CHAIN REACTIONS IN SOLUTION

by

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Summary

Two photochemical reactions in aqueous solution are the subject of this thesis. Both reactions have been shown to be chain reactions, with quantum yields in the range 0 to 50.

The photocatalysis of the electron exchange reaction between Tl(I) and Tl(III) in aqueous perchloric acid by ultraviolet light in the wavelength range in 230-270 mμ, has been shown to be a chain process with quantum yields in the range 1 to 500, and from a study of the dependence of the quantum yield on the concentration of reactants, the absorbed light intensity and other variables, a mechanism for the chain reaction has been postulated. The chain carrier Tl(II) is formed by dissociation of the charge-transfer excited state formed by photoabsorption of the Tl(III) species

$$\mathrm{TlOH^{2+}} + h\nu \xrightarrow{\phi_1} \mathrm{Tl^{2+}} + \mathrm{OH} \; .$$

It is proposed that the $\mathrm{Tl^{2+}}$ acts as a chain carrier in the propagation reactions

$$\mathrm{Tl^{2+}} + \overset{*}{\mathrm{Tl}}{}^{3+} \rightleftharpoons \overset{*}{\mathrm{Tl}}{}^{2+} + \mathrm{Tl^{3+}} \qquad (2)$$

$$\overset{*}{\mathrm{Tl}}{}^{2+} + \mathrm{Tl^{+}} \rightleftharpoons \mathrm{Tl^{2+}} + \overset{*}{\mathrm{Tl}}{}^{+} \qquad (3)$$

A detailed discussion of the termination processes is included as the dependence of quantum yield on the absorbed light intensity suggests a termination reaction involving both linear and quadratic termination. A value for the ratio of the rate constants of the propagation reactions (2) and (3) has been determined and compared to theoretical predictions of the Marcus and Hush theories on electron exchange reactions.

The ultraviolet induced chloride exchange reaction between platinum(IV) bisethylenediamine dichloride ion and free chloride ion exhibits quantum yields of up to 50. A quantitative study of the effect of several variables on the quantum yield, plus qualitative evidence on the effect of impurities on the reaction, have led to the conclusion that Pt(III) is the chain carrier involved in the reaction. The implications of the observation that the quantum yield is independent of the wavelength of irradiation are discussed in detail.

A subsidiary study of the net photolysis, has shown that release of chloride ion from the complex occurs with a quantum yield of .022.

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This thesis contains no material previously submitted for a degree or diploma in any University, and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

John K. Yandell
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INTRODUCTION

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SECTION I

CHAPTER 1: INTRODUCTION

Although the photochemistry of organic compounds has been studied fairly extensively in the last decade, relatively few photochemical studies have been made on inorganic systems (especially in condensed phases). The value of photochemical techniques in enabling specific reactions to be carried out, in organic preparative chemistry, possibly induced research in this field. The lack of any such stimulation in inorganic chemistry, may be a basic reason for the lack of interest in the photochemistry of inorganic compounds, despite the possibility of significant and interesting results. The absorption of light produces excited, reactive species which are of fundamental interest for comparison with stable compounds. Although most excited states of inorganic compounds are short-lived, a great deal of information about their chemical and physical properties may be obtained from photochemical studies. Considerably more effort has been exerted in the study of the species produced by high energy radiation, despite the greater theoretical and practical difficulties involved.

The possible use of photochemistry in the theoretical understanding of absorption spectrum has also received little attention, although a group of Italian research workers have recently approached the irradiation of some inorganic complexes from this angle. (Detailed studies of the photochemistry of gaseous systems have been made, but this is limited by the small number of gaseous compounds.) For example, a study of the photochemistry of aqueous solutions of halide ions by Stein$^{(1)}$ and co-workers, has helped to establish the existence of hydrated electrons, and enabled a sounder interpretation of the origins of the spectra of these ions.

The reactivity of unstable intermediates is also of great interest to chemical kinetics, as a comparison of the kinetics of two species (the ground and excited states) differing only in electronic or vibrational energy may give useful information on the effect of energy changes on the rates of reaction.

The two photochemical chain reactions reported in this thesis, were studied in an attempt to elucidate some aspects of the chemistry of the reactants and related intermediates.

1. The first system studied was the ultraviolet induced electron exchange reaction between Tl(I) and Tl(III) perchlorates in aqueous perchloric acid. The thermal electron exchange has been reported on by several research groups, but the role of the possible intermediate oxidation state Tl(II) was not established with any certainty. It was hoped that Tl(II) would be found, by irradiation in the charge transfer band of Tl(III). The reactions and properties of the Tl(II) so produced, could then be studied and compared to Tl(I) and Tl(III) and other related ions. The process of photoexcitation was also of intrinsic interest. The properties of the Tl(II) intermediate, and the process

of photoexcitation of Tl(III) were also of intrinsic interest.

2. The second system studied was the photoinduced chloride exchange reaction between platinum(IV) bisethylenediamine dichloride cation and free chloride ion in aqueous perchlorate solution. This reaction also was shown to be a chain reaction, with similar kinetic characteristics to the thallium electron exchange reaction. However the nature of the intermediate acting as chain carrier in this and similar reactions involving Pt(II) halide complexes, was not clear from the conflicting evidence previously reported.

The primary photochemical absorption process in these compounds is unusual, as apparently the products of photoadsorption are independent of wavelength and band of irradiation. This phenomenon is not predicted on a simple consideration of the usual assignation of electronic transitions to spectral bands. It was of interest to try and determine the excited states involved in the reaction in the hope of eliminating this apparent anomaly. Excited Pt(IV) complexes and Pt(III) species are the most likely intermediates in these Pt(IV) photochemical substitution reactions.

A discussion of previous photochemical studies and theories developed therefrom is made in the second chapter, leading up to the interpretation of present results on the platinum exchange reaction. Included in this chapter is a summary of present interpretations of inorganic complex spectra.

The third chapter is devoted to a summary of theories on electron transfer and ligand substitution reactions in solution. This material is aimed at enabling the results of the present study to be interpreted in terms of these theories.

SECTION I

CHAPTER 2: PHOTOCHEMISTRY

A. Spectra

The next section reports briefly the current state of the theory of the absorption spectra of inorganic complexes, which is obviously important in the understanding of photochemical excited states. The discussion is limited mainly to transition metal and near transition metal complexes, as these are of main interest to this thesis.

A molecular orbital diagram of an octahedral metal complex (Fig. I.1) is used to illustrate the theoretical principles of absorption spectroscopy. (From Figgis$^{(2)}$.) The usual assumptions of molecular orbital theory are made in drawing up this diagram. As well, π-bonding orbitals are not shown for simplification, and because they are unlikely to play a large role in the bonding and spectra of the complexes studied in this thesis. The d levels are split by electron interactions when the orbitals are occupied.

The two terminologies in common use for the five irreducible representations of group theory for octahedral symmetry are shown on the diagram as labels for the molecular orbitals. The subscripts u and g have their usual meaning. The superscripts b, n and a, refer to the bonding, non-bonding and antibonding character of the orbital respectively. The lines indicate the overlapping orbitals (or mixtures of orbitals) which form the molecular orbitals.

As the molecular orbital resembles the orbital nearest in energy to it, in most complexes the bonding orbitals have largely ligand orbital character. Similarly the t_{2g}^{n} and e_{g}^{a} molecular orbitals have mainly metal d character, and the a_{1g}^{a}, and t_{1u}^{a} orbitals have mainly metal s and p character, respectively.

The success of the ligand field approach to d-d absorption spectra is based on this assumption with respect to the t_{2g}^{a} and e_{g}^{a} orbitals. The high metal d character of these orbitals means that they can be treated as perturbed free metal ion orbitals.

The possible transitions within this diagram, and the nature of the excited states thus formed are discussed in the next few pages. The transitions are labelled by the term in most common use, although some of these terms do not have their origins in molecular orbital theory.

Charge-transfer absorption.

Jørgenson(3) has interpreted charge-transfer bands as corresponding to electronic transitions from the bonding molecular orbitals (e_{g}^{b}, t_{2u}^{b}, a_{1g}^{b}) to the lowest available energy level. In transition metal complexes this will be either t_{g}^{a} or the e_{g}^{a} orbitals. For example, Jørgenson assigns the charge-transfer bands of the PtX_6^{2-} group of ions (where X^- is Cl^-, Br^-, or I^-) to transitions from σ-bonding and π-bonding orbitals to the antibonding e_g orbitals. He has successfully interpreted the band structure of these platinum complexes in terms of these transitions.

The term, charge-transfer, comes from the theory of Mulliken(4), derived to account for the intense absorption bands occurring in mixtures of some compounds (e.g., Benzene/I_2), that do not occur with either of the components. The theory involves the interaction of a "no bond" ground state (DA) and a polar excited state (D^+A^-), to give a ground state wave function,

$$\psi_0 = \psi(DA) + \lambda\psi(D^+A^-)$$

and an excited state wave function,

$$\psi_1 = \psi(D^+A^-) + \mu\psi(DA)$$

The charge-transfer band is associated with the electronic transition between these two states. The theory is also applicable to the transition from a polar ground state to a "no bond" excited state.

The main characteristic of the theory, as implied by the name, is the large net displacement of charge, resulting in intense absorption bands. Some predictions of the theory are:

1. The charge-transfer band will be very intense ($\epsilon_{max} > 10{,}000$) due to the large change in dipole moment associated with the transition, and because the transition is completely allowed (not forbidden by any selection rules).

2. The energy of the charge-transfer absorption depends on the ease of oxidation of the donor (D) and the ease of reduction of the acceptor (A). Expressed mathematically,

$$h\nu = I - E + \delta$$

where $h\nu$ is the energy of the absorbed quantum, I is the ionization potential of the donor, E is the electron affinity of the acceptor, and δ

is a complex term which is predicted to be relatively constant for spectra of similar compounds.

3. The transition moment is the sum of two terms. The first is dependent on the dipole moment of the transferred charge and the hole left behind; and the stabilization of the ground state by interaction with the excited state. The second term can give rise to charge-transfer absorption without any bonding in the ground state. This type of absorption is called contact charge-transfer and may occur between two species in close proximity purely by chance contact.

The theory of charge-transfer spectra was reviewed by Murrell(5) in 1961. The high intensity ($\varepsilon > 5{,}000$), low wavelength bands of the spectra of complex ions have been attributed to charge-transfer absorption.(6) They exhibit the characteristic of dependence of wavelength (energy) on the ease of reducing the metal (acceptor), and the ease of oxidizing the ligand (the donor). For example, Barnes and Day(7) correlated the reduction potentials for the $M^{L+}/M^{(L-1)+}$ complex, with the energy of the first intense band of some complex metal ions (M^{n+}) with the same ligand, in agreement with their assignation as charge-transfer bands. The complexes involved were $Sm(III)X$, $Eu(III)X$, $Yb(III)X$, $Co(III)(NH_3)_5X$, $Cu(II)X$, where X was the ligands SCN^-, Br^-, $SO_4^{''}$, and H_2O. Since in the majority of transition metal complexes, neither the ground state nor the excited state are "no bond" states, the quantitative aspects of the theory have to be treated with some reservation.

Jørgenson's concept of transitions from bonding to non-bonding or antibonding orbitals is probably a more accurate concept, although possibly a less useful one. There are not many practical differences between the concepts. Both theories predict a transfer of charge from ligand to metal; the molecular orbital theory on the basis that the donor bonding orbitals have high ligand character and the acceptor orbitals have high metal character. Both predict intense absorption because the transitions are completely allowed with large transition moments. Both predict a dependence on the ease of oxidation of ligand and ease of reduction of metal. One significant difference is in the concept of the transition symmetry. The charge-transfer microsymmetry is linear, and the concept involves only the one bond between ligand and metal. However the molecular orbital model conceives, for an octahedral complex, an equal effect on all ligands. For a six-coordinated species which does not have octahedral symmetry (i.e. without all six ligands the same) the correct description undoubtedly lies somewhere between these concepts.

Other spectra which have been attributed to charge-transfer origins include the spectra of inorganic anions in solution (I^-, Br^-, Cl^-, $SO_4^=$, SCN^-, CN^-, etc.). Stein and co-workers have studied the photochemistry of some of these ions, and concluded that although the products of absorption are the oxidized ion plus an aquated electron, as expected from charge-transfer to solvent absorption, the initially formed excited state is spherically symmetrical, which conflicts with the concept of charge-transfer. In agreement with these ideas, Symons et al(8) proposed a model, termed the square well model, to account for the absorption spectrum of the solvated iodide ion.

Similarly the high intensity bands of the divalent states of the first row transition metal aquo ions have been attributed to reverse charge-transfer, i.e. charge-transfer from metal to ligand. These transitions are perhaps better described as metal d to metal s transitions, and will be discussed further under this section.

d-d absorption.

Transitions from the non-bonding $t_{2g}{}^{n}$ orbitals, to the anti-bonding $e_{g}{}^{a}$ are traditionally called d-d transitions, as they may be treated qualitatively at least as transitions between the d orbitals of free metal ion perturbed by the presence of the ligand "field". A combination of this approach (the crystal field model) and molecular orbital theory has been labelled ligand field theory. The theory has been very successful in predicting the number, position, and qualitatively the intensity, of the low intensity bands of transition metal spectra ($\epsilon_{max} < 1,000$).

d-s absorption.

These transitions on the molecular orbital diagram are from either the $e_{g}{}^{a}$ or $t_{1g}{}^{n}$ orbitals to the $a_{1g}{}^{a}$ orbital. Again they are called d to s transitions because of the similarity of these orbitals to d and s free metal ion orbitals.

In high oxidation states of transition metals, the energy difference between these orbitals is probably such that the absorption would appear at wavelengths beyond the accessible region of the spectrum. However charge-transfer bands could obscure any peaks due to these transitions. With ions in low oxidation states, absorption bands occur which have been attributed to charge-transfer to solvent. Dainton(9) found a linear dependence of the energy corresponding to the long wavelength edge of the first intense band of the first row transition metal divalent aquo ions,on the corresponding oxidation potential (M^{2+}/M^{3+}). The good agreement with the formula,

$$h\nu = -I + E + \delta$$

was taken as proof of the charge-transfer character of the absorption bands.

This interpretation is supported by photochemical studies of Fe(II)(1,16), that have shown that irradiation in this band leads to the formation of Fe(III) and hydrated electrons as expected from charge-transfer from metal to solvent. However the alternative explanation of these bands as being d-s in origin, is still tenable. Jørgenson(3), after referring to the work of Dainton, concluded that the transitions may be attributed to charge-transfer with accidently small transition moment (or spin forbidden). But, he still thought it was probable that the excited orbital has l=o to some extent and was the even Υ_1 (a_{1g}) orbital.

s-p transitions.

The next transition on the molecular orbital diagram is the $a_{1g}{}^{a} \rightarrow t_{1u}{}^{a}$ transition, called s-p transitions. These transitions may only be observed if the metal ion has a complete (n -1) d shell plus 1 or 2 electrons in the ns orbital. Tl(I) is the example of interest to this thesis. The ultraviolet absorption bands of Tl(I) ions in crystals and aqueous solution have been interpreted as charge-transfer bands, but are now generally regarded as s-p transitions.(10,3)

These are all the transitions that may take place within the scope of the molecular orbital diagram. However absorption bands of aqueous inorganic complexes may also arise from.

1. Transitions within a ligand.
2. Transitions from metal to π-acceptor levels on the ligands.
3. Transitions from outer sphere ion paired anions to the metal.

This form of charge-transfer spectrum probably conforms to the Mulliken charge-transfer model more closely than inner sphere charge-transfer. A well known example is the $Co(NH_3)_6I^{2+}$ ion pair which absorbs strongly in the near ultraviolet.

The occurrence of charge-transfer excitation between a metal and an outer sphere anion, introduces the possibility of electron transfer from solvent in the second coordination sphere. No evidence for this has been reported in the literature, but this may be due to the lack of effort directed towards finding the phenomenon.

A qualitative calculation, based on the assumption that $h\nu = -I + E + \delta$ is applicable, shows that as the $Co(NH_3)_6I^{2+}$ absorption occurs in the near UV, $Co(NH_3)_6H_2O^{3+}$ should absorb in the accessible region of the spectrum. A charge-transfer band does occur in the far ultraviolet, but it has been attributed to charge-transfer from NH_3 to the Co(III).(11)

B. Photochemical Reactions

Brief reviews of inorganic photochemical reactions have been published by Orgel(12) and Basolo and Pearson.(13) Adamson has recently reviewed the photochemistry of Cr(III) complexes.(17)

1. Qualitative effects.

The reactions of the various excited states and the theories predicting this behaviour are discussed qualitatively in this section. Of primary concern is the type of reaction products that may be expected to form from each type of excited state.

Now the thermal and photochemical reactions of metal complexes may be classified into two groups.

(a) Substitution type reactions.

Common reactions in this group are aquation, racemization, ligand exchange reactions; all occurring without an overall change in oxidation state of the metal ion. For example, the hydrolysis reactions of Co(III) salts such as

$$Co(NH_3)_5Cl^{2+} + H_2O \rightleftharpoons Co(NH_3)_5H_2O + Cl^-$$

are substitution type reactions.

(b) Redox reactions.

Reactions involving a change in the oxidation state of the metal ion. The usual products in photochemical redox reactions are a reduced metal ion and an oxidized ligand. The reduction of a metal ion may produce a labile oxidation state which hydrolyses, thus involving both types of reaction. Examples where the primary product of photoabsorption is a reduced metal ion and an oxidized ligand are numerous. Evans and Uri(14) detected Cl atoms from the photolysis of $FeCl^{2+}$. Similarly flash photolysis studies of Ce(IV) nitrate showed the production of Ce(III) and NO_3. As most photochemical reactions involve dissociation of the absorbing species, dissociation is discussed in some detail.

Dissociation reactions.

A complex ion usually dissociates by the loss of one ligand from the complex. No clear cut example (in inorganic complexes) of an excited state immediately dissociating into more than two fragments, has been reported. (Secondary dissociation of unstable products of the first dissociation is excluded.)

A ligand may dissociate from a complex either homolytically or heterolytically. With the usual definitions of homolytic and heterolytic fission of a bond, the products of homolytic fission of a coordinated ligand are redox products - reduced metal ion and oxidized ligand. Conversely, the oxidation state of the metal ion will not be changed by heterolytic fission, and substitution products will result.

Thus the problem is reduced to the mode of dissociation of the excited states. At this stage a digression into a general discussion of the relation between bonding and mode of dissociation is necessary. Very few molecules dissociate under thermal heat in the gas phase into ions. Similarly in the gas phase very few neutral excited states dissociate into ions. (One exception is thallous chloride, TlCl, which has an excited state which dissociates into Tl^+ and Cl^- in the gas phase.(15)) However, in solution the extra stability gained by solvation makes ionic dissociation a favourable process for ionic compounds. In the particular cases of interest to this thesis, more refined ideas may be necessary. The ground state of a complex such as $PtCl_6^{2-}$ is generally pictured as a central platinum ion with six chloride ions surrounding it. This model necessitates the conclusion that if bond breakage occurs an intact chloride ion will be released. In ions of this type thermal substitution type reactions probably involve heterolytic fission, but this is the replacement of one species by another, rather than just dissociation.

Dissociation of charge-transfer excited states.

Now considering a charge-transfer excited state, one model for this excited state involves an oxidized ligand attached to a reduced metal ion, for example, $PtCl_5^{2-}$...Cl. The model implies that bond cleavage will occur homolytically with products $PtCl_5^{2-}$ and Cl. The question arises whether this model is too simple and that dissociation in solution of charge-transfer excited states may occur homolytically.

Experimentally, either no reaction or homolytic fission is observed (with the possible exception of Pt(IV) complexes). Tables I.1 and I.2 list a number of typical quantum yields for the products of photolysis of inorganic complexes.

The molecular orbital model lends itself less readily to predictions of dissociation type; for the charge distribution in the excited and ground states is less clearly defined. The normal charge-transfer transition from bonding orbitals to non-bonding or antibonding orbitals only exhibits charge-transfer properties because of the ligand character of the bonding orbitals and the metal ion character of the acceptor orbitals. The same prediction of homolytic dissociation products would be made on this basis, if the assumption is also made that dissociation occurs with retention of the orbitals with similar character to the ligands by the ligand, and analogously by the metal.

Table I.1

Complex	Spectra λ_{max} and ϵ_{max} d-d band	Quantum Yields		Wavelength of Irradiation	Band Type	Ref.
		Product	ø			
$Mn(C_2O_4)_3^{3-}$	500 (120)	CO_2, Mn(II)	.5	<400	>500<1% C-T	29
			.3	500		
$Cr(C_2O_4)_3^{3-}$	420 (97) 570 (75)	Co(II) (N_2 atm.)	.016	254	Probably C-T >400 <1% C-T	38
Fe_{aq}^{3+}	240 (5000) 400 (.7) 550 (.1)	Fe(II)	.07	254	charge-transfer	33
$(FeOH^{2+})$	325 (5000) 450 (120)	Fe(II)	.15	310	charge-transfer	
$Ce(IV)(SO_4)$	320 (5600)	Ce(III)	.2	254	charge-transfer	31
$Ni(CN)_4^{2-}$		No photochem. reaction		254 313 365	charge-transfer d-d band	25
$Pt(CN)_4^{2-}$		"		254	C-T and d-d	25
$Cr(NH_3)_6^{3+}$	354 (50) 466 (40) 655 (.1)	$Cr(NH_3)_5H_2O$	.26	452	d-d band	32
			.29	652	"	32

Table I.2

			Quantum Yields							
	Spectra		Redox Products				Substitution Products			
Complex	λ_{max} (ϵ_{max}) d-d bands	Charge transfer (λ_{max})	Product	Quantum Yield	Irradiation Wavelength	Ref.	Product	Quantum Yield	Irradiation Wavelength	Ref.
$Co(en)_3^{3+}$	465(865)	211 (21,200)	Co(II)	.06-.17	254	23	hydrolysis	5×10^{-4}	370	21
	340(79.7)		2en, NH_3, HCHO	.07	254	24		0	254	23
$Co(C_2O_4)_3^{3-}$	606(170)		Co(II), CO_2	1.0	370	1	racemization	0	550	16
	420(220)			.007	550					
				.4	250	24				
				.35	300	24				
				.1	400	24				
$Co(NH_3)_6^{3+}I^-$	475(55)	<300	Co(II)	.77	370	21				
	340(98)			.001	550	21				
				.53	366	36				
				<.001	550	36				

(contd.)

Table I.2 (contd.)

			Quantum Yields							
	Spectra		Redox Products				Substitution Products			
Complex	λ_{max} (ϵ_{max}) d-d bands	Charge transfer (λ_{max})	Product	Quantum Yield	Irradiation Wavelength	Ref.	Product	Quantum Yield	Irradiation Wavelength	Ref.
$Co(NH_3)_5I^{2+}$	585(75)	287	Co(II), I_2	.12	550	21				
	380(1880)			.47	365	23				
				.5-1.0	254	26				
$Co(NH_3)_5Cl^{2+}$	530 (48)	227	Co(II)	.13-.34	254	23	$Co(NH_3)_5$-H_2O^{3+}	.05	370	20
	360 (45)			.003	365	21				
				.05	330	20		.007	550	20
				10^{-5}	550	20				

Reactions of d-d excited states.

The transitions involved in d-d absorption predict an excited state involving only a redistribution of charge within the d shell of the metal ion. On this basis, if dissociation is to occur it would be expected to be heterolytic with formation of substitution products.

In general irradiation in d-d bands does lead to the formation of substitution products. However some complexes dissociate into homolytic fission products when irradiated in d-d absorption bands. For example, $Co(C_2O_4)_3^{3-}$ yields Co(II) on irradiation at all wavelengths. A study of some of these reactions led Adamson(21) to discard the ideas discussed above, and postulate that d-d as well as charge-transfer excited states dissociate homolytically. Particular examples discussed by Adamson included the photolysis of $Co(NH_3)_5I^{2+}$ which, when photolysed with light of wavelength 550 mμ, gave Co(II) and I_2, although the nearest high intensity band was at 287 mμ.

A more detailed description of their proposed mechanism is shown diagramatically below.

$$\begin{tikzcd}
MA_5X^{n+} + h\nu \arrow[r, "(1)"] & MA_5^{(n-1)+}\ldots X \arrow[r, "(2)"] \arrow[dd, "(3)"', "A"] & MA_5^{(n-1)+} + X \\
 & & B \\
 & MA_5^{(n-1)+}H_2O\ X \arrow[r, "(4)"] & MA_5^{(n-1)+}H_2O + X^- \\
 & & C
\end{tikzcd}$$

The reactions involved are:

(1) Formation by absorption of light of the intermediate A, in which the M-X bond is homolytically broken.

(2) The fragments diffuse apart before they can react and redox products are formed.

(3) If the fragments do not move (due to their excess kinetic energy greater than thermal energies) very far apart, a water molecule imposes itself between the fragments. This is followed by,

(4) Back electron transfer leading to the formation of hydrolysis products.

This mechanism may be criticised on several grounds, especially in comparison to the more feasible mechanism which seems to be available. This mechanism is discussed in terms of the potential energy diagram in Fig. I. 2, before Adamson's mechanism is considered further.

The curves depict the potential energy of the bond between metal and ligand, as a function of the internuclear distance between the ligand and metal, for 'typical' ground states (g), d-d excited states (d) and charge-transfer excited states (c) and (c'). The products of dissociation are shown on the right hand side. The usual charge-transfer excited state is illustrated by the upper dotted profile (c'), which does not cross the lower energy profiles.

However the continuous charge-transfer profile (c) exhibits an important characteristic in that it crosses the d-d profile (d), even though the charge-transfer band energy (indicated by the vertical arrow) is considerably greater than that of the d-d band. In this situation ions excited in a d-d band may cross over (intersystem

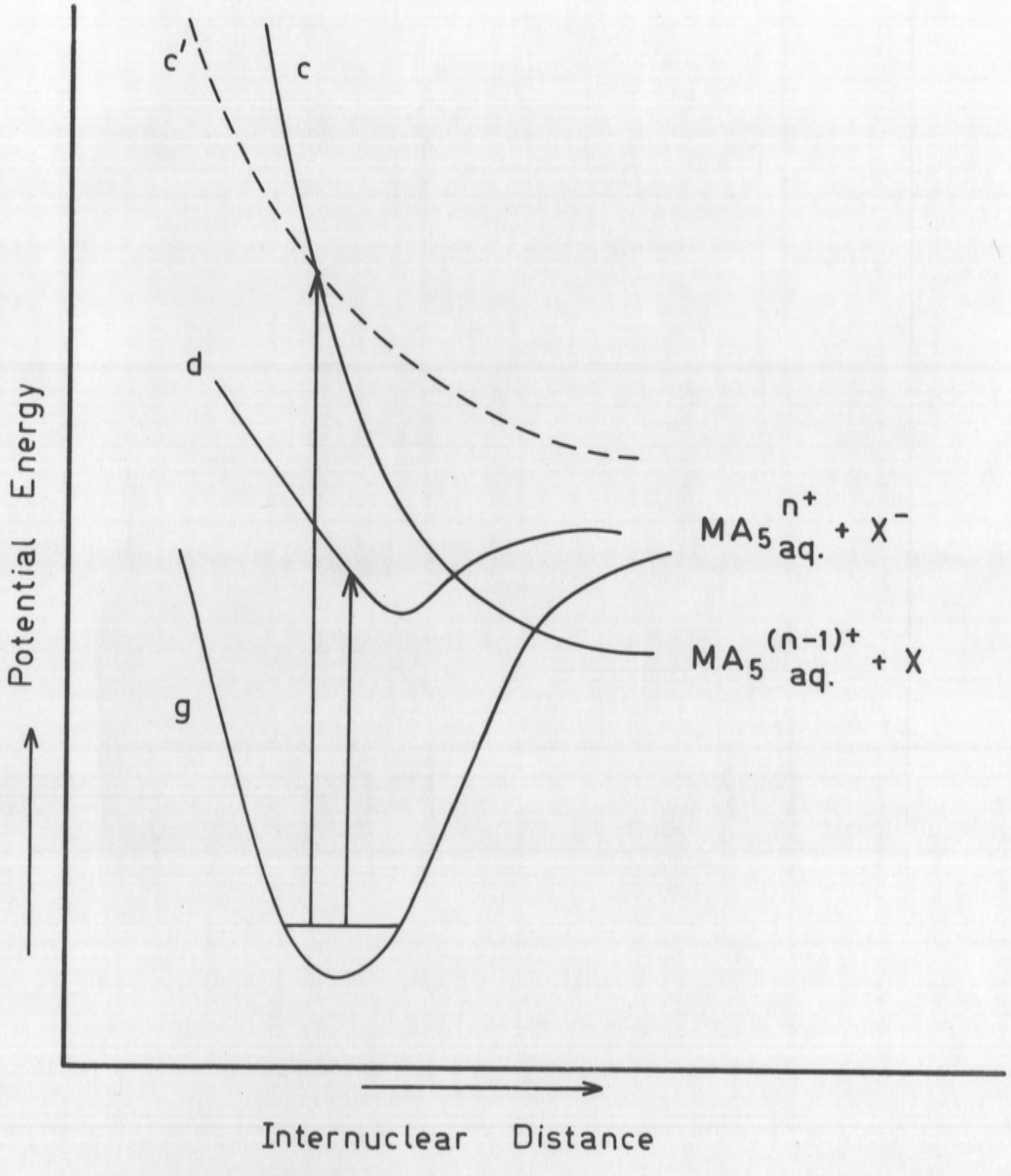


FIG. I·2 Potential Energy Diagram.

g Ground state
d d-d excited state
c & c′ Charge transfer excited states

crossing) to the charge-transfer profile, forming redox products. Thus the essential requirement is a cross over of the d-d and charge-transfer potential energy profiles. This is likely to occur when the ligand is easily oxidizable, and the metal is easily reducible. Consultation of Table I. 2 shows that the species which form redox products when irradiated in d-d bands have I^-, $C_2O_4^=$ as ligands, which are both easily oxidizable. This intersystem crossing was proposed by Porter et al$^{(24)}$ to explain the results of the photolysis of manganese(III) tris oxalate ion.

It can be seen from the potential energy diagram that the charge-transfer profile (c) crosses the ground state profile as well. This indicates that thermal electron transfer between ligand and metal, may be possible. In some cases this is observed; notably the manganese oxalate ion thermally decomposes to Mn(II). Some complexes which homolytically dissociate when irradiated in a d-d band, are thermally stable. This may be due simply to the high energy of activation required to reach the cross over point.

An alternative consideration is based on the observation that there is, in the more stable Co(III) complexes, a difference in the spin state between the oxidized and reduced metal ions. (Co(III) is low spin d_6, Co(II) high spin d_7.) This introduces a spin restriction for electron transfer which will reduce the probability of cross over to the charge-transfer profile, and hence increase the stability of the complex.

Returning to the homolytic fission mechanism of Adamson's; this may also be described in terms of potential energy diagrams. The d-d excited state (homolytically fissioned) must cross the ground state profile at large internuclear distances if a solvent molecule is interposed between metal and ligand at the cross over point.

Adamson's mechanism may be criticised on the grounds that,

(1) From our knowledge of absorption spectra, a d-d excited state with a charge distribution leading to homolytic products would seem less likely than one leading to heterolytic fission.

(2) The number of excited states that have their cross over point with the ground state at a suitable internuclear separation, might be expected to be small.

(3) The interaction between the departing ligand and metal would be relatively small when a solvent molecule is interposed, with a consequent reduction of the probability of crossing from the excited state to the ground state (i.e. low probability of back electron transfer).

On this basis both homolytic and heterolytic products might occur for the one system on irradiation at one wavelength in a d-d band, as further dissociation of those species which escape back electron transfer will lead to homolytic products.

These points suggest that the mechanism of Adamson's is less probable than the alternative mechanism postulated.

It may be concluded that since cross over from one potential energy curve to another may occur, the exceptions to the rule of d-d excitation leading to substitution products and charge-transfer absorption leading to redox products, do not disprove the general conception of the mode of dissociation of these states.

In this discussion it is assumed that there is a significant difference between the electronic states of the charge-transfer excited state and the d-d excited state, even when they have the same energy, i.e. at the cross over point. In this context it is well to keep in mind a point raised by Figgis. He noted that the distinction between ligand field and charge-transfer spectra cannot be made sharply if there is extensive mixing of the metal and ligand wave functions in the molecular orbitals of the complex. In particular, the mixing in the tetrahedral oxyanions MO_4^{n-} is so extensive that it is not proper to describe the bands which are observed as either ligand field or charge-transfer in origin.

Only the possibility of dissociation of excited states due to their excitation energy, this dissociation leading to the formation of products has been considered so far. It is worth noting, however, that d-d excited states may react to form substitution products by normal thermal reaction paths, which may not be distinguishable from photochemical dissociation paths. Essentially photosubstitution of excited states may occur if the excited state is labile.

Both crystal field and molecular orbital models predict an increase in the lability of d-d excited states. The transition from t_{2g} to e_{2g} is a transition on the crystal field model, from orbitals spatially orientated between the ligands to orbitals orientated towards the ligands. The electronic repulsion is expected to weaken the bonding and increase the lability. Similarly the molecular orbital model predicts a decrease in bond strength due to the transferred electron being in an orbital of higher antibonding character. The decrease in bond strength does not necessarily increase the lability of a complex, but there is some correlation between lability and bond strength in transition metal complexes.

An interesting point which may play an important role in the lability of excited states of some complexes, is that the excited states of some complexes are expected to be Jahn-Teller distorted (with increased lability), although the ground states are not distorted.

The reactions of d-s and s-p excited states.

These transitions may be qualitatively described as excitation from one metal orbital to a higher energy metal orbital.

Two possible photochemical consequences may occur:

(1) The excited electron is ionized off leaving an oxidized metal ion and a reduced ligand or solvent molecule. The formation of Fe(III) from photolysis of aqueous Fe(II) is an example of this reaction. The mechanism envisaged for this process is analogous to the photolysis of anions in aqueous solution postulated by Stein and co-workers.(1,27)

They found that the photolysis of anions such as I^- led to formation of I atoms and hydrated electrons (e^-_{aq}). The mechanism they proposed to account for their results involved the initial formation of a spherically symmetrical excited state, followed by charge asymmetrization to form the products.

(2) From the molecular orbital model it might be predicted that excitation from, for example, a non-bonding to an antibonding orbital would decrease the bond strength, and hence possibly increase the lability of the complex. Dissociation of the complex would also be expected.

2. Quantitative effects.

The first part of this chapter has been devoted to a discussion of the relationship between the type of reaction expected and the nature of the excited state. In the remainder of the chapter, the factors affecting the quantitative yield of products are considered.

The first step of all photochemical reactions is the absorption of a quantum of light to produce an excited state. The quantum yield for the formation of products, then depends on the competition between reactions leading to the formation of products, and other means of energy loss by the excited state.

The discussion is facilitated by reference once more to the potential energy diagram of Fig. I.2.

An excited state may lose energy in four ways.

(1) Dissociation. Some energy is transferred to kinetic energy of the fragments but the fragments may still be vibrationally and electronically excited. This will probably occur within a vibration time (10^{-13} sec). The vertical line in Fig. I.2 indicates a transition from the ground state to an excited state. As this transition occurs without change in internuclear distance (Franck-Condon principle), and the potential energy of excited states is usually at a larger internuclear distance than the potential energy minimum of the ground state, the excited state is often formed in a repulsive state with sufficient energy to cause dissociation. Exceptions to this are discussed in more detail under charge-transfer absorption.

(2) Radiative degradation to the ground state or lower energy excited state (fluorescence). Fluorescence has been reported for some inorganic complexes.(37) The 'allowedness' of the electronic transition, as measured by the integrated intensity of the corresponding absorption band is related approximately to the 'allowedness' of the reverse process, i.e. fluorescence (Turro(28)). The inherent radiative lifetime τ_o (in seconds) of an excited state is given approximately by the formula,

$$\tau_o = \frac{3.5 \times 10^8}{\bar{V}_m^2 \int \epsilon . a\bar{V}} \approx \frac{3.5 \times 10^8}{\bar{V}_m^2 \, \epsilon_m \Delta V_{\frac{1}{2}}}$$

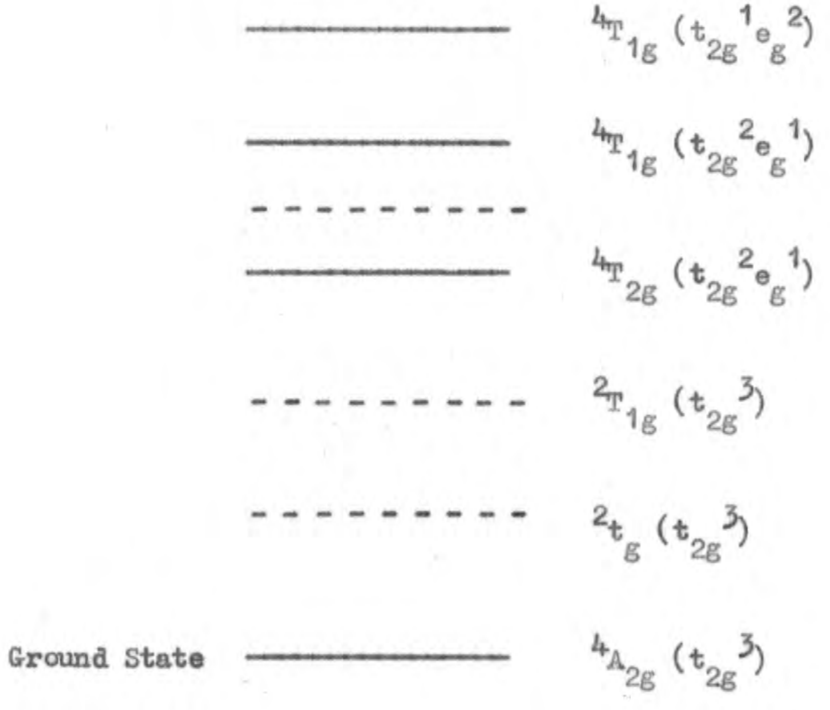
where $\bar{V}_m$ is the wavelength of the maximum for the absorption band (in cm^{-1}), $\Delta V_{\frac{1}{2}}$ is the half-width (in cm^{-1}), and ϵ_m is the maximum extinction coefficient of the band. Choosing maximum values for the oscillator strength, for low ultraviolet bands, the radiative lifetime is approximately 10^{-8} sec. This represents a minimum time for radiative decay to occur for most excited states. (Adamson(17) has criticised the application of the approximate formula to some transition metal absorption bands.)

(3) If the excited state potential energy profile crosses another potential energy profile, a finite probability exists that the system will cross to the other profile. The probability of crossing from one state to another depends on the same factors that control the probability of absorption of light. (Mixing of orbitals, selection rules, etc.) If the crossing is from one excited state to another in the same spin state, it is referred to as internal conversion. Internal conversion between excited states is generally very efficient in organic systems. Radiative decay from states other than the lowest energy excited state has only been observed in one or two cases.(40) Internal conversion may compete with dissociation.

If the crossing involves a spin change, it is known as intersystem crossing. This is less efficient than internal conversion. It may compete with degradation to the ground state, but not with dissociation.

An instructive example taken from the literature, is the study of the photolysis of Cr(III) reported by Plane et al(34) and Adamson, and discussed by Schlafer(41) and Adamson.(17) An energy level diagram for the d-d excited states for Cr(III) complexes is illustrated in Fig. I.3.

Fig. I.3



The four solid lines are all quartet states, and transitions from the ground state to the upper states produce three quartet-quartet absorption bands of moderate intensity (ϵ_{max} (10-1000)). The dotted lines are doublet states. Transitions to this excited state result in weak spin forbidden absorption bands at long wavelengths ($\epsilon_{max} < 10$).

The Cr(III) complexes undergo photosubstitution reactions with a wide range of quantum yields. For the octahedrally symmetrical complexes, the quantum yields for irradiation in the quartet-quartet bands are independent of wavelength of irradiation. A plausible explanation of this observation was suggested by Schläfer.(41)

Irradiation in any of the quartet-quartet bands, produces an excited quartet which by internal conversion returns rapidly (10^{-10} sec) to the highest excited quartet ($^4A_{2g}$). The quantum efficiency of this process is assumed to be one. Two processes compete for the quartet; (i) internal conversion to the ground state, (ii) intersystem crossing to the doublet state. The fraction of species that undergo each process will be independent of wavelength. Because of the long radiative lifetime, and the inefficiency of internal conversion to the ground state, the doublet state has a long lifetime (10^{-3} sec). Thus hydrolysis of this state may occur, before it returns to the ground state, and a constant quantum yield for hydrolysis is observed.

Irradiation in the quartet-doublet band produces the doublet with unitary efficiency, and hence a quantum yield for hydrolysis of one, if hydrolysis is rapid as compared to other possible reactions of the doublet.

Adamson(17) in a complete review of Cr(III) photochemistry, points out that this simple idea needs modification, especially in complexes of symmetry lower than octahedral. He considers that the quartet states must also hydrolyse in some cases. Another possibility is that conversion to the ground state leaves the ground state in a high vibrational energy level, which may hydrolyse more rapidly than the thermally equilibrated state.

Returning to the discussion of energy loss by excited states, the fourth means of loss of energy is:

(4) Energy transfer to another species. This may occur by radiative transfer (emission and absorption), but the rate controlling step is the fluorescent emission, which is discussed under point (2). Another means of energy transfer called resonant energy transfer, may occur at large distances between species with overlapping absorption bands, by a non-radiative process. No reports appear to be available on the importance of this form of loss of energy in inorganic complexes.

The quantitative effect of competition between product formation and other thermal equilibration processes is illustrated in more detail below, for d-d and charge-transfer absorption.

d-d absorption.

A general example is given to illustrate the principles involved. If ϕ is the quantum yield for the formation of products in the reaction scheme,

$$X + h\nu \xrightarrow{\phi_1} X^{\neq} + A \xrightarrow{K_1} \text{products} \qquad (1)$$

$$X^{\neq} \xrightarrow{K_2} X \qquad (2)$$

where $X^{\neq}$ is an excited state, which is formed by absorption with quantum efficiency ϕ_1. And if the reaction is in competition with an energy loss reaction (say, internal conversion to the ground state), with unimolecular rate constant K_2, then $\phi = \phi_1 \left\{\frac{K_1 A}{K_1 A + K_2}\right\} = \phi_1 \left\{\frac{1}{1 + K_2/K_1 A}\right\}$. The lifetime of the excited state in the absence of reaction (1) is proportional to K_2^{-1}, so that the longer lived species will yield a larger quantum yield. This sort of situation arises when the formation of product is a bimolecular reaction.

Charge-transfer absorption.

Dainton(42) has discussed some aspects of charge-transfer photochemistry of relevance to this section. The formation of redox products following charge-transfer involves dissociation of the excited state. The dissociation is in competition with the other forms of energy loss, but as dissociation is very rapid, competing processes are often too slow to reduce the quantum yield significantly. Charge-transfer absorption usually produces a species in a highly repulsive state, so that the species is expected to dissociate within a vibration time. However there may be conditions, where the charge-transfer excited state has a much longer lifetime. If the excited state is formed with little repulsive energy in the vibrational mode of dissociation, or if the excited state has a significant potential energy minimum; it is possible that no dissociation or delayed dissociation will occur. In a solvent, the surrounding solvent molecules may cause a potential energy barrier to dissociation. This 'cage' effect(44) may increase the lifetime of excited states so that competing processes, such as internal conversion to ground state, become important.

All these considerations apply to the excited state while it is still within the 'solvent cage', that is before solvent has become interposed between the fragments of dissociation. The processes returning the excited state to the ground state within the solvent cage is termed primary recombination, and the fraction of excited states which escape primary recombination (i.e. that dissociate), is sometimes called the primary quantum yield. This term has, however, been used in a different sense later in this thesis.

In most photochemical reactions the products of reaction are found by the reaction of a scavenger with one or both fragments of dissociation. Thus, the quantum yield for the formation of products will be equal to the primary quantum yield (as defined above), if all the fragments are scavenged. However when recombination of the fragments is rapid, then the recombination reaction may compete with the scavenging reaction, reducing the quantum yield. Noyes(42) has discussed recombination and scavenging competition in several papers; in terms of three stages of recombination; primary, secondary and tertiary (my term) recombination. Primary recombination (recombination within the solvent cage), has been considered in the last few pages. In the next section, the ideas of Noyes on recombination of fragments that have escaped the solvent cage are reviewed.

1. Secondary recombination.

Noyes observed that two fragments from a single dissociation, diffusing apart with kinetic energy greater than thermal energy, will in most cases reach thermal equilibrium with the solvent at a small distance apart. Then, under the influence of random diffusive movements, there is quite a high probability that the two fragments will re-encounter one another. If the fragments have a high probability of reaction per encounter, a significant fraction of the fragments will recombine reducing the quantum yield for the products of scavenging reactions. This recombination is called secondary recombination.

Noyes developed a simple quantitative theory to calculate the probability of secondary recombination. His model included the following features. A molecule AB absorbs a quantum of light, $h\nu$, and dissociates. The kinetic energy of the fragments is assumed equal to $h\nu - E$, where E is the difference in energy between AB and A and B separately. The fragments diffuse apart under the influence of this kinetic energy, but are slowed down by the viscous drag of a continuous medium. The distance between the fragments, when their kinetic energy is reduced to thermal energies is calculated from this model and termed the separation distance s. Noyes then calculates the probability of the two fragments encountering each other again, assuming random diffusive displacements of frequency a. For a separation distance of zero, the probability of re-encounter calculated by Noyes is .527 (for $\Upsilon = 1$, where Υ = ratio of the encounter diameter to the root mean square displacement distance). β, the probability of re-encounter of two fragments from separation distance s, was shown by Hamill(32) to be proportional to the reciprocal of s. β', the probability of secondary recombination was shown by Noyes to be,

$$\beta' = \alpha\beta_0 \ (1 - \beta + \alpha\beta)$$

where α is the probability of reaction per encounter, and β_0 is the probability of re-encounter of two fragments after a non-reactive encounter. Unless $\alpha > .1$, β' will be small, so that if the recombination reaction is not close to diffusion controlled, secondary recombination (recombination of geminate fragments) will be unimportant.

If all the fragments that escape secondary recombination, are scavenged, then the quantum yield will be $1 - \beta'$. Noyes(43) compared the results of his theory to quantum yields obtained for the photodissociation of I_2, and obtained satisfactory agreement considering the simplicity of the model.

Quantitatively the Noyes model is likely to break down in more complicated dissociative reactions. The biggest source of error probably lies in the assumption that the excess energy over that required to break the bond is imparted to the fragments as kinetic energy. In polyatomic molecules this assumption is unlikely to be true; other modes of vibration receiving significant quantities of energy. The possibility that the fragments of dissociation may be electronically excited should also be kept in mind.

The assumption of a continuous medium, is also suspect in consideration of microscopic effects. However, it might be pointed out that at least in a semi-quantitative sense, the Noyes' theory is very useful.

Tertiary recombination.

Some geminate fragments will escape both primary and secondary recombination, and become randomly distributed through the solution. If there are no competing processes, the fragments may still recombine by normal reaction paths, a process labelled tertiary recombination.

The competition between scavenging reactions and primary, secondary, and tertiary recombination is of considerable interest to this thesis. On the basis of the theory outlined above, Noyes(43a) has discussed in detail the dependence of the quantum yield on the rate of scavenging and the rate of recombination.

Scavenging may compete with tertiary recombination at concentrations of scavenger down to 10^{-9} mole l^{-1}. For the common reaction scheme,

$$A + h\nu \rightleftharpoons A^{\neq} \xrightarrow{\phi_1} B + C$$

$$B + C \xrightarrow{K_1} A \qquad (1)$$

$$B + X \xrightarrow{K_2} \text{Products} \qquad (2)$$

where $A^{\neq}$ is a photochemically excited state, B and C are fragments of dissociation of $A^{\neq}$, and X is a scavenger. K_1 and K_2 are the rate constants for the recombination reaction (1), and the scavenging reaction (2). Applying the steady state approximation to the concentration of B, the quantum yield for the formation of products, ϕ

is given by

$$\phi = \phi_1\left\{\frac{K_2[X]}{K_1[C] + K_2[X]}\right\} \qquad (i)$$

where ϕ_1 is the quantum yield for fragments escaping secondary and primary recombination, [C] is the concentration of a fragment of dissociation, and [X] is the concentration of scavenger. As [C] is usually much less than [X], an efficient scavenger (high K_2) will react with all the fragments even when the recombination rate constant, K_1, is at a maximum.

The case of more interest and difficulty is the competition between secondary recombination and scavenging reactions. Noyes concluded that only very efficient scavengers will compete, and then only at concentrations greater than .1 mole $l.^{-1}$. As this point is of importance in the thallium work, it is discussed in more detail in the relevant section.

Scavengers are not expected to compete with primary recombination, unless very reactive and in high concentration. Noyes considered that only reactive solvent scavengers would compete significantly.

I have attempted in this chapter to outline some of the factors which affect the quantum yields of photochemical reactions. In the next chapter rates of chemical reactions are discussed, as the relative rates of reactions control quantum yields in most photochemical reactions.

SECTION I

CHAPTER 3: THE RATES OF REACTION OF INORGANIC COMPLEXES IN SOLUTION

The discussion is limited to electron transfer and substitution reactions of transition metal and near transition metal complexes in aqueous solution, as these reactions are of importance to this thesis. Within these fields, specific emphasis is placed on the reactions of species similar to the compounds and their excited states observed in this study.

A. Electron Transfer Reactions

These reactions involving the mutual oxidation and reduction of two species have been the subject of many experimental and theoretical reviews.(45) No single mechanism has been found for electron transfer reactions; in fact three types of reactions, broadly based on the distance of interaction of the two reacting species, have been distinguished theoretically.

(i) Long range interaction. Grotthus mechanism.
The electron transfer is proposed to occur between species up to 100 Å apart.

(ii) Outer-sphere electron transfer reactions.
The two species approach within 5-20 Å of each other, but there is little overlap of inner coordination spheres. The interaction of donor and acceptor orbitals is small, e.g. $\mathrm{Co\ en_3^{3+}}$ - $\mathrm{Co\ en_3^{2+}}$.

(iii) Inner-sphere electron transfer.

The two reactants are considered to form an activated complex involving a single coordinated ligand bridge. For example, the activated state for the reaction between Cr^{2+}_{aq} and $Co(NH_3)_5Cl^{2+}_{aq}$ is considered to be on the basis of wide experimental evidence,

$$H_2O\ Cr^{2+}...Cl...Co(NH_3)_5.$$

These three types of reactions are considered in more detail below.

(i) The Grotthus mechanism.

The mechanism is based on the mechanism proposed by Grotthus in 1928, to account for the anomalously high mobility of the proton in aqueous solution. In electron transfer reactions, the charge is carried from one ion to another by a mechanism analogous to the transfer of charge by protons from one electrode to another during conduction. This type of mechanism, first proposed by Reynolds and Lumry,(47) may carry a charge from the reductant to the oxidant over fairly large distances.

R.A. Horne(46) has presented some strong evidence supporting this type of mechanism in the electron exchange reactions between Fe(II) and Fe(III) ions. However the mechanism has not been suggested for any other ions. Characteristics of the Fe(II) - Fe(III) exchange reaction which, according to Horne, show that the reaction is Grotthus controlled are:

(a) Very little variation in the rates and activation energies of a large number of substituted species, except where both species have no water molecules in the inner coordination sphere.

(b) Comparatively slow rate of electron transfer in non-aqueous solvents. An exception, recently reported by Reynolds et al,(37) is the rate of exchange in dimethyl sulphoxide, which was found to be very similar to the rate of the exchange in water. The exchange rate is also independent of traces of water.

(c) The activation energy plot for the reaction shows no discontinuity at the phase change, in going from aqueous solution to an ice.(46b, 48,49) The reactants are supposed to be trapped more than 100 Å apart in the ice, so that exchange must be occurring over a long distance.

(d) Deuterium isotope effects on the exchange rate have the same magnitude as isotope effects on the mobility of protons.

In the Grotthus mechanism the transfer of charge is slow enough to consider the bridging waters nuclear motions to be temporarily in equilibrium with the transferring charge. However if the charge-transfer is rapid, the Franck-Condon principle may hold so that the charge crosses the intervening water molecules without change in nuclear configuration. It is interesting to speculate on the relationship of this rapid electron transfer to resonant energy transfer.

(ii) Outer-sphere electron transfer reactions.

Probably many reactions are of this type, but mostly only those involving reactants with a strongly bound, substitution inert inner-coordination sphere can be placed in this category with any certainty. Examples are the $MnO_4^-/MnO_4^=$, $Co(en)_3^{3+}/Co(en)_3^{2+}$ exchange reactions.

Outer-sphere electron transfer reactions have been the subject of several theoretical papers. Early workers in the field include Libby, Weiss, R.J. Marcus et al and Laidler.(45) More recent and more extensive theoretical studies have been made by Marcus,(50) Hush(51) and Doganadze.(52)

Some common assumptions of the main theories are:

(a) The actual electron transfer process takes place under conditions where the Franck-Condon principle holds.

(b) Small overlap between donor and acceptor orbitals so that the splitting, due to their interaction, is small.

(c) The configurations from which electron transfer occurs are in thermal equilibrium with the remaining configurations.

Marcus has critically reviewed the theories up to 1963. (No major changes in theory have been reported since then, but Ruff(53) has put forward an entirely new theory.) Marcus concluded that the theories of Hush and Doganadze are basically equivalent to his own, although their approach to the subject is quite independent.

<u>Factors affecting the activation energy.</u>

All the theories aim at predicting the activation energy and rate of outer-sphere electron transfer reactions from first principles. To do this the activation energy is considered to be the sum of three terms:

a. Reorganization energy.
b. Coulombic repulsion energy.
c. Free energy of reaction.

a. <u>Reorganization energy</u>.

This term arises because of the application of the Franck-Condon principle. If electron transfer occurs between two species in their equilibrium configurations, the oxidized and reduced species thus formed will be in excited non-equilibrium configurations because of the change in their charge. Hence the energy of the products will be greater than the energy of the reactants, which is obviously not possible for an exchange reaction where $\Delta G^{\circ} = 0$. For example, if electron exchange occurs between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$, the Co-N bond lengths must be the same in both complexes in the transition state, or the energy of the state before electron transfer will be less than the energy of the state after electron transfer.

The reorganization energy may be divided according to Marcus into three terms:

(a) The solvent around a highly charged ion will have a different orientational and vibrational polarization than an ion with lower charge. Hence the solvent around the two ions must reorganize to a situation between that of the two ions ($\Delta G^{\neq}_{or}$).

(b) As pointed out above, the bond lengths of the ligand to metal bonds must reach a position between that of the reactant and product. This is called internal reorganization ($\Delta G^{\neq}_{ir}$).

(c) A small reorganization term arises from changes outside the inner coordination sphere due to changes inside the sphere in bond lengths etc. ($\Delta G^{\neq}_{s}$).

Marcus points out that only his theories take all three points above into account. However Hush only neglects the last point, which is probably small. Doganadze et al only took the first point (a), into consideration.

b. Coulombic repulsion.

The energy required to bring two ions to the activated state, due to the coulombic repulsion (or attraction) of the charges, contributes another factor to the activation energy, $\Delta G^{\neq}_{t}$. The assumption is made in the calculation of this value, of dielectric saturation inside the first coordination sphere.

c. ΔG^{o}, the free energy change for the reaction contributes a term $\Delta G^{o}/2$ to the activation energy. Hence $\Delta G^{\neq}$, the activation energy for the reaction is the sum of these terms.

$$\Delta G^{\neq} = \Delta G^{\neq}_{t} + \Delta G^{o}/2 + \Delta G^{\neq}_{or} + \Delta G^{\neq}_{ir} + \Delta G^{\neq}_{s}$$

The rate constant for reaction (k_r) may then be calculated from

$$k_r = \frac{kT}{h}\, e^{-\Delta G^{\neq}/RT}$$

where k, T, and h, have their common meaning. The theories also calculate the entropy of activation ($\Delta S^{\neq}$).

Adiabicity and non-adiabicity.

All these terms represent the energy required to bring the reactants to the activated state. If the reaction behaves adiabatically in a quantum mechanical sense, there is a high probability that all configurations of the activated state will proceed to form products. Alternatively if the probability is low, the reaction is termed non-adiabatic. The theories of R.A. Marcus and Hush are adiabatic theories, whereas Doganadze et al and R.J. Marcus et al, have considered non-adiabatic conditions. The non-adiabatic theories have to calculate the probability of the formation of products from the transition state. The results of R.A. Marcus and Hush's calculations have been compared to experimental activation energies and rate constants, and with some exceptions show reasonable agreement with experimental data. ($\Delta G^{\neq}$ within 3 kcal mole^{-1}.) (References 45d, 54, 50.) One such reaction is the Co(II) - Co(III) exchange, which may be slow due to the spin restriction discussed below.

The theory of Marcus also predicts that for similar reactions the relationship,

$$K_{12} = (K_{11}\, K_{22}\, K_{12})^{\frac{1}{2}}$$

will hold,

where K_{12}, K_{11}, K_{22} are the rate constants for the reaction between

A and B, A and A', B and B' respectively

$(A + B \rightarrow A' + B')$,

and K_{12} is the equilibrium constant for the reaction. This expression has been found to hold on some fast outer-sphere reactions.(54) The Marcus theory is most successful for reactions between large strongly bound anions. (Example, $IrCl_6^{3-}$ - $IrCl_6^{2-}$ exchange), where presumably, the conditions of outer-sphere electron transfer hold most rigorously.

Another factor which may play an important role in the rate of electron transfer reactions, is the spin multiplicity restriction as in the Co(III) - Co(II) exchange reactions. As Co(II) is spin free $(t_{2g}^5\ e_g^2)$, in the ground state, and Co(III) is spin paired (t_{2g}^6), a reorganization energy term is required to either spin pair the Co(II) or spin free the Co(III), so that they are in the same spin state. This spin restriction may also contribute a term to the activation energy of other reactions involving spin changes. If the energy gap between the spin free and spin paired states is small then the activation energy increase will also be small. Sutin and others(45c) have discussed the problem.

The ideas of spectroscopy may also be applied to arrive at the same conclusion. In this case a slower rate is predicted as a consequence of the reduced probability of crossing from one energy level to another, since the crossing is spin forbidden.

(iii) Inner-sphere electron transfer reactions.

Defined as reactions involving large overlap of the inner coordination spheres. The distinguishing feature of these reactions is that they often involve simultaneous ligand transfer. For example, the reactions of Co(II) with a number of oxidizing agents such as $FeCl^{2+}$, have been shown to be inner-sphere reactions by the formation of $CrCl^{2+}$. The substitution inert Cr(III) species could not have formed through substitution by a free Cl^-, so it is assumed to be substituted during electron transfer through the inner-sphere bridged intermediate $Cr^{2+}...Cl...Fe^{3+}$. Reactions that do not have a substitution inert product are difficult to categorize as inner or outer-sphere. However, Sutin(45d) has suggested some empirical rules to distinguish between the two mechanisms.

Factors affecting inner-sphere reaction rates.

1. Obviously the bridging ligand will have a large influence on the rate of reaction, through its ease of formation of the bridge and the conductivity of the bridge. The role of bridging groups has been discussed by Taube(45e).

2. The non-bridging ligands may also affect the reaction either (a) sterically: by the interaction with the other reactant hindering the formation of a bridge, or (b) second order ligand field effects, determining bond strengths of the bridging ligand.

3. One reactant must be substitution labile. For example, the Cr(II) aquo ligands are labile. It is possible that some reactions are controlled by the substitution-like process involved in forming

the activated complex. Taube et al(55) proposed a conjugation mechanism for inner-sphere reactions with conjugated bridging ligands. Halpern and Orgel(56) have attempted to put the theory into quantitative form.

A recent paper of remarkable interest is the paper of R.A. Marcus(57) on the chemiluminescent electron transfer reactions. Several reactions have been reported where products in electronically excited states are formed, which emit photons on returning to the ground state. Chandross and Sonntag(58) report some chemiluminiscent reactions between radical anions. For example, the reaction between 9,10 diphenylanthracene radical anion with benzoyl peroxide. Marcus discusses these reactions in terms of the accessibility of the intersection of the excited state orbital of the acceptor with the donor orbital. If the potential energy curve of the excited state of the acceptor intersects that of the donor at a reasonable energy level, then electron transfer to an excited state may occur, followed by luminescent return to the ground state. According to Marcus, the rate of reaction proceeding via the excited state may be much greater than the rate of reaction through the two ground states.

Chemiluminescent reactions are predicted to occur for very exothermic reactions.

It is probable that the formation of excited states occurs more often than is now known, because it is probable that in some systems, luminescent return to the ground state is too weak to be observed, or that non-radiative paths to the ground state predominate.

The reverse of the above process, electron transfer from an electronically excited state to the ground state, is also of interest theoretically. Photochemically produced excited states of reactants are likely to show different reaction rates than the ground states.

B. Substitution Reactions in Aqueous Solution

Included under the general heading of substitution reactions are all reactions which involve alteration of the inner coordination sphere of a complex ion (aquation, isomerization, exchange, etc.) without change in oxidation state. Some recent reviews of substitution reactions include Basolo and Pearson(60), Sutin,(45d) Sykes,(45f) and Wilkins.(61,62)

From the great body of research on these reactions qualitative relationships between various parameters, (such as bond strength, ligand charge and size, ligand polarizability, etc.) have been established. However it is not proposed to discuss here, all the results and theories of substitution reactions, but rather to consider selected fields of particular interest to this thesis.

(i) Direct substitution.

The majority of substitution reactions have a mechanism involving only the interaction of complex, substituting species and solvent. Table I.3 lists some rate constant data, which give an indication of the order of magnitude of the rate constants for the metal oxidation states recorded. (Most of the data are for reactions involving aquo ligands.) The figures in brackets are quoted by Sutin(45d) as characteristic rate constants for the replacement of a coordinated water molecule from hydrated metal ions. From the data two factors affecting the rate of substitution are observed.

Firstly, the rate of substitution shows a strong correlation with electronic configuration. Basolo and Pearson(60a) put the configurations in the following approximate order of increasing lability:- d_3; low spin d_6; d_8; low spin d_4; low spin d_5; the remaining configurations are more labile. Substantial agreement with this order of reactivity is found in the rate of water exchange of the hydrated ions.(45d) Basolo and Pearson have shown that this order is well explained on the basis of the relative contribution of the crystal field stabilization energy to the activation energy.

Secondly, the oxidation state and the charge on the ion influence greatly the rate of exchange. The higher oxidation states are generally less labile than lower oxidation states with the same electronic configuration.

Another general trend worth mentioning, is the increase in stability of complexes on going from the first to the third row transition elements, with a commensurate decrease in lability.

Table I.3

Orders of Magnitude of Substitution Rate Constants

	Bivalent Ions			Trivalent Ions		
d^1				V(IV)	10^3	(10^3)
d^2				V(III)	10^2	
d^3	V(II)	10	(2×10^2)	Co(III)	10^{-4}	(3.3×10^{-6})
d^4	Cr(II)	10^2	(7.4×10^9)			
d^5	Mn(II)	10^7	(3×10^7)	Fe(III)	10^2	(3×10^3)
d^6	Fe(II) low spin	1		Co(III)	10^{-4}	$(< 10^3)$
	high spin	10^4–10^7	(3×10^6)	Rh(III)	10^{-5}	(1.7×10^{-4})
d^7	Co(II)	10^6	(1.1×10^6)			
d^8	Ni(II)	10^3	(2.7×10^4)			
d^9	Cu(II)	10^7	(8.3×10^9)			
d^{10}	Zn(II)	10^7				
d^{10}	Hg(II)	10^9		Tl(III)		$(> 3 \times 10^9)$

A further factor, connected to the electronic structure, that affects reaction rates, is Jahn-Teller stretching, which increases the lability of some complexes. The effect, which is important in high spin d_4, low spin d_7, and d_9 complexes, is due to increased lability of the axial ligands; and hence of all ligands if the interchange of axial and equatorial positions is sufficiently rapid.

Of particular interest to this study are the low spin d_6, d_7, and d_8 configurations of the Pt(IV), Pt(III), and Pt(II) species, and the d_{10} configuration of Tl(III). Considering d_{10} configurations first, all the d_{10} complexes are very labile including Tl(III). The reactions of Pt(IV) show unusual characteristics so that comparison to other d_6 complexes is not justified, but low spin d_6 complexes are very inert and Pt(IV) is no exception. Few low spin d_7 complexes have been definitely characterised, and little is known of their lability. Jahn-Teller stretching might be expected to increase the lability of these complexes.

Mechanisms of substitution reactions.

1. Direct substitution.

Some general tendencies in the micro-mechanism of substitution reactions have been observed. Apart from reactions which react via small concentrations of a more labile oxidation state, many substitution reactions of octahedral complexes in aqueous solution have been found to proceed via an aquo species. For example, the substitution of $Co(NH_3)_5NO_3^{2+}$ by CNS^-, was shown spectrophotometrically to involve an aquo intermediate.(63) This is probably a result of the generalization that the incoming ligand does not have a large effect on the rate constant for substitution, so that substitution by water is more rapid because of the high concentration of the solvent molecules.

In general the rate of substitution is controlled more by bond breaking in the complex, than bond formation. This is particularly true in the more inert complexes of Cr(III), Co(III), and Ni(II). As Pt(IV) is isoelectronic with Co(III), the substitution reactions of Pt(IV) might be expected to be controlled by the same factors as Co(III) complexes. But the reactions of Pt(IV) complexes are catalysed by Pt(II), so that no comparison with Co(III) can be made.

In square planar complexes such as Pt(II), however, the rate of substitution may be controlled more by bond formation than bond breaking. For example, see Belluco.$^{(29)}$

Ion association is important in some reactions, the reaction of ion pairs such as $\text{Co en}_2(\text{H}_2\text{O})_2{}^{3+}.\text{SO}_4{}^{=}$ being rate determining, rather than direct reaction between the $\text{Co en}_2(\text{H}_2\text{O})_2{}^{3+}$ and the substituting $\text{SO}_4{}^{=}$.

2. Atom substitution.

The reactions discussed so far have been for the substitution of stable ligands, generally species with rare gas structures. (For example, Cl^-, SCN^-, H_2O.) A point of some concern to this study is whether unstable (reactive) species without rare gas structures will substitute in complexes. In particular, the possibility of exchange of Cl atoms with coordinated chloride has been considered. Little information appears to be available in the literature on substitution reactions involving such species. Two reactions which may have atom substitution mechanisms are the exchange reaction reported by Douglas,(64)

$$AgBr_2 + \overset{*}{B}r_2 \rightleftharpoons Ag\overset{*}{B}r_2 + Br_2$$

and the chloride exchange reactions between gaseous HCl and solid metal chlorides(65) ($SnCl_4$, $MgCl_2$, $CoCl_2$). The possibility of this type of reaction is much stronger in photochemical studies, as species such as Cl atoms are often present.

3. Catalysis of substitution reactions.

Some reactions are catalysed by the presence of cations such as Na^+, Mg^{2+} and H^+. Most substitution reactions do not exhibit this catalytic effect, but according to Basolo and Pearson, complexes with ligands that are strongly basic or have a large tendency to hydrogen bond, are often acid catalysed. An example is the acid hydrolysis of $Co\ en_2F_2^+$.

A few substitution reactions are catalysed by other oxidation states of the same metal. For example, Pt(IV) substitution reactions are well known to have a mechanism involving Pt(II). This type of reaction is actually a redox process.

SECTION I

CHAPTER 4: CHAIN REACTIONS

As this thesis describes a study of two chain reactions, it is worth considering the general characteristics of chain reactions, and in particular, exchange reactions with chain mechanisms.

1. General properties.

In broad terms, a chain reaction consists of one reaction (initiation) which initiates through the production of a reactive species (chain carrier), a series of other reactions (propagating reactions) leading to the formation of products; so that product formation is more rapid than the initiating process.

More specifically then, a chain reaction must have at least one initiation reaction producing a chain carrier, and one propagation reaction. With the exception of explosive reactions, most chain reactions with continuous initiation also have a termination step involving the destruction of chain carriers.

As discussed by Dainton(59) in his monograph on chain reactions, two types of chain reactions may be distinguished, branched and unbranched chain reactions. Branched chain reactions, where the number of chain carriers is increased by the propagation reactions, are not involved in the present study. (In branched chain reactions the rate of reaction increases with time.)

2. Exchange reactions.

A more detailed outline of the mechanism of an exchange reaction with a chain mechanism may be deduced from the nature of exchange reactions.

The chain carrier in a chain exchange reaction must have the following properties. It must be capable of inducing exchange between the exchanging species A and B, without being destroyed in the reaction (or at least producing a new chain carrier). (The ground states of A and B cannot act as chain carriers.) As exchange between A and B must involve both A and B, a chain carrier must react with both A and B. Assuming that a three-body collision mechanism is unlikely, two reactions must be involved. Three basic reaction paths for the reaction of the chain carrier C with reactants A and B, leading to exchange, may be envisaged.

(i) The simplest mechanism involving exchange between the chain carrier and both exchanging species,

$$\overset{*}{A} + C \rightleftarrows \overset{*}{C} + A$$

$$\overset{*}{C} + B \rightleftarrows \overset{*}{B} + C$$

where the * indicates a labelled species. An example might be,

$$\mathrm{P\overset{*}{t}Cl_6}^{2-} + \mathrm{Cl} \rightleftarrows \mathrm{PtCl_6}^{2-} + \overset{*}{\mathrm{Cl}}$$

$$\overset{*}{\mathrm{Cl}} + \mathrm{Cl}^- \rightleftarrows \overset{*}{\mathrm{Cl}}{}^- + \mathrm{Cl}$$

(ii) Chain carrier forms a 'complex' (association) with either A or B.

$$\overset{*}{A} + C \rightleftarrows \overset{*}{A}C$$

$$\overset{*}{A}C + B \rightarrow A + \overset{*}{B} + C$$

An example is the Pt(II) catalysed exchange between Cl^- and Pt(IV) complexes.

$$Pt(en)_2^{2+} + \overset{*}{C}l^- \rightleftarrows Pt(en)_2\overset{*}{C}l^+$$

$$Pt(en)_2\overset{*}{C}l^+ + Pt(en)_2Cl_2^{2+} \rightleftarrows Pt(en)_2\overset{*}{C}l_2^+ + Pt(en)_2^{2+} + Cl^-$$

where $Pt(en)_2^{2+}$ is acting as a chain carrier. Note: In practice this may not be described as a chain reaction as there is no initiating reaction. However if, for example, the Pt(II) was created by irradiation, then the system would have all the characteristics of a chain reaction.

(iii) Chain carrier induces exchange between associated A and B.

$$\overset{*}{A} + B \rightleftarrows \overset{*}{A}B$$

$$\overset{*}{A}B + C \rightarrow A + \overset{*}{B} + C$$

A possible mechanism for the chloride exchange above is,

$$Pt(en)_2Cl_2^{2+} + \overset{*}{C}l^- \rightleftarrows Pt(en)_2Cl_2.\overset{*}{C}l^+ \text{ (ion pair)}$$

$$Pt(en)_2Cl_2\overset{*}{C}l^+ + Pt(II) \rightarrow Pt(en)_2^{2+} + Cl^- + Pt(en)_2\overset{*}{C}l_2^{2+}$$

Of course, other more complicated reaction paths may be imagined, but they will all correspond to one of the above forms, except where more than one chain carrier is involved. All these reaction schemes involve two reactions, which is the minimum number of chain propagating steps in a chain exchange reaction.

Mathematical treatment of chain reactions.

For non-branched reactions with constant initiation rates, simple long time reaction kinetic principles are applicable, after sufficient time has elapsed to obtain a steady state concentration of chain carrier. The treatment of time dependent conditions is fully developed in Dainton's monograph and will not be reproduced here.

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SECTION II

THE INFLUENCE OF ULTRAVIOLET LIGHT ON THE ELECTRON EXCHANGE REACTION BETWEEN Tl(I) AND Tl(III) IONS IN AQUEOUS SOLUTION

Summary

The ultraviolet catalysed electron exchange reaction between Tl(I) and Tl(III) perchlorates in aqueous perchloric acid has been studied and found to be a chain reaction. A mechanism involving Tl(II) as a chain carrier is proposed to account for the observed dependence of quantum yield on the experimental variables.

A brief review of the literature relevant to the study is presented in the first chapter.

SECTION II

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SECTION II

CHAPTER 1: INTRODUCTION

A. Properties of Aqueous Thallous and Thallic Perchlorate Solutions

Essential to a discussion of the reactions involved in the exchange reaction is a knowledge of species present in solution.

(a) Tl(I) species.

The only Tl(I) species present in significant quantities in a solution 1 molar in perchloric acid is the aquated Tl^+ ion. Lindsay(1) has determined the stability constant for the TlOH ion pair to be $3.0\ l\ mole^{-1}$ at 25°C, i.e.

$$\frac{[TlOH]}{[Tl^+][OH^-]} = 3.0\ l\ mole^{-1}$$

From this equation $[TlOH] < 3.0 \times 10^{-13}\ [Tl(I)]$ for solutions 1 mole l^{-1} in $[H^+]$, which is considered negligible.

Freeman et al(2) reported the chemical shifts of the thallium nuclear magnetic resonance for solutions of thallium hydroxide, fluoride, acetate, formate, nitrate and perchlorate. The perchlorate anion showed the smallest chemical shift. The authors suggested from their results that thallous perchlorate is completely dissociated. This is expected as the association between the perchlorate anion and cations is generally weak, presumably partly because of the small charge and large radius of the anion. Very few coordination complexes containing perchlorate ion have been prepared.(3) Association between highly charged cations and perchlorate (e.g. Tl(III) and perchlorate ion), is also found to be weak, so that the interaction with a singly charged species is expected to be extremely weak.

(b) Tl(III) species.

The greatest amount of information about the thallic species present in solution is obtained from a study of thallic perchlorate spectra by Waind and Rogers.(4) The spectra of aqueous thallic and thallous solutions are shown in Fig. II.1 (determined on a Unicam SP800 automatic spectrophotometer).

Waind and Rogers studied the acid dependence of the thallic spectrum over a perchloric acid concentration range of .5 to 6.0 mole l^{-1}. The variation in apparent extinction coefficients with acid concentration (at constant ionic strength) could be explained over the whole range, by the existence of two absorbing species in equilibrium. The equilibrium proposed was

$$Tl^{3+} \rightleftharpoons TlOH^{2+} + H^+ \qquad k_1$$

They found no evidence for the existence of the dihydroxy species, $Tl(OH)_2^+$. The k_1 values determined were in agreement with the values determined potentiometrically by Biederman.(5) (The value found by Waind and Rogers at 25°C and ionic strength of 3 was $K_1 = .069 \pm .004$. Biederman reported a value of .073 under the same conditions.)

Waind and Rogers interpreted the effect of sodium perchlorate

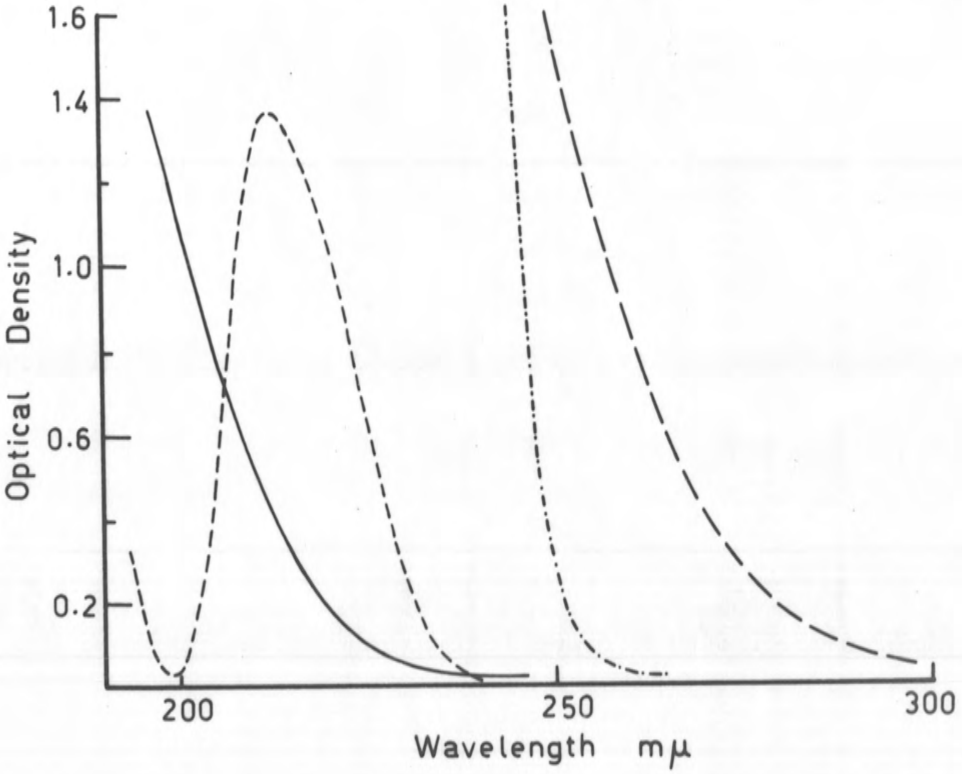


FIG. II·1 Absorption Spectra of [Tl(1)] and [Tl(III)] Perchlorates in aqueous Perchloric Acid.

—— [Tl(III)] = 3.2×10^{-4} mole $l.^{-1}$ ---- [Tl(1)] = 1.6×10^{-4} mole $l.^{-1}$

— — [Tl(III)] = 4.0×10^{-2} " " -·-·- [Tl(1)] = 8.0×10^{-2} " "

concentration on the spectrum in terms of ionic strength effect on the acidity constant K_1. Thus perchlorate-thallic interaction does not affect the spectrum in the region studied. But, although outer-sphere ion pair formation does give rise to strong absorption bands, in the case of perchlorate ions this absorption may well occur below 200 mμ, and thus would not be detected. Waind and Rogers also reported that the thallous and thallic spectra were independent, suggesting no interaction between the thallous and thallic cations.

Figgis(6) studied the complexing of various anions with thallic ion in aqueous solution, by the application of nuclear magnetic resonance spectroscopy. From the chemical shifts of the Tl^{205} NMR spectrum he concluded that Cl^-, Br^-, I^- and SO_4^{2-} complexed strongly with thallic ion, but no evidence for complexing was found with perchlorate and fluoride.

The thallic aquo ion may be hexa-coordinated, by analogy to other complex ions of thallic, such as the Cl^-, Br^- and N_3^- complexes, which are probably hexa-coordinated. However, work on the chloride and bromide complexes indicates that two ligands may be more weakly bonded than the other four.(7)(18b)

Both thallous and thallic perchlorate solutions are kinetically stable at room temperature to oxidation or reduction by light or oxygen. Hermann and von Grube(8) in 1920 reported that thallic sulphate solutions reduced in visible light. However, no evidence of reduction has been found in later studies or in this thesis.

(c) Perchloric acid.

Many studies of aqueous perchloric acid have been reported, including a recent review by Pearson.(9) Perchloric acid is a very strong acid and is regarded as completely dissociated up to about a concentration of 3 mole l^{-1}.

Although perchlorate salts in the presence of oxidizable organic matter act as powerful oxidizing agents, the perchlorate ion itself shows no oxidizing properties in solution.

The aqueous acid is stable under normal conditions, and in fact, may be heated to 100°C without any appreciable decomposition, at all concentrations of acid up to the commercially available, constant boiling, 72% mixture.

B. The Exchange and Redox Reactions of Thallium Ions

(a) The thermal exchange reaction between Tl(I) and Tl(III).

The thermal exchange reaction has been studied under a wide variety of conditions. The rate of exchange has been determined as a function of acidity, ionic strength, and the concentration of the anions Cl^-, Br^-, CN^-, $SO_4^{=}$ and NO_3^-, as well as ClO_4^-.

As the thallium system has the unusual property of involving two electron transfer, a great deal of effort has been put into trying to determine whether the mechanism of exchange involves simultaneous two electron transfer (one stage reaction), or two separate (in time) single electron transfers (two stage). In the latter case, the Tl(II) oxidation state is present as an intermediate. The theories of Marcus and Hush predict that this mechanism will be more energetically favourable than a one stage mechanism. The kinetic evidence strongly suggests that a separate ion, Tl(II), does not exist as an intermediate in the thallium(I)-thallium(III) exchange reaction. However, the kinetics cannot distinguish between simultaneous two electron transfer, and two separate electron transfers occurring without dissociation of the Tl(II)-Tl(II) pair formed after the transfer of one electron.

The next section discusses the results and conclusions that have been drawn from the thallium electron exchange studies. Apart from the question of Tl(II) as an intermediate, interest is also focussed on the categorization of the reaction into inner or outer-sphere mechanisms.

The exchange reaction in aqueous perchloric acid has been studied by Prestwood and Wahl(10), Gilks et al(12b), Dodson(13,17), Born et al(14), Wiles(20), and Teresa Palma Donas(16). Apart from Born et al, they agree that the main reactions (in the range 1.0 to 6.0M $HClO_4$) are

$$\overset{*}{Tl}{}^{3+}_{aq} + Tl^{+}_{aq} \rightleftarrows Tl^{3+}_{aq} + \overset{*}{Tl}{}^{3+}_{aq} \qquad (1)$$

and

$$\overset{*}{Tl}OH^{2+}_{aq} + Tl^{+}_{aq} \rightleftarrows TlOH^{2+}_{aq} + \overset{*}{Tl}{}^{+}_{aq} \qquad (2)$$

The rate constants for these two reactions are of the same order of magnitude. For example, Roig and Dodson(17b) reported the rate expression:

$$R_{ex} = .253\ [Tl(I)][Tl^{3+}] + .089\ [Tl(I)][TlOH^{2+}]$$

at 25°C and ionic strength 3.68. Born et al(14) from some results at low acid strength, concluded that ClO_4^- anion was directly affecting the rate by ion pairing. However their conclusion is drawn from very few results, and other evidence would suggest little interaction between Tl(III) and ClO_4^-.

The studies in the presence of anions may be divided into two groups:

1. $SO_4^{''}$ (23,20) and $NO_3^{''}$ (10) and ClO_4^- (10-17), may be included in this group. A linear increase of rate with increase in the concentration of the anion is observed with these three anions.

2. Cl^-(12a, 17-19, 21a), Br^- (21b), and CN^- (22). A more complex dependence on anion concentration is reported for these anions. They all show a decrease in rate at low concentrations, followed by an increase at high concentrations. The results may be explained by different rates of reaction for the different complex species present. For example, the decrease in rate at low anion concentrations is explained by the assumption that the rate of reaction between the first ion-paired thallic species (e.g. $TlCl^{2+}$) and thallous ion is slower than the reaction between the aquated ions.

The decreased rate with the monosubstituted species is possibly not predicted on the basis of the theory of Marcus, as the lower charge on the reactant is expected to increase the rate of exchange. However the presence of the associated anion necessitates the apparent transfer of the ligand in the overall mechanism. This may occur by (i) atom transfer during the exchange process or (ii) by the normal processes of association following electron transfer with non-zero free energy change.

Higginson(24) suggested that if Tl(II) was an intermediate in the reaction, a high entropy of activation would be expected, because of the expected large radius of the lone s electron orbital of the Tl(II) ion. This assumes that the activated state has the charge distribution approximating that of Tl(II). The value of $\Delta S^{\neq}$ of approximately -20 e.u. would not, on this argument, be consistent with Tl(II) as intermediate.

Stronger evidence that Tl(II) is not involved comes from the study of redox reactions of thallium with other cations.

The lability of thallous and thallic complex ions has not allowed a distinction between outer or inner-sphere mechanisms to be made.

(b) The redox reactions of thallium ions.

Table II.2 lists many of the redox reactions reported in the literature with a note on the mechanism postulated by the authors. The reactions show different characteristics dependent on the number of equivalents per mole of reactant shown in the usual redox reactions of these ions. Generally Tl(II) is found to be an intermediate

Table II.2

Reactants	Non-Thallium Product	Suggested Mechanism	Reference
Tl(III) - Fe(III)	Fe(II)	2 stage	25
V(IV)	V(V)	"	36,38
V(III)	V(IV)	"	36,38
$Ru(Ophen)_3^{2+}$	Ru(III)	"	28
U(IV)	U(VI)	1 stage	39,29
Hg(I)	Hg(II)	"	30
V(II)	V(IV)	"	41
Cr(II)	$(Cr(III))_2$	"	31
Sn(II)	Sn(IV)	"	32
N_2H_4	N_2, H_2O	"	33
SO_3''	SO_4''	"	40
Tl(I) - Co(III)	Co(II)	2 stage	35
Ce(IV)	Ce(III)	"	35,37

when a one equivalent reactant is used, but two equivalent reactants convert one thallium species to the other directly.

One equivalent reactants.

The authors' evidence for suggesting Tl(II) as an intermediate is in all examples (except Tl(III) - V(III) reaction), based on the observation of retardation of the rate of reaction by the presence of the non-thallium product. The retardation is consistent with a two stage mechanism. For example with the Tl(III) - Fe(II) reaction, the mechanism

$$\mathrm{Tl(III)} + \mathrm{Fe(II)} \rightleftarrows \mathrm{Tl(II)} + \mathrm{Fe(III)}$$

$$\mathrm{Tl(II)} + \mathrm{Fe(II)} \rightarrow \mathrm{Tl(I)} + \mathrm{Fe(III)}$$

is consistent with the reported rate law,

$$\mathrm{Rate} = \frac{k[\mathrm{Tl(III)}][\mathrm{Fe(II)}]}{[\mathrm{Fe(III)}]}$$

An analogous kinetic expression is reported for the reduction of Tl(III) by Hg(I). However, in this case the authors favour the alternative mechanism,

$$(\mathrm{Hg(I)})_2 \rightleftarrows \mathrm{Hg(II)} + \mathrm{Hg(0)}$$

$$\mathrm{Hg(0)} + \mathrm{Tl(III)} \rightarrow \mathrm{Tl(I)} + \mathrm{Hg(II)}$$

and hence a single stage mechanism.

With two equivalent reactants (U(IV), Sn(II)) the kinetic evidence supports a one stage mechanism. The Tl(III) - U(IV) reaction is thought to be a single stage mechanism, as added scavengers for Tl(II) or U(III) (Cu^{2+}, Hg^{2+}, Ag^{+}), did not affect the reaction rate. Similarly in the Sn(II) - Tl(III) reaction, the absence of any effect of added Co(III) as a scavenger for Sn(III), led the authors to support a single stage mechanism.

A single stage mechanism for two equivalent reactants is inituitively most likely, as the intermediate after transfer of one electron (two unstable oxidation states in close proximity), would probably transfer the second electron rapidly. The high free energy difference favouring the formation of products is likely to result in very low activation energies for the second electron transfer.

Perhaps the group of reactions with the strongest evidence supporting their mechanistic classification, is the group in which the non-thallium reactant forms different products on reaction with one or two equivalent redox species. The reactants in this group are hydrazine (N_2H_4), sulphite (SO_3'') and Cr(II). In all cases on reaction with thallium(III) the products expected for two equivalent oxidants are found. Thus, with the possible exception of the Tl(III) - V(IV) reaction, in all examples where the non-thallium reactant has an accessible oxidation state different by two equivalents, the reaction with thallium probably proceeds by a one stage mechanism.

Dorfman and Gryder, from their results on the Tl(I) - Ce(IV)(35) reaction, put forward an interesting argument which strongly supports a one stage mechanism for the thallium(I) - thallium(III) exchange reaction. If both reactions proceed by a two stage mechanism, the rate of reduction of Ce(IV) by Tl(III) should not be less, in the presence of Tl(III), than the rate of exchange between Tl(I) and Tl(III), as both reactions are controlled by the concentration of Tl(II).

The observation that the rate of the exchange reaction was much less than the reduction rate, led the authors to conclude that both reactions could not be two stage reactions. Further evidence suggesting that the Ce(IV) - Tl(III) reaction was a two stage reaction, thus necessitates that the exchange reaction has a single stage mechanism.

Sykes(36) using a similar argument applied to the V(IV) - Tl(III) reaction, came to the same conclusion. He noted that since Tl(I) has no effect on the above redox reaction, Tl(II) cannot be produced by the exchange reaction, as an increase in Tl(II) concentration would increase the rate of the V(IV) - Tl(III) reaction.

The evidence for inner or outer-sphere reactions is also inconclusive in these reactions. The Cr(II)(21,29) reaction would normally give information on the nature of reaction because of the inertness of the products (Cr(III) complexes). However, the suggested mechanism for reaction via a Cr(IV) species still leaves the question unanswered.

The mechanisms of electrochemical reactions are closely related to redox reactions, so that it is interesting to look at electrochemical studies on thallium. Catherino and Jordan(42) studied the electrolysis of thallous and thallic perchlorate solutions at smooth platinum electrodes, and concluded that Tl(II) was an intermediate in the electrolysis of these ions. A similar conclusion was reached by Vetter and Thiemke(43) from electrolysis studies of thallium(I) and thallium(III) in sulphuric acid. However James,(44) in a later study stated that the above workers had misinterpreted their results. James concluded that evidence for Tl(II) as an intermediate could not be deduced from electrochemical experiments.

C. Photochemical and Radiation Studies

Probably the most instructive information, from the point of view of this thesis, may be obtained from several papers on studies of irradiation of thallium solutions. Two very similar studies to this thesis both suggest Tl(II) as an intermediate in exchange reactions between Tl(I) and Tl(III) species. Schäfer(45) studied the action of ultraviolet light on the rate of electron exchange between Tl(I) and Tl(III) in aqueous hydrobromic acid. Quantum yields greater than one were found and the following chain mechanism postulated:

$$\mathrm{TlBr}^{+} + h\nu \xrightarrow{k_1} \mathrm{TlBr}^{+} + \mathrm{Br} \tag{1}$$

$$\mathrm{TlBr}^{+} + \overset{*}{\mathrm{Tl}}{}^{+} \overset{k_2}{\rightleftarrows} \mathrm{Tl}^{+} + \overset{*}{\mathrm{Tl}}\mathrm{Br}^{+} \tag{2}$$

$$\mathrm{TlBr}_2{}^{+} + \overset{*}{\mathrm{Tl}}\mathrm{Br}^{+} \overset{k_3}{\rightleftarrows} \overset{*}{\mathrm{Tl}}\mathrm{Br}^{+} + \mathrm{TlBr}_2{}^{+} \tag{3}$$

$$\mathrm{TlBr}^{+} + \mathrm{Br} \rightarrow \mathrm{TlBr}_2{}^{2+} \tag{4}$$

However, the observed dependence of quantum yields on the rate of light absorption I,

$$\phi \propto \frac{1}{\mathrm{I}} \frac{1}{[\mathrm{Tl(III)Br}]}$$

is not consistent with this mechanism. The mechanism is analogous to the one postulated for the present study in the absence of Br^- ions.

Irradiation at 450 mμ, where the species TlBr was said to absorb, had no effect upon the reaction.

Challenger and Masters(46) irradiated a mixture of Tl(I) and Tl(III) in sulphuric acid with x-rays. Their results for the rate of exchange were fitted to the empirical expression,

$$\text{Rate} = K\ [\text{Tl(III)}]^{.503} I_{abs}^{\ .670}\ ,$$

where I_{abs} is the intensity of the x-rays. They suggested a Tl(II) chain carrier, in a chain mechanism of the type,

$$\overset{*}{\text{T}}\text{l(III)} + \text{Tl(II)} \rightleftharpoons \text{Tl(III)} + \overset{*}{\text{T}}\text{l(II)}$$

$$\overset{*}{\text{T}}\text{l(II)} + \text{Tl(I)} \rightleftharpoons \text{Tl(II)} + \overset{*}{\text{T}}\text{l(I)}$$

Challenger and Masters reported the high G value of 32 ions/100 e.v. in the absence of additives, which fell to .2 ions/100 e.v. in the presence of .0167M Fe(II) ion. This high G value indicates a chain reaction, as the G value for the formation of primary radiation products in water is less than 5.(47)

No dependence on Tl(I) concentration was found in the range of concentrations studied, in contrast to the present study, but in sulphuric acid complex thallic-sulphate species are almost certainly present.

Recently Cercek et al(48) published a pulse radiolysis study of thallous sulphate solutions. In de-aerated 10^{-2}M thallous solution at pH 6.5, an absorption spectrum with two peaks was observed at the end of a pulse of 4 MeV electrons. From various effects of

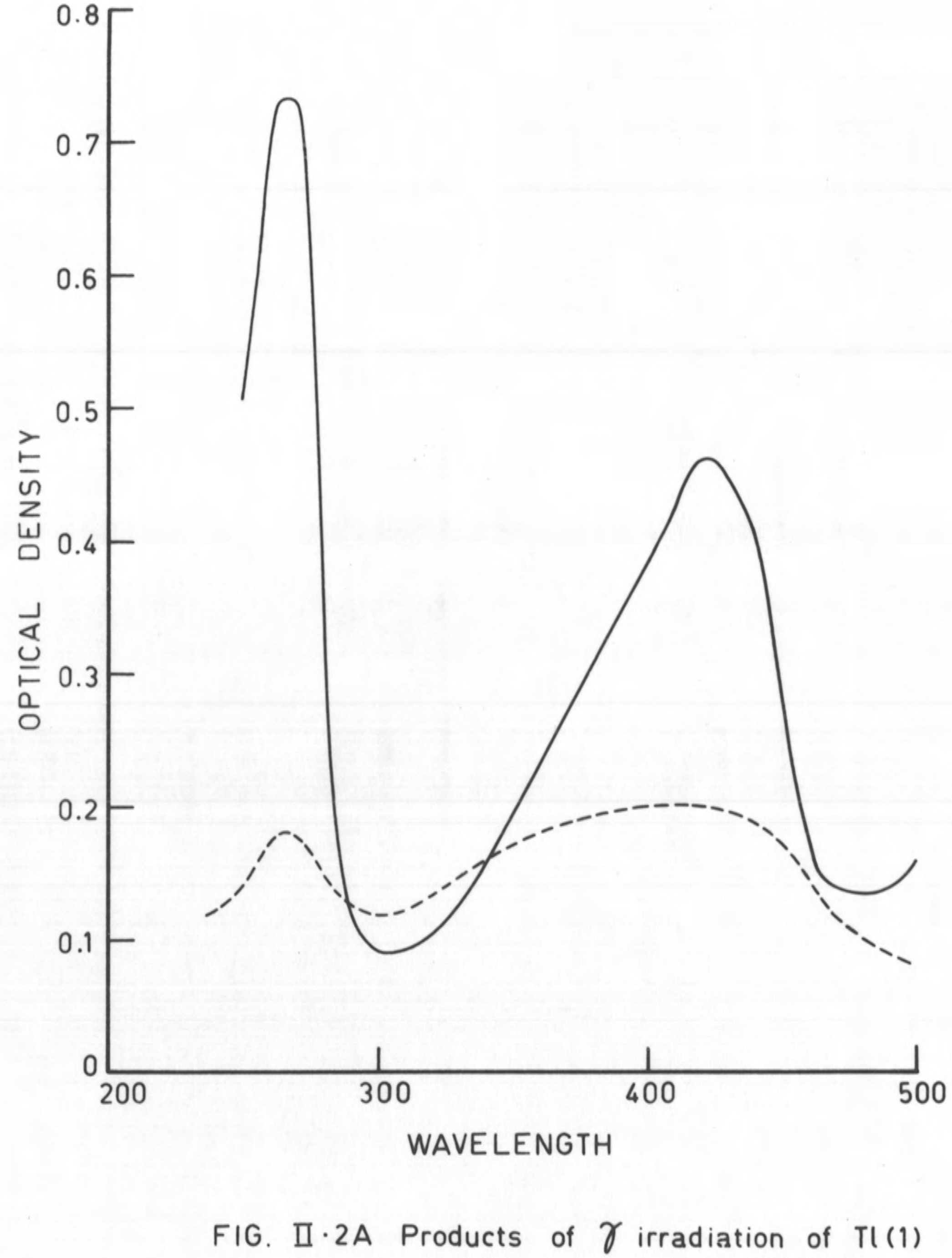


FIG. II·2A Products of γ irradiation of Tl(1)
—— Brown and Dainton (49)
---- Cercek et. al. (48)

scavengers, and arguments based on knowledge of the primary radiation products of water, they assigned the peak at 400 mμ to a Tl_2^+ species and the peak at 260 mμ to Tl^{2+}. The Tl_2^+ is predicted to form from the reaction of hydrated electrons with Tl^+. The species is unlikely to occur in the present study.

The spectrum of the Tl^{2+} species is reproduced in Fig. II.2A. The molar extinction coefficient of Tl^{2+} was found to be 5400 l mole^{-1} cm, and the band width (δ+) approximately 20 mμ. The most likely observable band for a thallium(II) ion would be an s-p transition. The corresponding transition in Tl(I) has a maximum at 210 mμ with maximum extinction coefficient (9×10^3), and a half-width of 20 mμ. From the time decay of the Tl(II) peak, the rate constant for the reaction

$$Tl(II) + Tl(II) \rightarrow Tl(III) + Tl(I)$$

was found to be $2.3 \pm .8 \times 10^9$ l mole^{-1} sec^{-1} at zero ionic strength. Dainton and Brown$^{(49)}$ reported the results of γ-irradiation of thallous ion trapped in a frozen sulphuric acid matrix.

The spectrum of the resultant ice is also shown in Fig. II.2A. The authors state "The peaks with λ_{max} = 417 and 267 mμ may be correlated with the absorptions reported by Cercek in the liquid phase and assigned to Tl^0 and Tl^{2+} respectively".

Conclusions drawn from thallium literature.

There is substantial evidence suggesting Tl(II) as an intermediate in some thermal thallium redox reactions, which together with the results of radiation studies, strongly support the conclusion of the existence of a Tl(II) species in aqueous solution, albeit a short lived species.

Several deductions about the nature of the Tl(II) may be made from the available data.

1. The reaction between Tl(II) and water is slow, i.e. it does not compete with the disproportionation.

2. The comparative reaction rates of Tl(II) with various other species have been determined. The one of interest to this thesis is the rate constant ratio reported for the reactions of ferrous and ferric ions,(25)

$$\left\{\frac{K\ Fe(II)}{K\ Fe(III)} = 27\right\} .$$

3. The rate of the disproportionation reaction,

$$Tl^{2+} + Tl^{2+} \rightleftharpoons Tl^{3+} + Tl^{+}$$

is very rapid with a rate constant quoted by Cercek et al(48) of $2.3 \pm .8 \times 10^{9}$ l mole^{-1} sec^{-1} at $\mu = 0$.

Object of present research.

The present study was started for its interest in two fields.

1. In photochemistry, it was of interest to see whether the absorption of light by the $TlOH^{2+}_{aq}$ species produced appreciable

quantities of Tl(II). If this was the case, the method might prove to be a useful means of producing Tl(II), and possibly may be extended to the preparation of other unstable oxidation states.

2. The reactions of Tl(II) with itself and Tl(I) and Tl(III) were of importance in the complete understanding of the thermal redox reactions of thallium. For example, a knowledge of the rate constant for the reaction,

$$\mathrm{Tl(II)} + \mathrm{Tl(II)} \rightarrow \mathrm{Tl(III)} + \mathrm{Tl(I)} \qquad (1)$$

would help to establish the feasibility of a mechanism for the thermal exchange reaction involving initial transfer of one electron, followed by rapid transfer of the second electron.

$$\mathrm{Tl(III)} + \mathrm{Tl(I)} \rightarrow \mathrm{Tl(II)}\ldots\mathrm{Tl(II)} \rightarrow \mathrm{Tl(II)} + \mathrm{Tl(III)}$$

If reaction (1) is diffusion controlled, Tl(II) is unlikely to form as a single entity, as the two Tl(II) species could destroy each other before dissociation can occur.

The rates of the exchange reactions,

$$\mathrm{Tl(II)} + \mathrm{Tl(I)} \rightleftharpoons \mathrm{Tl(II)} + \mathrm{Tl(I)}$$

$$\mathrm{Tl(II)} + \mathrm{Tl(III)} \rightleftharpoons \mathrm{Tl(III)} + \mathrm{Tl(II)}$$

were of interest to compare to the theoretically predicted rates of Hush and Marcus.

The thallous-thallic system has some practical advantages for this sort of study.

(i) The two valence states are stable over long periods.

(ii) The electron exchange reaction is slow so that catalysis may be observed without severe interference by the thermal reaction.

With this introduction, the next chapter deals with the experimental methods used in the study.

SECTION II

CHAPTER 2: EXPERIMENTAL

A. Introduction

The determination of the quantum yield for exchange

$$\phi_{ex} = \frac{R_{ex}}{I_{abs}}$$

requires the experimental determination of three independent parameters.

1. The rate of exchange R_{ex} (in units of mole l^{-1} min^{-1}).
2. The absorbed light intensity I_{abs} (in units of Einstein absorbed per litre of reactant solution per unit time).

In turn, this is determined by the product of two terms; the incident light intensity and the fraction of light absorbed. The incident light intensity was determined by chemical actinometry, and

3. The fraction of light absorbed was determined from data in the literature, and experimental measurements of extinction coefficients of reactant solutions.

These three techniques are discussed in different sections of the chapter. Some details of techniques particularly applicable to small sections of the results, have been left until those results have been discussed. One other section on the preparation and standardization of the reactant solution is included at the beginning.

B. Preparation of Reactant Solutions

In all preparations doubly distilled water was used. Three solutions,

A. thallic perchlorate,

B. thallous perchlorate, and

C. perchloric acid,

were independently prepared and analysed, and reactant solutions prepared by quantitatively mixing the three solutions.

(a) Thallic perchlorate.

Two methods were used for the preparation of thallic solutions.

1. Thallic oxide (BDH Lab. Reagent) was dissolved in 72% $HClO_4$ acid at approximately 80°C. The solution was kept at this temperature with an infrared lamp, or on a water bath for several days to effect solution.

2. Thallous perchlorate (prepared from thallous carbonate, BDH Lab. Reagent) solutions were electrolysed to thallic with cylindrical platinum gauze electrodes at 25 volts and .2 amps. The thallous perchlorate was oxidized at the anode in one beaker, which was connected to a second beaker containing perchloric acid (approximately 1 mole l^{-1}) by an inverted U tube filled with the same perchloric acid (approximately 1 cm diameter, 10 cm length). Glass sinters at the end of the tube prevented rapid diffusion of solution to and from the tube. At the end of electrolysis no thallous could be detected with CrO_4^{-}/CN^{-} precipitating mixture (discussed later).

The upper limit of thallous concentration in the thallic, of concentration ca. 3×10^{-2} mole l^{-1}, was therefore ca. 10^{-4} mole l^{-1}.

Standardization of thallic solutions.

The thallic perchlorate had to be standardized for perchloric acid concentration as well as thallium concentration.

1. Acid.

Three methods were used for the acid standardization of thallic solutions.

(i) The acid was titrated against standard .1N NaOH, to a methyl red end point, in the presence of a large amount (several gm) of acid free NaCl. The NaCl prevented precipitation of Tl_2O_3 which masked the end point. However, this method was only satisfactory if the thallic concentration was less than 10^{-4}M.

(ii) The second method involved the reduction of the thallic ion to thallous ion with SO_2 gas (from a cylinder), and boiling off the excess SO_2 (more than ½ hour boiling) before titrating the acid with standard NaOH. This method gave slightly inconsistent results (2% variation) for unknown reasons.

(iii) The best method was the potentiometric titration of the acid against standard NaOH. The thallic oxide precipitated in the pH range (4-5), but when all the hydroxide had precipitated the titration was carried out in the normal fashion. Allowance for the precipitated thallic hydroxide had to be made in the calculation. The end point was determined by plotting the differentials ($\Delta pH/\Delta v$) against volume (v), where ΔpH is the change in pH for a change Δv in the added volume of base.

2. Thallic ion determination.

Three methods for the determination of thallic ion concentration were used.

(i) Thallic ion was determined gravimetrically as the 8-hydroxyquinoline complex of Tl(III). The method of Moeller and Cohen(50) was followed except that the complex was dried at less than 100°C as charring occurred at the recommended temperature.

(ii) (51) The thallic was reduced to thallous with SO_2 gas (the solution boiled to remove excess), and the thallous was determined volumetrically against standard KIO_3. Because of some doubt about this method a third method was used.

(iii) The method was developed by Daugherty.(27) The thallic was reacted with a known excess of standard ferrous solution, warmed to ca. 80°C on a water bath for a few minutes and cooled to less than room temperature. A known excess of ceric ammonium sulphate (in H_2SO_4) was then added, and the excess back titrated against the standard ferrous solution using ferroin as indicator. This was the easiest method to use, but the gravimetric method was the most reproducible ($< \frac{1}{2}\%$).

On one solution all three methods of determination gave consistent results (within 1%).

(b) Preparation of thallous perchlorate.

Thallous perchlorate was prepared from BDH laboratory reagent by dissolution in dilute perchloric acid. The solution was standardized volumetrically by titration against standard KIO_3 to an iodine monochloride end point.(53) The acid strength was determined by titration against standard NaOH.

In later preparations the thallous carbonate was recrystallized from triply distilled H_2O.

In one case, solid thallous perchlorate was prepared by dissolution of thallous carbonate in dilute perchloric acid, at concentrations greater than the solubility of thallous perchlorate. The precipitated solid was dried at approximately 120°C. At this temperature fuming was observed which was attributed to excess perchloric acid. On dissolving the thallous perchlorate in water, a yellow precipitate formed. This was shown to be thallous chromate. The weight of precipitate represented less than 1% of the total thallous. The appearance of thallous chromate under these circumstances was attributed to the oxidation of Cr(III) impurity by the hot perchloric acid during drying. This solution was filtered to remove the thallous chromate and used to prepare a reactant solution, which gave results consistent with solutions prepared in the normal manner.

(c) Perchloric acid.

Some batches of perchloric acid were twice distilled under vacuum at pressures of less than 1 cm and temperatures less than 100°C. At this temperature according to Pearson,(9) there is no appreciable decomposition to yield chloride ion. Otherwise the A.R. acid was used without purification. Some locally produced A.R. acid gave low results before distillation. Baker Analysed Reagent was used without distillation.

Preparation of active tracer. (thallous and thallic)

The tracer Tl^{204} was prepared by neutron irradiation of thallous carbonate in the Lucas Heights reactor, yielding a specific activity of 20 mc/gm. 40 mg (.8 millicurie) was dissolved in 100 ml of dilute perchloric acid, giving a solution of $Tl(I)^{204}$ perchlorate.

$Tl^{204}\ (ClO_4)_3$ was produced by oxidation of thallous active solution by ozone(65) or electrolytically at platinum electrodes (see thallium(III) preparation). Two to three drops per 10 ml was sufficient for one kinetic run.

C. Experimental Arrangement for Photolysing Solutions

The experimental arrangement is illustrated in Fig. II.2. The silica reaction cell (cylindrical 2.5 cm diameter, 1 cm length) was reproducibly placed approximately 3 cm from a flat silica window (6 x 6 cm square) in the wall of the perspex water bath. The water bath containing deionized water was thermostatted to ± .1°C. The light source was a low pressure mercury arc (Hanovia portable ultraviolet

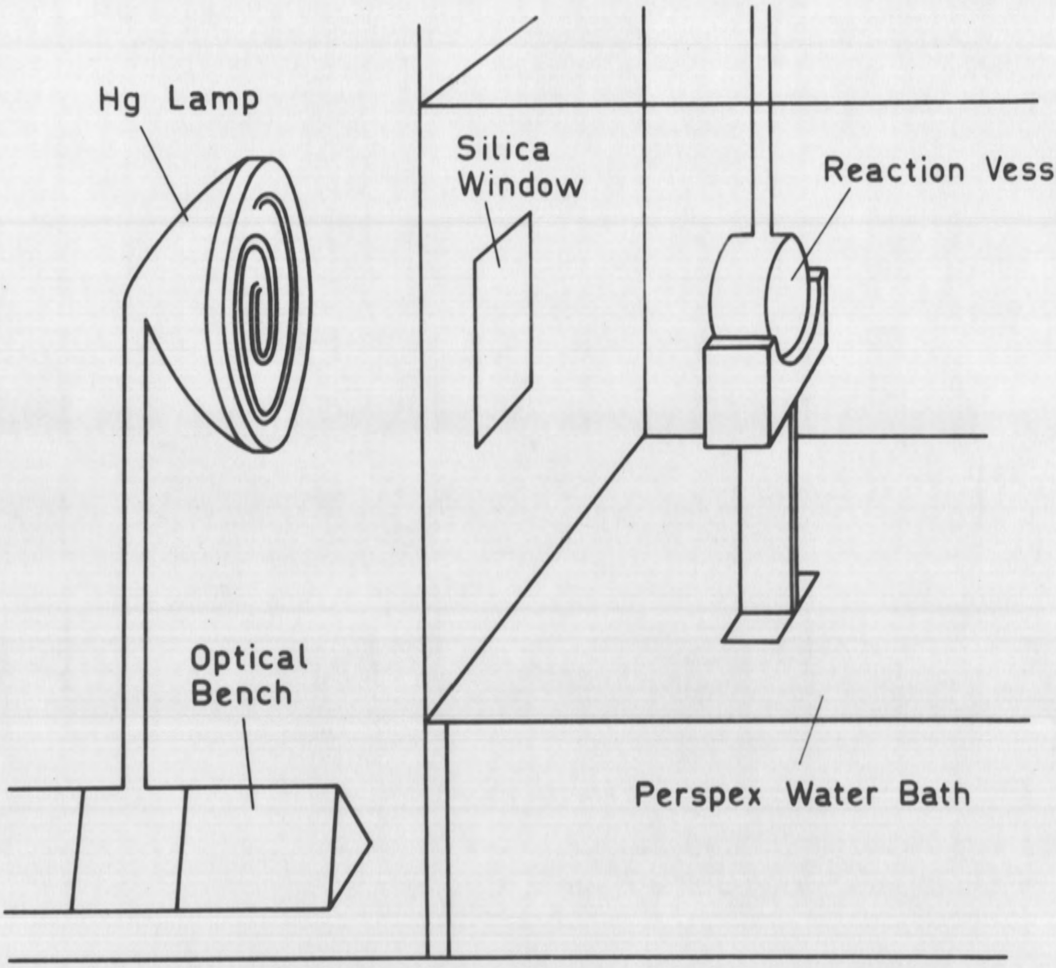


FIG. II·2 Irradiation Apparatus.

lamp) in the form of a spiral arc (3 cm diameter, 15 cm length). The lamp was firmly fixed on an optical bench outside the water bath.

D. Determination of the Rate of Exchange

Approximately 5 ml of reactant solution (without tracer) was pipetted into the reaction cell, (previously cleaned with chromic acid and stood overnight in distilled water). The cell and solution were placed in the water bath and irradiated for 1 to 1½ hours. After this period (pre-irradiation) 2 to 3 drops of the tracer solution was added to the reactant mixture, (after shutting off the light). The intensity of the light was known for several fixed positions of the light on the optical bench. One of these positions was selected and the run started by removing a shutter from the light beam. Samples of approximately $^{1}/_{3}$ ml were taken at known times (including before the start of the run), and subjected to the separation technique discussed below.

Separation of the oxidation states.

In exchange reactions the two exchanging species must be separated and one or both radioactively assayed.

The method developed by Prestwood and Wahl(10), involving precipitation of thallous chromate, was used in this study to separate thallium(I) from thallium(III), as it was quick and reproducible. In detail: The reaction sample was delivered into the precipitating mixture (5 ml of a solution of Na_2CrO_4, (.5 mole l^{-1}), NH_3 (8 mole l^{-1}) and alcohol (10%), plus 2 ml of 6M sodium cyanide - all cooled to 0^oC in an ice bath). Immediately following the sample, 1 ml of thallous perchlorate carrier was added. After standing for approximately 10 minutes the thallous chromate was collected on a porosity 5 sinter glass filtration apparatus. The thallous chromate was washed with a dilute sodium chromate solution containing approximately 10% alcohol. The filtrate and washings containing Tl(III) were collected directly in a 50 ml standard flask. The solid thallous chromate precipitate was dissolved in conc. sulphuric acid (5 ml), and the solution washed into a second 50 ml standard flask.

Radio-assay.

Both the thallous and thallic fractions were assayed for radioactivity in a liquid Geiger-Muller tube. A Philips scaler and H.T. supply were used. All tubes were operated at approximately 50 volts above the lower edge of the plateau region in the voltage against count rate curve. The background radioactivity (20 counts/min) was checked at intervals.

For all samples (except very low counts), the time required for 10,000 counts was determined, which results in a constant counting error. A maximum count rate of 6,000 counts per min^{-1} was used, up to which the counter was shown to be linear. That is, the counts were proportional to the concentration of activity in this region (and possibly higher). No correction was necessary for the decay of activity over the time of assay as the half time for Tl^{204} decay is 3.5 years. Sulphuric acid was also shown to have a negligible effect upon the count rate.

E. Determination of Light Intensity

(a) Actinometry.

A chemical actinometer was used to determine the light incident on the reaction vessel. Ferrioxalate actinometer developed by Hatchard and Parker(54) was chosen for its accuracy, ease of use, and speed as compared to the older uranyl oxalate. The actinometer is based on the photochemical reduction of ferric to ferrous, followed by the spectrophotometric determination of ferrous as ferrous phenanthroline. As complete absorption of the light entering the cell occurs, the rate of absorption of light is given by

$$\frac{D}{\epsilon \phi}$$

where D is the optical density per unit time, ϵ the extinction coefficient of the ferrous phenanthroline complex, and ϕ is the quantum yield for reduction.

The detailed technique was the same as that recommended by Hatchard and Parker, except for the following details. 2 ml samples of irradiated actinometer were taken and pipetted directly into 25 ml standard flasks containing a mixture of 5 ml of the acetate buffer, 2 ml of o-phenanthroline and 10 ml of water. After standing for more than $\frac{1}{2}$ hour in the dark the optical density of the resulting ferrous phenanthroline solutions was determined on a Shimadzu manual spectrophotometer, (see spectra for more details) at 510 mμ.

The extinction coefficient of ferrous phenanthroline produced by this technique was checked with Hatchard and Parker's value by quantitatively diluting a standardized solution of ferrous ammonium sulphate. The resulting optical density versus concentration curve is shown in Fig. II.3. The extinction coefficient (11,030) agreed within experimental error ($\frac{1}{2}$%) with Hatchard and Parker's value (11,050).

(b) Spectrum of the light source.

The low pressure mercury arc emits light mainly at two wavelengths, 185 mμ and 254 mμ, although some light at higher wavelengths is observed in the spectrum. The spectrum of the source was photographed on a Hilger quartz medium spectrograph, with and without a $^1/_4$ inch plate of soda glass in the light beam, at 3 different exposure times, (see Fig. II.4). The significance of the soda glass filter will be considered later.

The light emitted at 254 mμ was isolated during kinetic studies by the experimental arrangement. The light of wavelength 189 mμ was absorbed by the water in the water bath and the wavelengths longer than 254 mμ were not absorbed by the thallium reactant solutions, so

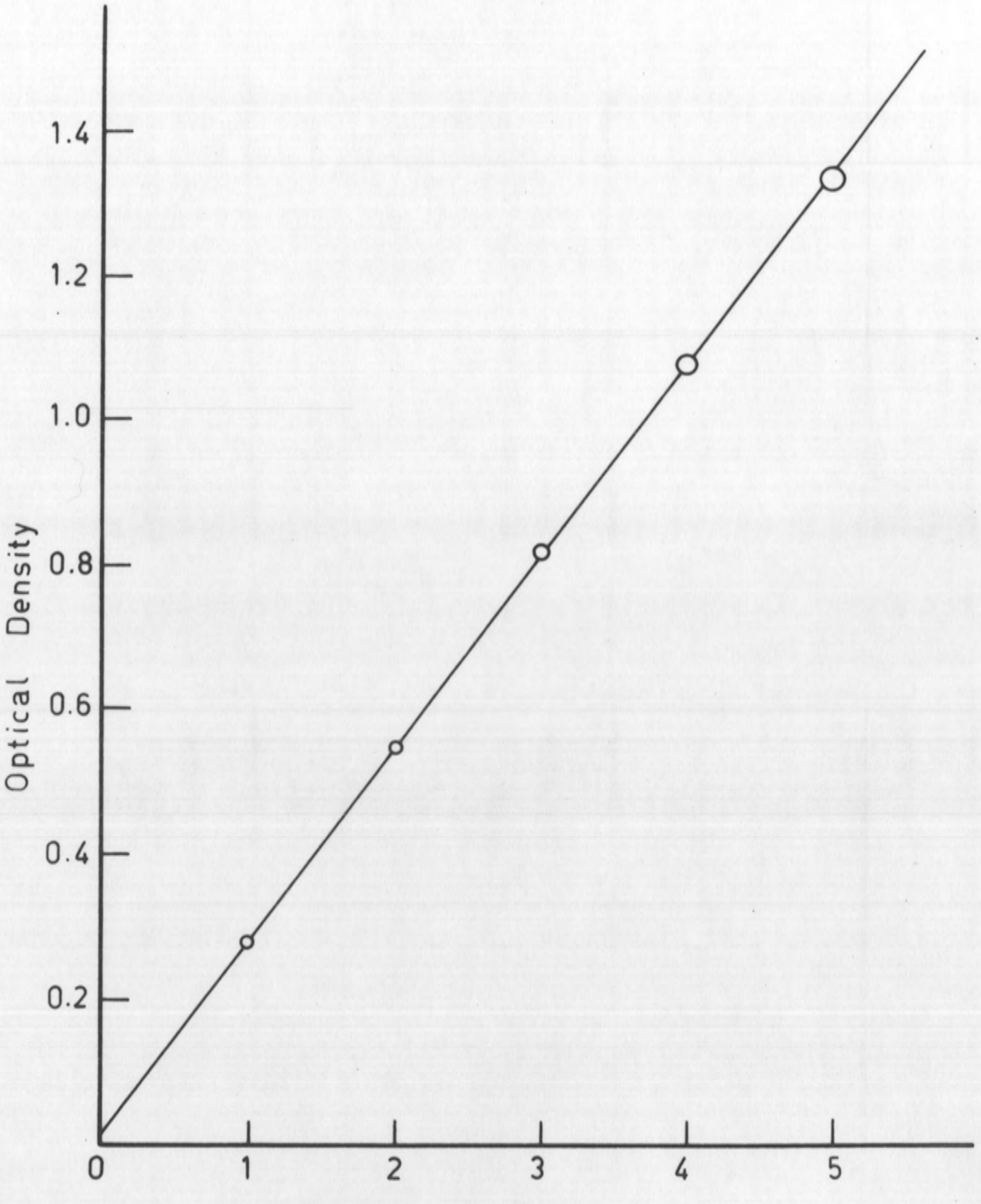
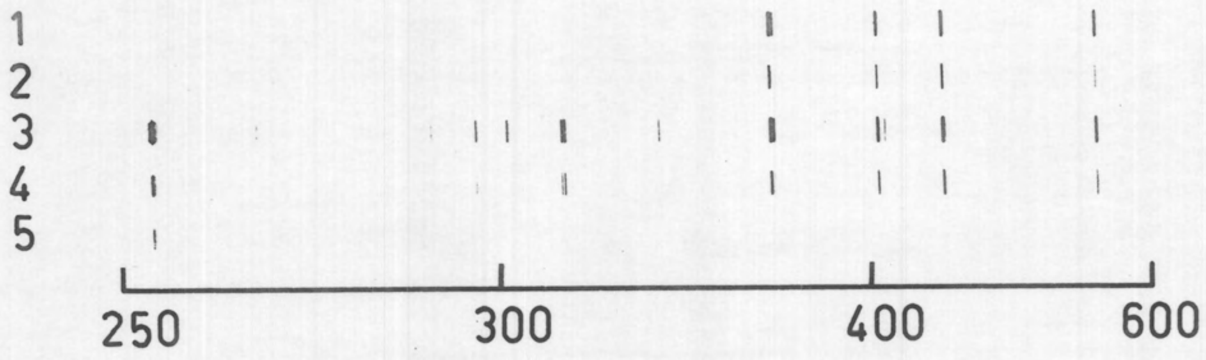


FIG. II·3 Fe(II) Phenanthroline Extinction Coefficient.



Wavelength mμ

FIG. II·4 Spectrum of Source.

1. 30 sec. exposure with glass filter.
2. 5 " " " " "
3. 60 sec. exposure.
4. 5 " "
5. 1 " "

were ineffective in the reaction.

However the actinometer solution absorbs up to 500 mμ in the visible region, so that the actinometer measured the intensity of the longer wavelength lines as well as the emission at 254 mμ. Hence it was necessary to determine the intensity at these longer wavelengths independently, and subtract it from the total intensity as measured by actinometry. This was mainly done by repeating the actinometry with the 1/4 inch plate glass, referred to on p. 89 in the light beam. From the relative density of the lines of the spectrum, with and without the glass plate, it was possible to estimate the intensity of light (2%) which was absorbed by the soda glass but emitted above 254 mμ. The actinometry with the glass filter measured the light intensity of the remainder of the light above 254 mμ (.8%). The technique also determines the intensity of any stray visible light from internal sources. Thus a 10% correction was made to the total light intensity as measured by the actinometer.

(c) Stability of the light source.

A thermopile connected to a sensitive galvonometer was used to check the stability of the light source. The thermopile was placed in the water bath in the position of the cell. The difference between the galvonometer readings with and without a shutter in the light beam was taken to be proportional to the light intensity falling on the thermopile. After the first half hour, the current from the thermopile remained steady within 2%, for more than four hours. Long term instability was shown to be less than 7% from actinometry over more than a year.

The effect of mains voltage variation was also checked by deliberately altering the mains voltage with a variac, and observing the effect on a thermopile. A 10 volt drop in the 240 volt mains supply produced less than a 2% drop in the light intensity.

The temperature of the outside of the source is supposed(55) to greatly affect the output of low pressure mercury arcs, but actinometry over a long period with no temperature control showed only a 7% variation (which may be attributed to other factors as well as temperature variation). However all runs were done at laboratory temperatures of less than 25°C, and with few exceptions greater than 15°C.

(d) Spectra.

Spectral measurements were taken on a manual Shimadzu photoelectric spectrophotometer, model QR50. The cell block was thermostatted to ± .2°C, and the temperature of the solution in the cells was brought up to this temperature. 1 cm and 4 cm silica cells were used in the measurements. The wavelength scale was calibrated against the lines of an inbuilt mercury arc. It was shown to be less than 3 Å out at 2537 Å. The absorbance scale was calibrated by a research worker in this Department with standard neutral density filters provided by the Commonwealth Bureau of Standards. The scale was found to be correct within the tolerance quoted by the manufacturers.

The optical density of solutions were determined against distilled water. A small correction ($<$ .01 optical density units) was sometimes made to the optical density measurement, to allow for dust. The correction was made on the basis of the optical density measurements at 400 mμ, where the absorption by thallium species is negligible. (The method of correction may not be completely justified as light scattering increases as the wavelength decreases, but the correction is small anyway.)

SECTION II

CHAPTER 3: RESULTS

A. Introduction

The quantity of most interest to the photochemist is the quantum yield, a measure of the number of reactions occurring per quantum of light absorbed. The quantum yield for exchange is defined as

$$\phi_{ex} = \frac{R_{ex}}{I_{abs}}$$

in this study, where R_{ex} is the rate of exchange and I_{abs} is the absorbed light intensity. These two quantities were determined independently, the rate of exchange from kinetic studies, and the absorbed light intensity from a combination of chemical actinometry and reactant spectra. The first two sections discuss the calculation of the results obtained for the quantum yields of the thallium(I)-thallium(III) electron exchange reaction, when irradiated by light of 254 mμ.

B. Calculation of the Absorbed Light Intensity

The absorbed light intensity (the rate of absorption of light) is determined from the product of the incident light intensity by the fraction of light absorbed.

(a) Actinometry.

The incident light intensity was determined by actinometry.

Values of quantum yield for the actinometer (1.26 at 254 mμ), and the extinction coefficient of ferrous phenanthroline (11,050) used in the calculation are those reported by Hatchard and Parker(54).

Some typical results are reported in Table II.3. Optical densities of ferrous phenanthroline solutions per minute irradiation, per ml of irradiated solution are recorded for five positions of the light on the optical bench.

Table II.3

optical densities min^{-1} ml^{-1}	.0209	.00588	.00360	.00227	.00180
	.0204	.00584	.00362	.00230	.00172
	.0215				
	.0208				
	.0202				
	.0210				
Average	.0206	.00586	.00361	.00229	.00176
o.d. min^{-1} ml^{-1} with glass	1.63×10^{-3}	4.7×10^{-4}	3.8×10^{-4}	1.66×10^{-4}	
$I_o \times 10^5$	3.35	.950	.582	.372	.284

I_o is the incident light intensity (Einstein l^{-1} min^{-1}). It is calculated directly from the optical density measurements by the expression,

$$I_o = \frac{25 . D}{\epsilon . \phi} ,$$

where D, ϵ, and ϕ are defined on page 88. 10% is subtracted to allow for non-useful light of wavelength greater than 254 mμ. Dainton et al$^{(57)}$ determined an 8% correction for light of longer wavelengths than 254 mμ, for a similar light source. Due to an alteration of geometry, light intensities had to be redetermined for some later work. The results are recorded with the relevant kinetic data.

Error.

The random error in the individual light intensities may be judged from the results in position 1. A variation of < 7% was observed for these results over a year. Hence for the other positions which have been duplicated an error of ± 2% is probably justified. For position 1 the accuracy is probably better than this, because of the number of values determined.

Systematic errors: The error in Hatchard and Parker's determination of quantum yield is probably ± 2%. The error in the extinction coefficient is ± 1%. Therefore the error in the correction for non-useful light is probably ± 1% of the total light intensity. The random error in the actinometry is therefore of the order of ± 3%, and the systematic error ± 4%.

(b) Spectra.

(i) Thallic spectra.

The spectrum of thallic perchlorate in perchloric acid was reported by Waind and Rogers.(4) Values of molar extinction coefficients for Tl^{3+}_{aq} and $TlOH^{2+}_{aq}$ between 280 and 210 mμ were determined from the acid dependence of thallic perchlorate spectra by these authors. The following values of $\epsilon_{Tl^{3+}}$ and $\epsilon_{TlOH^{2+}}$, the molar extinction coefficients of Tl^{3+} and $TlOH^{2+}$ respectively, were taken from a graph in Rogers' and Waind's paper.

Table II.5

Wavelength (mμ)	$\epsilon_{TlOH^{2+}}$ mole^{-1} cm^{-1}	$\epsilon_{Tl^{3+}}$ mole^{-1} cm^{-1}
270	145-155	4-4.5
260	290-300	5.5-6.0
250	515-525	10.5-11.5
240	775-785	36.5-37.5
230	1030 By extrapolation	224 By calculation
2537	415 ± 10	8.0 ± .5

These values were used to calculate ϵ_{app}, the apparent molar extinction coefficient for thallic perchlorate solutions using the following equations:

$$\epsilon_{app} = \epsilon_{TlOH^{2+}} [TlOH^{2+}] + \epsilon_{Tl^{3+}} [Tl^{3+}]$$

and from

$$[TlOH^{2+}] = \frac{K_1 [Tl^{3+}]}{[H^+]}$$

$$\epsilon_{app} = \left\{ \frac{\epsilon_{TlOH^{2+}} \cdot K_1 + \epsilon_{Tl^{3+}}}{[H^+]} \right\} \frac{1}{1 + K_1/[H^+]}$$

Values of K_1 are reported by Waind and Rogers at 25°C as

Ionic strength $\mu = 1.5$ $K_1 = .086 \pm .004$ mole l^{-1}

$\mu = 3.0$ $K_1 = .069 \pm .004$ mole l^{-1}

As most work in this thesis has been done at an ionic strength between 1.2 and 1.3, an extrapolated value for K_1 of .089 was used in the calculations.

The calculated ϵ_{app} values used in this study are shown in Table II.6. They were checked against some experimentally determined values (shown on the right-hand side of Table II.6). Four thallic solutions made up, but not used in kinetic work, yielded values of the ϵ_{app} in agreement with the values calculated from Rogers and Waind's data.

(ii) Thallous spectra.

The extinction coefficient of thallium(I) at various wavelengths were determined experimentally: the results are shown in Table II.6 and Figs. II.5 and II.6.

The optical densities of some reactant solutions are shown in Fig. II.7. The values are in good agreement with the extinction coefficients in Table II.6.

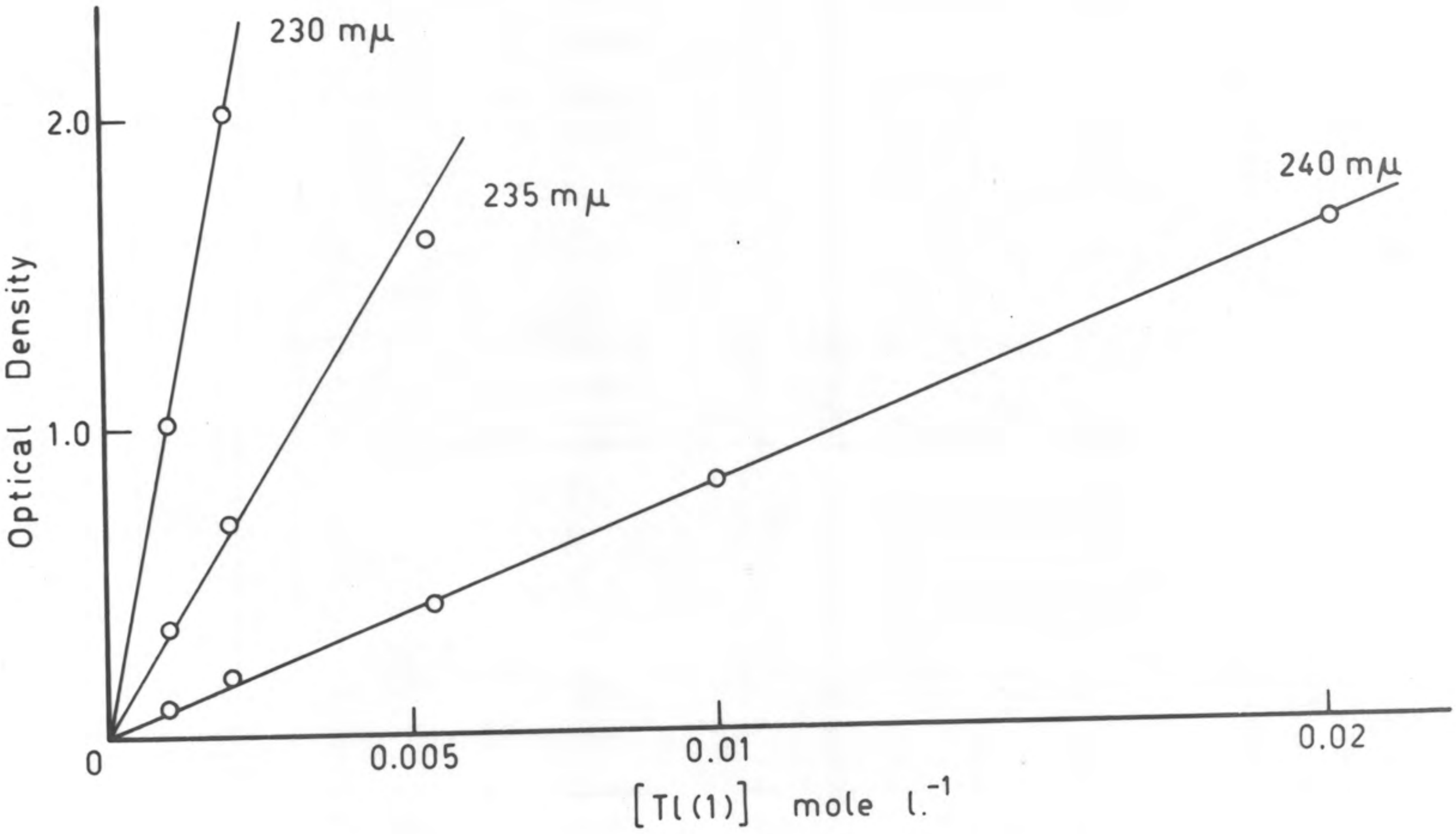


FIG. II·5 Extinction Coefficients of $TlClO_4$

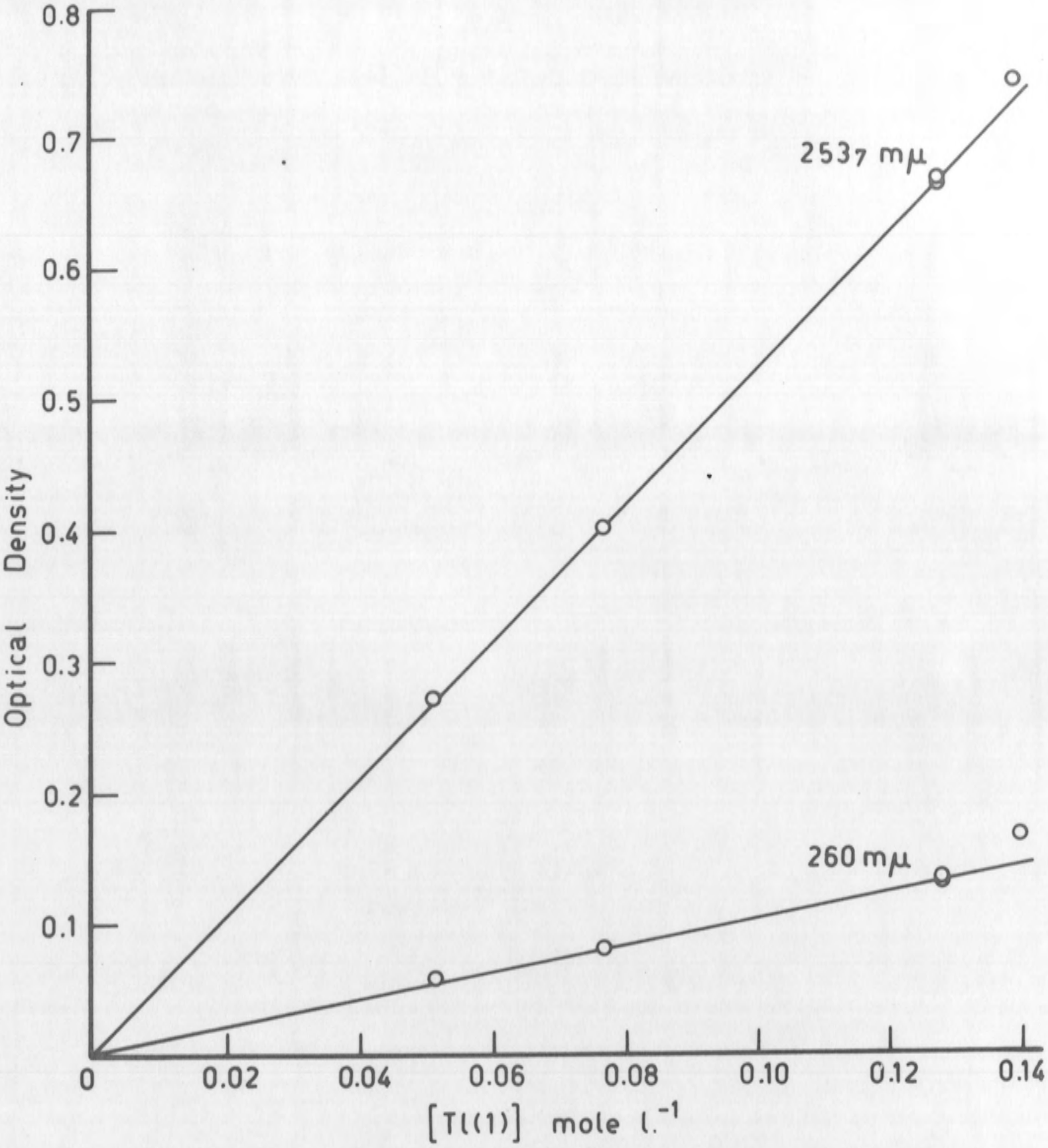


FIG. II·6 Extinction Coefficients of $TlClO_4$

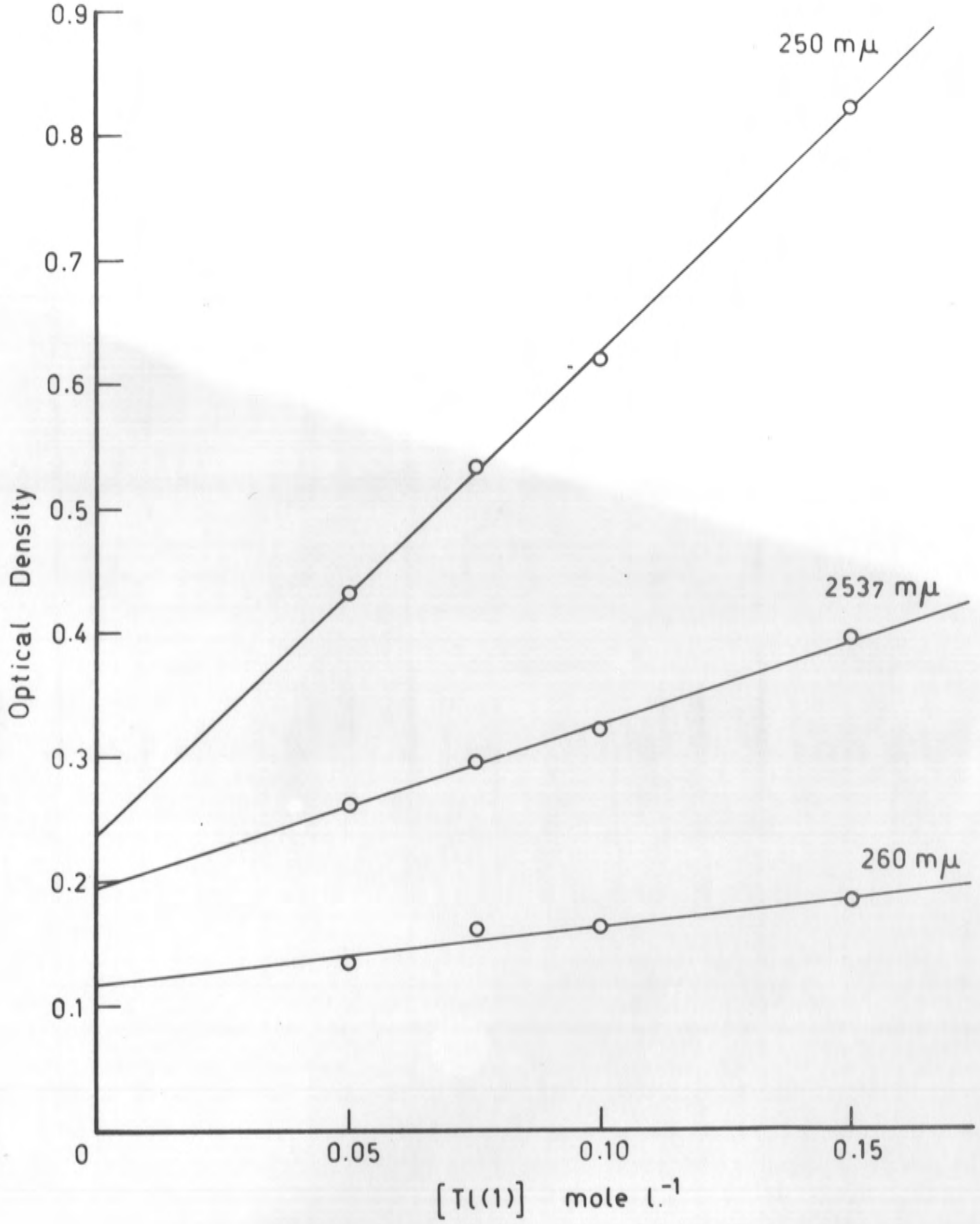


FIG. II·7 Spectra of Reactant Solutions.
[Tl(1)] = 0.005 , [H^+] = 1.10 mole $l.^{-1}$

Table II.6

Extinction Coefficients

Wavelength ($m\mu$)	$\epsilon_{Tl(I)}$ mole^{-1} cm^{-1}	$\epsilon_{Tl(III)}$ mole^{-1} cm^{-1} Calculated	Observed
270	$8.9 \pm 1 \times 10^{-2}$	15.5 ± 2	
260	$.25 \pm .02$	28 ± 3	27.6 ± 1
250	3.9 ± 1	49 ± 3	48.5 ± 1
240	$8.1 \pm .5 \times 10$	92 ± 5	
230	$9 \pm 2 \times 10^2$	280 ± 50	
253_7	$1.30 \pm .03$	38.4 ± 2	39 ± 2

Temperature: 25°C; $[HClO_4] = 1.10$ mole l^{-1}.

The errors quoted in these values are

(i) for $\epsilon_{Tl(I)}$ calculated graphically from the Beer's law plots.

(ii) for $\epsilon_{Tl(III)}$ the error is in reading the graphs in Waind and Rogers' paper.

The fraction of the light absorbed by Tl(III) in a solution containing both thallous and thallic may be determined from equation (1). As the presence of Tl(I) absorbs some of the light incident on the absorbing solution, it is necessary to correct for this absorption in the calculation of the light absorbed by Tl(III).

$$\frac{I_{abs}}{I_o} = \frac{\epsilon_{Tl(III)}[Tl(III)]\left(1 - 10^{-(\epsilon_{Tl(III)}[Tl(III)] + \epsilon_{Tl(I)}[Tl(I)])l}\right)}{(\epsilon_{Tl(III)}[Tl(III)] + \epsilon_{Tl(I)}[Tl(I)])} \qquad (1)$$

where I_{abs} is the absorbed light intensity and I_o is the incident light intensity determined from actinometry. The absorption by $TlOH^{2+}$ in the presence of Tl^{3+} was calculated from an analogous equation.

C. Rate of Exchange and Quantum Yield

The rate of exchange was calculated from the McKay(56) equation,

$$\text{Rate of exchange} = R_{ex} = \frac{\ln(1 - F)}{t} \; \frac{ab}{a + b}$$

where a and b are the concentration of exchanging species and F is the fraction of exchange at time t.

F was calculated from the expression $\frac{A_t - A_o}{A_\infty - A_o}$, developed by Prestwood and Wahl,(10) for zero time exchange which is due to separation induced exchange. They applied the expression to some precipitation separation techniques, involving much larger separation induced exchange, than observed in this study.

Prestwood and Wahl reported 5% zero time exchange for the $CrO_4^=$ separation method. With the method employed in this thesis, 1-2% zero time exchange was observed when the activity was initially in the thallous form, but 6-8% with the activity in the thallic form. The difference is probably due to the use of thallous carrier in the precipitation.

Some typical results are shown in Table II.8.

Now a plot of log $(1 - F)$ against t should be a straight line. Experimentally, good straight line plots up to at least two $\frac{1}{2}$ times were observed. Two typical curves are plotted in Fig. II.8, including the results in Table II.8 (Curve A).

Induction period.

The plots should also pass through the point $(1 - F = 1.0, t = 0)$. However as is illustrated by curve B, an induction period was observed when the solutions were not pre-irradiated. The induction period is thought to be due to the destruction of chain carrier by impurities (probably organic). This hypothesis is supported by the observations on the effect of pre-irradiation. An alternative explanation of slow build-up of chain carriers may be discarded as the introduction of a shutter for short periods during a run has no effect on the rate plots.

The half-time for exchange was determined from the McKay plots, as $t = t_{\frac{1}{2}}$ when $1 - F = .5$. Substitution of $t_{\frac{1}{2}}$ in the equation,

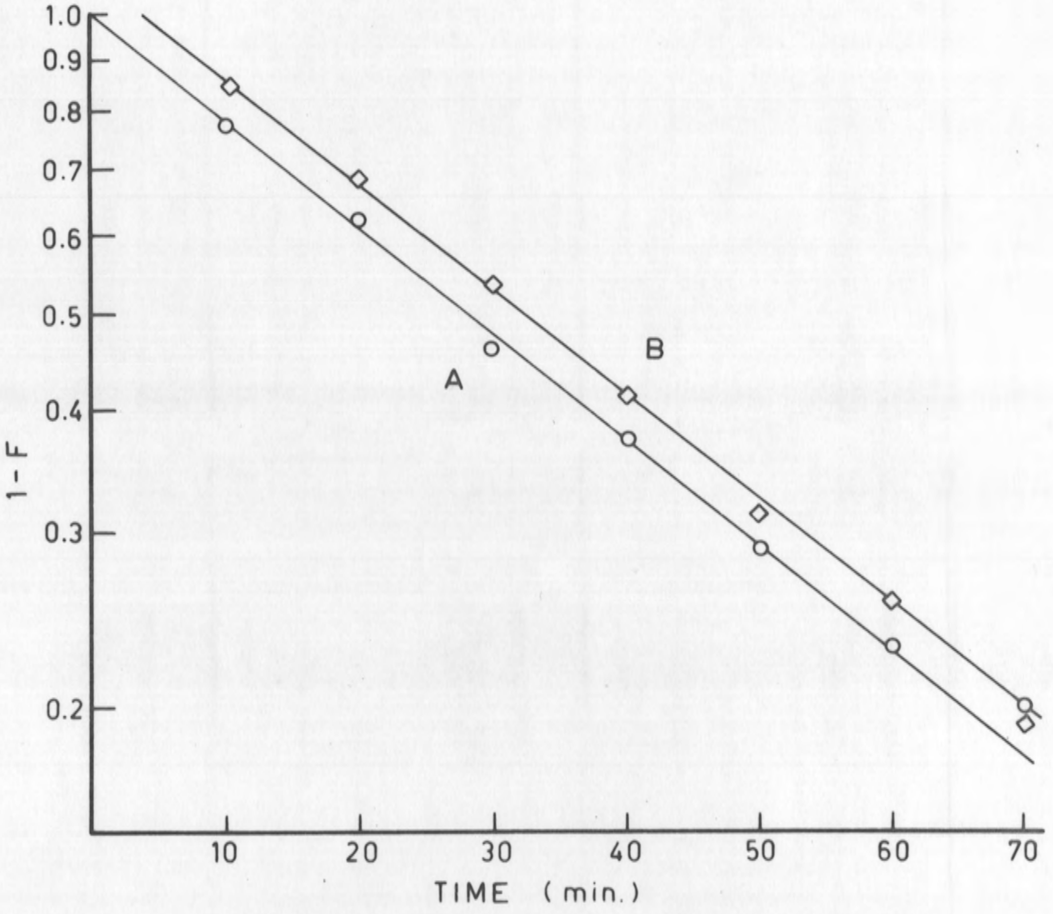


FIG. II·8 Typical Rate Plot.

A $[Tl(III)] = 0.005$ mole $l.^{-1}$, $[Tl(I)] = 0.0051$ mole $l.^{-1}$ $[\overset{*}{Tl}(I)]$

B $[Tl(III)] = 0.0051$ mole $l.^{-1}$, $[Tl(I)] = 0.005$ mole $l.^{-1}$ $[\overset{*}{Tl}(III)]$

A Pre-irradiated

B Not Pre-irradiated

Table II.8

Time	Tl(III) Activity		Tl(I) Activity				
(min)	a_1	a_2	b_1	b_2	A_t	F	1 - F
0	1012/10	101	2.213	4519	15		
10	5903/10	590	2.450	4082	121	.226	.774
20	8694/10	870	3.027	3304	192	.379	.621
30	7.766	1288	2.872	3482	269	.540	.460
40	6.948	1440	3.150	3475	310	.627	.373
50	6.677	1497	3.620	2762	350	.712	.288
60	6.472	1546	3.946	2534	377	.770	.230
70	5.570	1795	3.512	2855	391	.800	.200

a_1, b_1 are the actual times recorded for 10,000 counts in the thallium(III) and thallium(I) fractions respectively.

a_2, b_2 are the count rate in counts/min calculated from a_2 and b_2.

A_t: $A_t = \frac{a_2'}{a_2' + b_2'} \times 10^3$ where a_2', b_2' are a_2 and b_2 corrected for background activity.

F: Fraction of exchange = $\frac{A_t - A_o}{A_\infty - A_o}$,
where A_∞ is the calculated value of A_t at infinite time.

Conditions:

$[Tl(I)] = .0051$; $[Tl(III)] = .005$; $[HClO_4] = 1.10$ mole l^{-1}.

Temp.: = 25°C.

$$R_{ex} = \frac{.693}{t_{\frac{1}{2}}} \frac{ab}{a + b}$$

$$= \frac{.693}{t_{\frac{1}{2}}} \frac{[Tl(I)]\ [Tl(III)]}{[Tl(I)] + [Tl(III)]}$$

yields the rate of exchange R_{ex}.

The McKay equation applies to exchange systems where the concentration of exchanging species is constant throughout reaction. To determine whether any overall change in concentration occurs on irradiation, some solutions were irradiated for periods much greater than the half-time for exchange. No change in the equilibrium value of the ratio of thallous to thallic activity was observed. The infinite time values determined in these experiments lay within experimental error of the calculated infinite times.

A small correction to the photochemical rate was made, where necessary, to allow for the relatively slow thermal rate. A small correction for the concentration of tracer, significant only at low concentrations, was made to the concentration of reactants.

Quantum yield for exchange (ϕ_{ex}).

ϕ_{ex} was then calculated from

$$\phi_{ex} = \frac{R_{ex}}{I_{abs}}$$

using the values of R_{ex} and I_{abs} determined in the manner discussed above.

D. Errors

The error in the quantum yield is the sum of fractional errors in the rate of exchange and the absorbed light intensity.

(a) $\underline{I_{abs}}$ error.

I_{abs} = fraction of absorbed light x I_o

$$\frac{\delta I_{abs}}{I_{abs}} = \frac{\delta I_o}{I_o} \times \frac{\delta \text{ fraction}}{\text{total fraction}}$$

where δ is the error from the mean of the particular variable. Now $\delta I_o/I_o$ is the fractional error in the incident light intensity, which was estimated to be ± 3% random error, and ± 4% systematic error. The second term in the expression above varies with the value of the % light absorbed. When nearly all the light is absorbed the error in the % light absorption is small. However, at lower % absorption the error in this value is significant, as the error in the extinction coefficient of the reactant solution is significant. Thus, for example, the % error for the solution .005 mole l^{-1} in Tl(III) and .05 mole l^{-1} in Tl(I) is calculated to be ± 5%. This is a constant error when the concentration of reactants are fixed, but is partially a random error when comparing results at different concentrations. Including it with the systematic error, a total systematic error of ± 9% is observed. The total random error is ± 3%.

(b) Error in rate of exchange.

The error determined graphically from the possible variation in slope of the McKay plot is usually less than ± 5%. However the observed variation in rate is greater than this; of the order of ± 10%. This may be due, in part, to light intensity variation, but there is no way of determining this.

Two other sources of error in the rate of exchange are in the calculation of the infinite time value and in the concentration of reactants. Obviously these two factors are connected, both being dependent on the concentration of reactants. For example, take the reactant solution [Tl(III)] = .005M and [Tl(I)] = .05M (with Tl(III) activity). If the actual concentration of Tl(III) is less (say, .004) than assumed, two effects will be observed:

(1) the rate of exchange will be less as R_{ex} is roughly proportional to [Tl(III)] in this region.

(2) The actual infinite time value of the activity ratio will be less than the calculated value. Hence use of the calculated infinite time ratio will increase the apparent rate of exchange. (The concentration error (.001) would produce a 3-7% increase in the rate of exchange at the specified conditions.) The effect is greater if the values of the concentrations of reactants were closer. For example, for [Tl(III)] = .005 mole l^{-1} = [Tl(I)], an error of .001 in the Tl(III) concentration, will apparently increase the half-time of exchange by 15%. This will be compensated for by the actual decrease

in rate due to the decrease in concentration, so that the total error in the rate will be less than the error in the concentration of 20%. As the error in concentration in this study is less than ± 1%, the error in the rate due to concentration error will also be less than 1%.

The random error in the rate is thus calculated to be less than ± 10% with 90% confidence, i.e. I expect 90% of my values to lie within ± 10% of the mean values.

(c) Error in quantum yield.

$$\phi_{ex} = \frac{R_{ex}}{I_{abs}} .$$

The observed random error in R_{ex} also reflects the random error in I_{abs}. So that at one light intensity, the random error in ϕ_{ex} will be ± 10%. To this may be added a systematic error of ± 4% + (error dependent on % absorption).

However when comparing results at different light intensities these figures become ± 12% random error, and ± 2% + (error...etc.) systematic error.

Note: A further error may arise here due to the high optical densities used in some cases. Based on the discussion in Leighton and Noyes,(52) a calculation of the maximum error in this sytem gave a value of 13% (see Appendix for details). As the error was shown to have little effect on the rate constants determined from the results, it has been neglected.

E. Preliminary Runs

Preliminary runs were performed to test the effect on the rate of exchange of the following variables.

1. Oxygen.

Argon was bubbled through a reactant mixture for 2 hours before commencing the run. No difference in the rate of exchange within the limits of error (± 10%) was detected.

2. Stirring.

(a) The bubbling above also acted as a stirrer and produced no effect.

(b) A small but vigorous mechanical glass stirrer also did not affect the rate of exchange.

3. Pre-irradiation.

This was shown to remove the induction period but not affect the rate of exchange appreciably. Fig. II.8 shows the lack of affect of pre-irradiation on the rate of exchange.

F. [Tl(I)] Dependence

Table II.9 shows the results obtained for the variation of quantum yield ϕ_{ex} with thallium(I) concentration, assuming (1) both Tl^{3+}_{aq} and $TlOH^{2+}$ are photoactive species (ϕ^{1}_{ex}) and (2) the $TlOH^{2+}$ is the only photoactive species (ϕ^{2}_{ex}). The values of the quantum yield at [Tl(I)] = .05 and .10 mole l^{-1} were taken from the graphs of ϕ_{ex} against I_{abs} for the respective Tl(I) concentrations.

Table II.9

Dependence of ϕ_{ex} on Tl(I) Concentration

[Tl(I)] mole l^{-1}	$t_{\frac{1}{2}}$ min	$R_{ex} x10^5$ mole l^{-1} min	Corrected for Thermal Rate R_{ex}	$I_o x10^6$ Einstein l^{-1} min^{-1}	$\frac{I_{abs}}{I_o}$	Tl(III) Abs. I_{abs} x 10^6 Einstein l^{-1} min^{-1}	ϕ_{ex}^{1}	ϕ_{ex}^{1} Corrected	$TlOH^{2+}$ Abs. ϕ_{ex}^{2} Corrected
.0011	32 ± 4	1.95	1.95	36.3	.354	12.9	1.51	1.55	1.88
.0026	31 ± 3	3.71	3.70	33.6	.353	11.8_5	3.12	3.10	3.75
.005	29,30	5.94	5.92	33.6	.360	12.1	4.90	4.90	5.95
.0051	33,33, 31, 29,31	5.47	5.45	33.6	.352	11.8_0	4.65	4.62	5.62
.010	42	5.57	5.53	33.6	.358	12.0	4.61	4.61	5.61
	28	8.35	8.31				6.94	6.94	8.43
.020	28	12.3	12.1	33.6	.353	11.8_5	10.0_2	9.47	12.1
.050		Taken from I_{abs} Dependence						11.6 ± .5	
.075	11.0	30.1	29.8	115	.328	37.7	7.9_0	11.8	14.3
.10		Taken from I_{abs} Dependence						13.4	
.15	11.0	30.6	30.0	115	.298	34.3	8.75	12.7	15.4

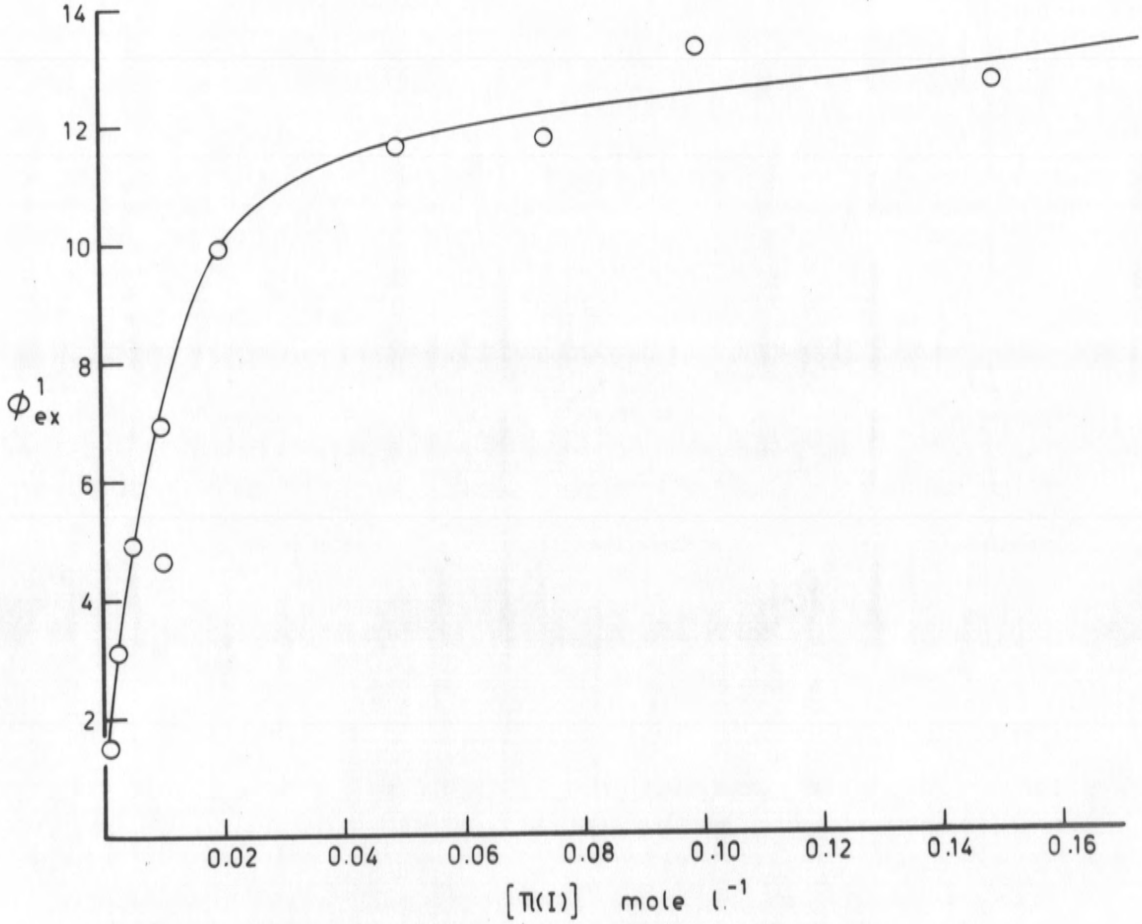


FIG. II·9 [Π(I)] Dependence

All the values have been corrected to an I_{abs} value of 12.0×10^{-6} Einstein l^{-1} min^{-1} for Tl(III) absorption and 9.86×10^{-6} Einstein l^{-1} min^{-1} for $TlOH^{2+}$ absorption, using the equation,

$$\phi_{ex} = K\, I_{abs}^{-.35}$$

where K is a constant. This equation is derived from other results. Only two values are significantly affected by the correction. The error in the half-time of exchange as determined from the variation in slope of the McKay slot is generally less than ± 5%. In those cases where the error is greater, it is quoted as a ± figure in the half-time of exchange.

In general, errors are not plotted on the graphs, as the random variation of the points gives a better idea of the magnitude of errors, than error bars determined from known sources of error.

G. [Tl(III)] Dependence

Table II.10 and graph II.10 show the dependence of the quantum yield for exchange on Tl(III) concentration, at constant Tl(I) concentration = .050 mole l^{-1}. $[HClO_4]$ = 1.10 mole l^{-1} and temperature = 25.0°C. Again two values of ϕ_{ex} are tabulated.

(1) For total Tl(III) absorption (ϕ_{ex}^{1}), and

(2) For $TlOH^{2+}$ absorption only (ϕ_{ex}^{2}).

Table II.10

Dependence of $\not{O}_{ex}$ on Tl(III) Concentration

Tl(III) mole l^{-1}	$t_{\frac{1}{2}}$ min	R_{ex} mole l^{-1} min^{-1}	R_{ex} corrected mole l^{-1} min^{-1}	$\frac{I_{abs}}{I_o}$	Tl(III) Abs. I_{abs}^{1} Einstein l^{-1} min^{-1}	$\not{O}_{ex}^{1}$	$TlOH^{2+}$ Abs. I_{abs}^{2} Einstein l^{-1} min^{-1}	$\not{O}_{ex}^{2}$
.0011	49	1.52	1.48	.336	2.86	5.18	2.35	6.30
.0021	47	2.92	2.84	.333	5.14	5.54	4.21	6.73
.0051	23	13.9	13.7	.330	11.3	12.1	9.28	14.8
.0101	20 17	29.1 34.2	28.7 33.8	.550	18.4	15.6 18.4	15.1	19.0 22.4
.0151	17	47.2	46.6	.691	23.2	20.1	19.1	24.4
.0201	17	55.2	54.4	.785	26.3	20.7	21.6	25.2
.0424	21	76.2	75.1	.940	31.5	24.2	25.8	29.2

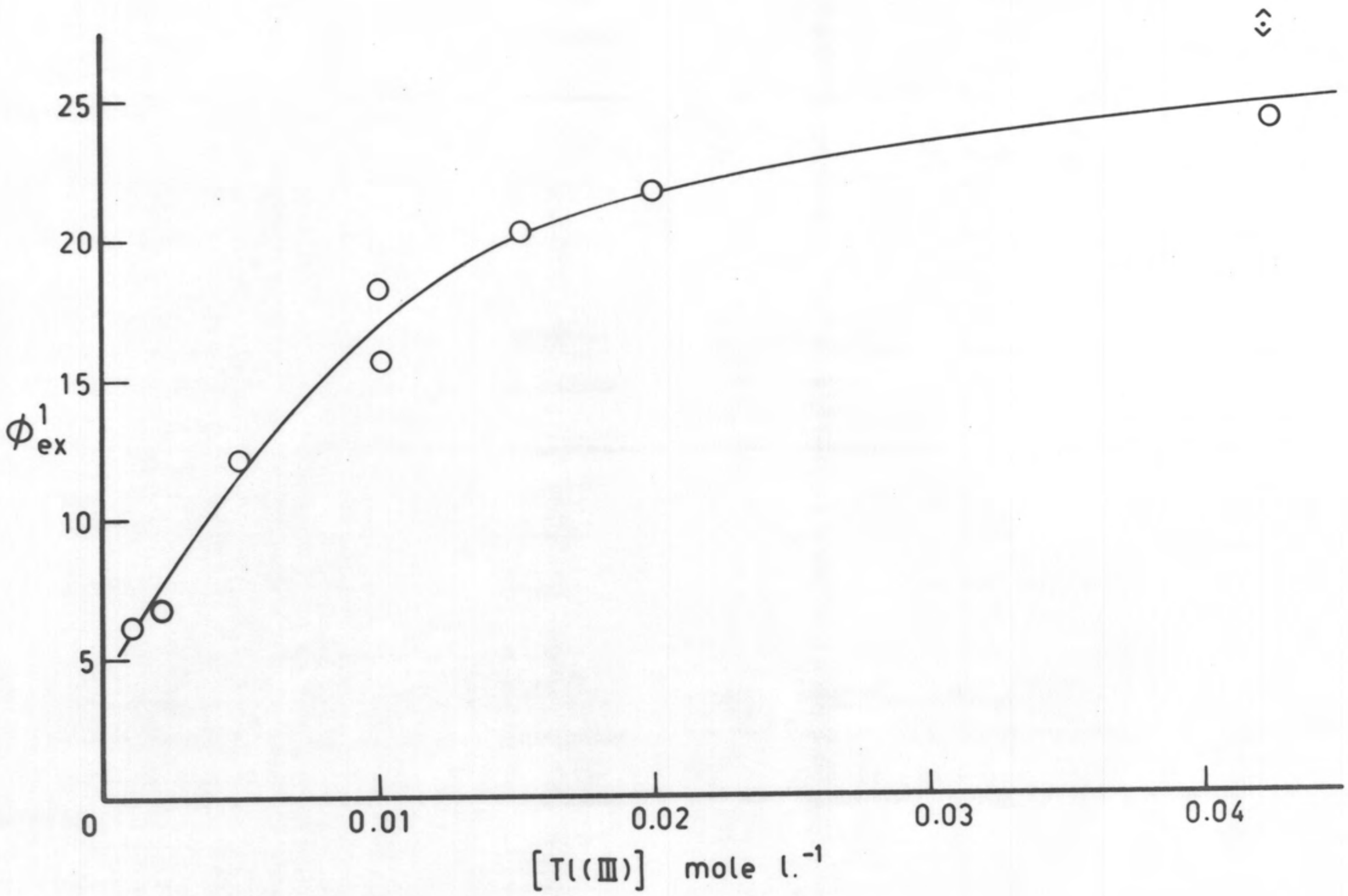


FIG. II·10 [Tl(III)] Dependence

⇕ Correction for non-uniform absorption.

H. Light Intensity Dependence

The dependence of ϕ_{ex} on I_{abs} has been determined at four concentration ratios of Tl(I) and Tl(III).

(a) $[Tl(I)] = .050_0$ mole l^{-1}, $[Tl(III)] = .005$ mole l^{-1}
(b) $[Tl(I)] = .100$ mole l^{-1}, $[Tl(III)] = .0051$ mole l^{-1}
(c) $[Tl(I)] = .0031_5$ mole l^{-1}, $[Tl(III)] = .041_2$ mole l^{-1}
(d) $[Tl(I)] = .0051$ mole l^{-1}, $[Tl(III)] = .040_0$ mole l^{-1}.

All runs were done at $[HClO_4] = 1.10$ mole l^{-1} and a temperature of 25.0°C.

Tables II.11 (a), (b), (c), (d) list the relevant figures. Corresponding graphs of ϕ_{ex}^{1} against I_{abs} are given.

Table II.11(a)

I_{abs} dependence; [Tl(I)] = .05; [Tl(III)] = .0051 mole l^{-1}

$I_o \times 10^6$	219	115	52.0	12.6	7.61
$t_{\frac{1}{2}}$ min	7.1	10.5	16.0	42	64
$R_{ex} \times 10^5$	44.9	30.3	19.8	7.43	4.31
$I_{abs}^{1} \times 10^6$	73.8	37.8	17.5	4.25	2.56
ϕ_{ex}^{1}	6.08	8.01	11.3	17.5	18.8
$I_{abs}^{2} \times 10^6$	60.6	31.0	14.4	3.49	2.10
ϕ_{ex}^{2}	7.39	9.77	13.8	21.3	23.0
$I_o \times 10^6$ Einstein l^{-1} min^{-1}	33.5	9.50	5.82	3.72	2.84
$t_{\frac{1}{2}}$ min	23	53	73	92	126
$R_{ex} \times 10^5$	13.7	5.86	4.20	3.29	2.35
$I_{abs}^{1} \times 10^6$	11.3	3.20	1.96_3	1.25	.956
ϕ_{ex}^{1}	12.1	18.3	21.4	26.4	24.6
$I_{abs}^{2} \times 10^6$	9.30	2.63	1.61	1.02_8	.786
ϕ_{ex}^{2}	14.7	22.3	26.1	32.1	29.9

R_{ex} mole l min^{-1}

I_{abs} Einstein l^{-1} min^{-1}

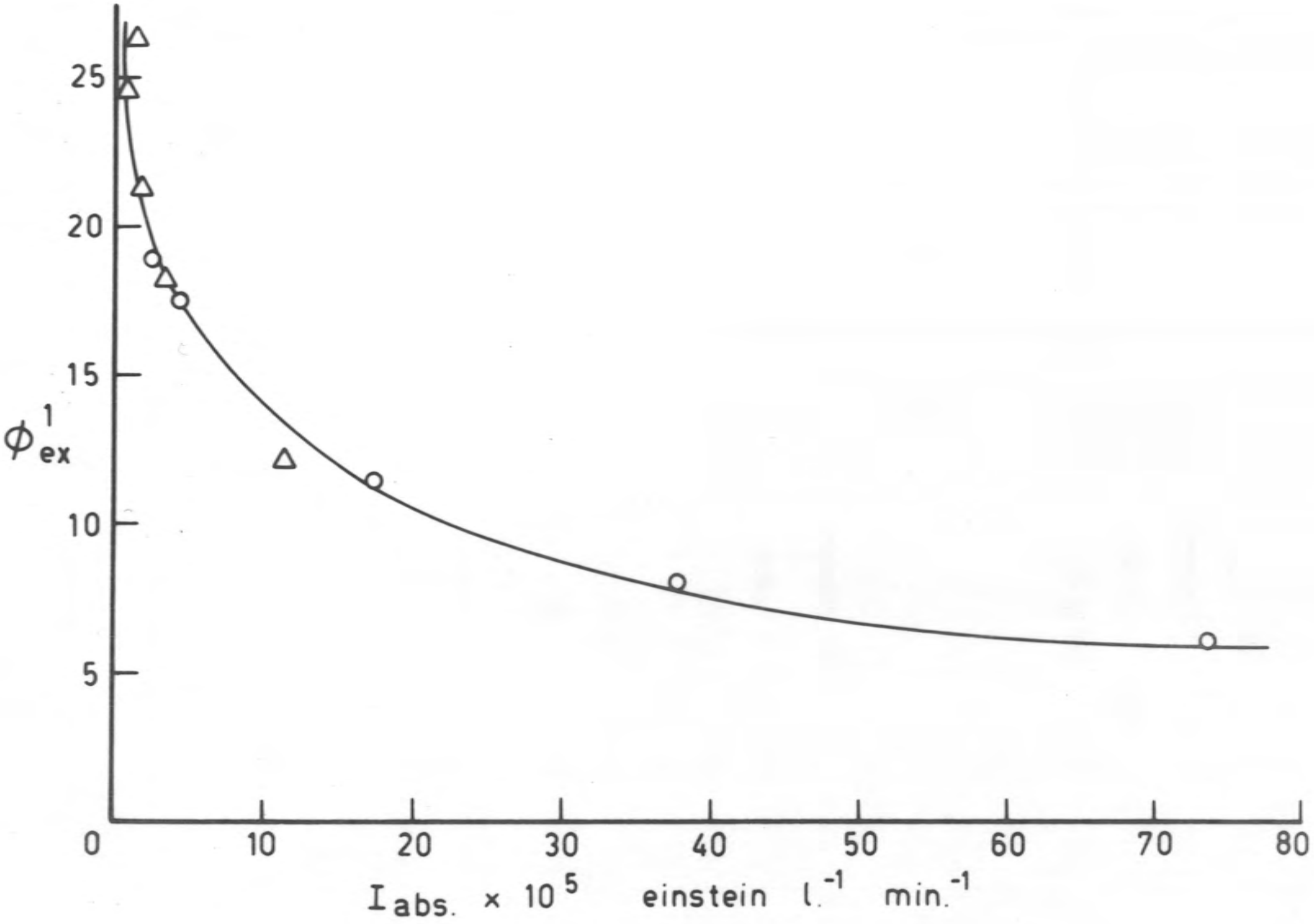


FIG. II·11 (a) $I_{abs.}$ Dependence
$[Tl(I)] = 0.050$ $[Tl(III)] = 0.005$ mole $l.^{-1}$

Table II.11(b)

I_{abs} dependence; $[Tl(I)] = .100$; $[Tl(III)] = .0051$ mole l^{-1}

$I_o \times 10^6$ Einstein l^{-1} min^{-1}	115	36.3	33.5	9.50	5.82	3.72	2.84
I_{abs} ($I_{abs}/I_o = .315$)	36.2	11.4	10.5_5	2.99	1.84	1.17	.895
$t_{\frac{1}{2}}$ (min)	11.5	20	37	80	118	135	190
	13.3	22	32			142	
$R_{ex} \times 10^5$ mole l^{-1} min^{-1}	28.8	16.2	8.99	3.82	2.46	2.11	1.39
	24.8	14.9	10.1	3.8		1.90	
ϕ_{ex}^{1}	7.95*	14.2*	5.50	12.8	13.4	18.0	15.5
	6.85	13.1	9.56			16.9	

* These four results were determined on a solution prepared from Tl_2CO_3. The remainder were determined on a solution prepared from Tl_2O_3.

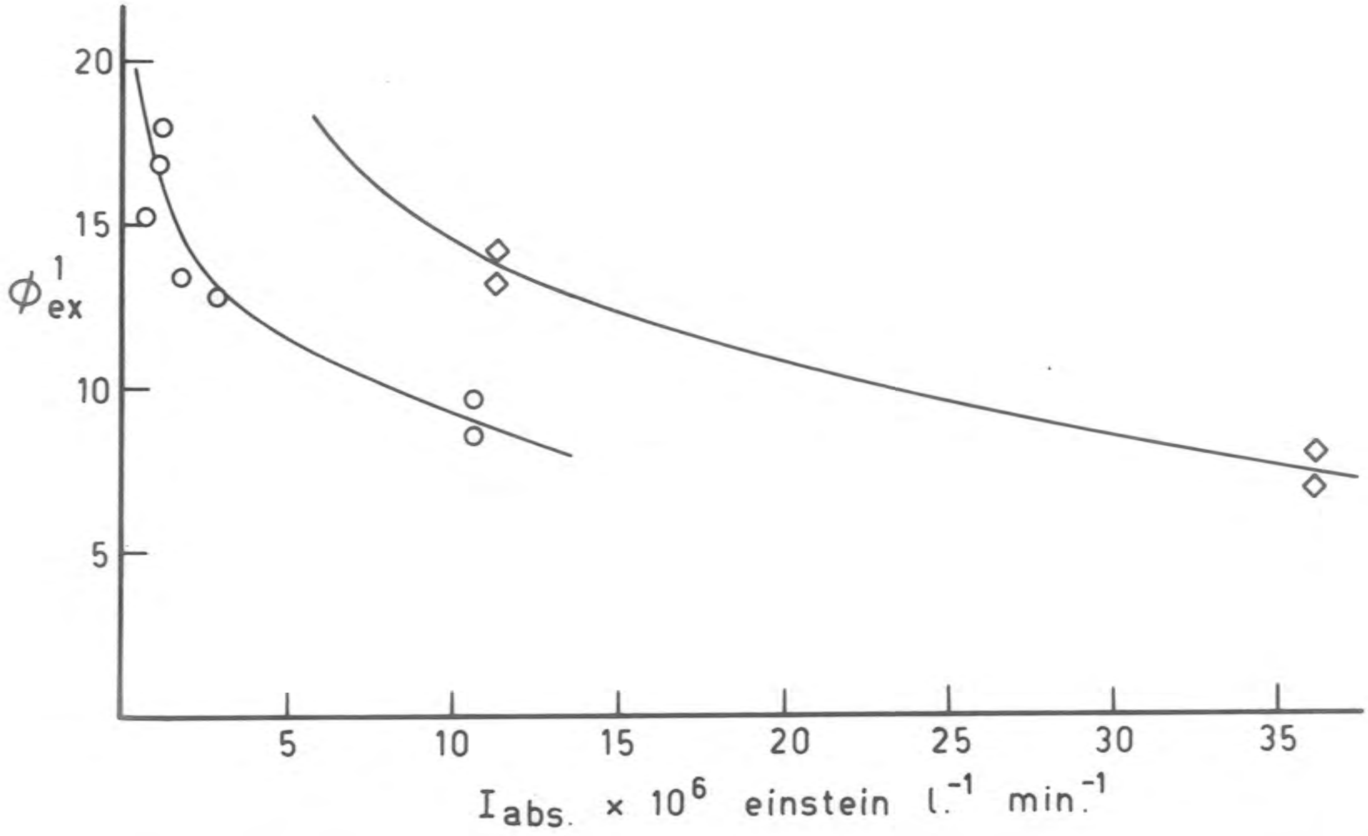


FIG. II·11 (b) $I_{abs.}$ Dependence [Tl(I)] = ·100 [Tl(III)] = ·0051 mole l.$^{-1}$

○ Solution prepared from Tl_2O_3

◇ Solution " " Tl_2CO_3

Table II.11(c)

I_{abs} dependence; [Tl(III)] = .0412; [Tl(I)] = .00315 mole l^{-1}

$I_o \times 10^6$	134	36.3	10.37	6.30	3.16
$R_{ex} \times 10^5$ mole l^{-1} min^{-1}	22.5	10.6 8.30	5.50	4.10	2.30
$I_{abs}{}^1 \times 10^6$	130	35.3	10.1_0	6.14	3.08
ϕ_{ex}^1	1.73	3.00 2.35	5.45	6.69	7.47
$I_{abs}{}^2 \times 10^6$	107	29.0	8.30	5.05	2.53
ϕ_{ex}^2	2.10	3.66 2.86	6.64	8.12	9.09

I_o, I_{abs} Einstein l^{-1} min^{-1}

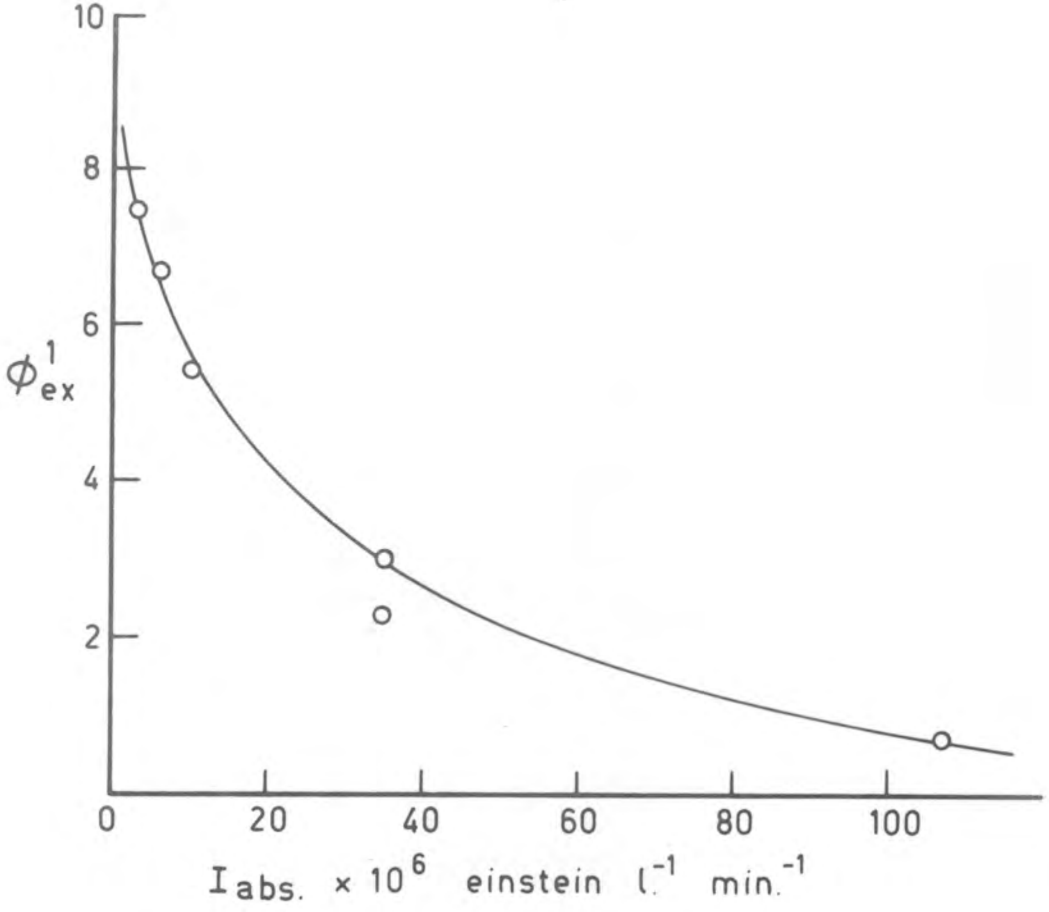


FIG. II·11 (c) $I_{abs.}$ Dependence.
[Tl(I)] = 0.0051 [Tl(III)] = 0.0412 mole l.$^{-1}$

Table II.11(d)

I_{abs} dependence; $[Tl(I)] = .0051$; $[Tl(III)] = .0400$ mole l^{-1}

$I_o \times 10^6$ Einstein l^{-1} min^{-1}	33.5	9.50	5.82	3.72	2.84
$R_{ex} \times 10^5$ mole l^{-1} min^{-1}	10.4	6.13	4.33	3.15	2.70
I_{abs}^{1}	32.3	9.15	5.60	3.59	2.24
ϕ_{ex}^{1}	3.22	6.70	7.73	8.78	9.86
I_{abs}^{2}	26.6	7.51	4.60	2.95	2.25
ϕ_{ex}^{2}	3.96	8.35	9.75	11.2	12.7

I. Temperature Dependence

Table II.12 shows the temperature dependence of the quantum yield for exchange. This work was done at an early stage in the study, and the solutions were not pre-irradiated. The reliability of the results is less than in the pre-irradiated solutions.

Calculation.

The rate of exchange was determined in the usual manner. The temperature dependence of the fraction of light absorbed I_{abs}/I_o, was calculated from the values of the extinction coefficients and acidity

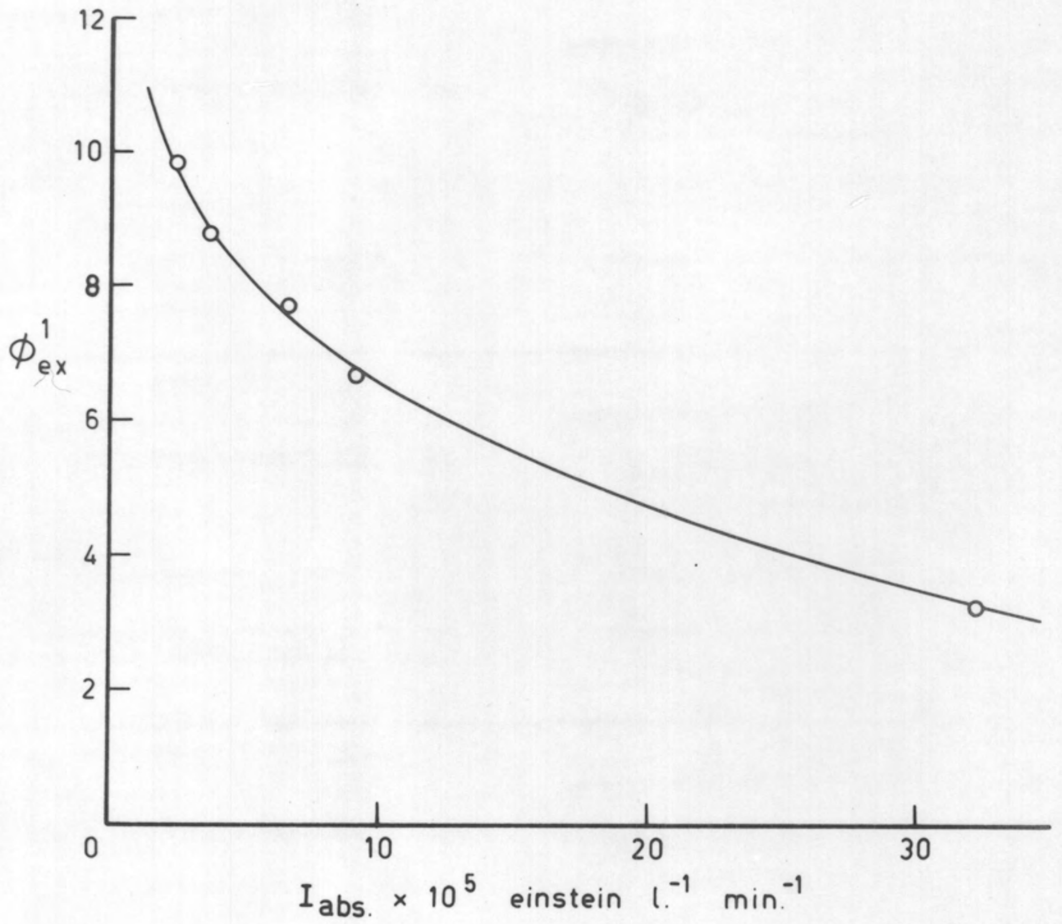


FIG. II · 11 (d) $I_{abs.}$ Dependence

[Tl(I)] = 0.0051 [Tl(III)] = 0.0400 mole l.$^{-1}$

Table II.12

Temperature Dependence

$[\mathrm{Tl(III)}] = .005$ mole l^{-1} $[\mathrm{Tl(I)}] = .0051$ mole l^{-1}

$[\mathrm{H}^{+}] = 1.10$ mole l^{-1} $I_o = 3.35 \times 10^{-5}$ Einstein l^{-1} min^{-1}

Temp. °C	$t_{\frac{1}{2}}$ min	Rate x 10^{-3} mole l^{-1} min^{-1}	I_{abs}/I_o	ϕ_{ex}^{1}
15.2	48	3.61	.258	4.19
20.1	47	3.69	.298	3.70
25.0	31	5.57	.344	4.84
29.1	26	6.66	.374	5.32
35.0	23	7.52	.454	4.95
35.0	20.5	8.46	.454	5.57
41.4	17	10.2	.505	6.02
48.0	13.5	12.8	.583	6.55

At 40°C, $\epsilon_{\mathrm{Tl}^{3+}} = 10$; $\epsilon_{\mathrm{TlOH}^{2+}} = 590$; $K = .101 \pm .006$

At 25°C, $\epsilon_{\mathrm{Tl}^{3+}} = 8$; $\epsilon_{\mathrm{TlOH}^{2+}} = 415$; $K = .089 \pm .004$

constants at 25°C and 40°C taken from Waind and Rogers (see Table II.12 for values). The apparent extinction coefficients for Tl(III), calculated from these values were plotted against temperature, assuming the same small curvature as the optical density versus

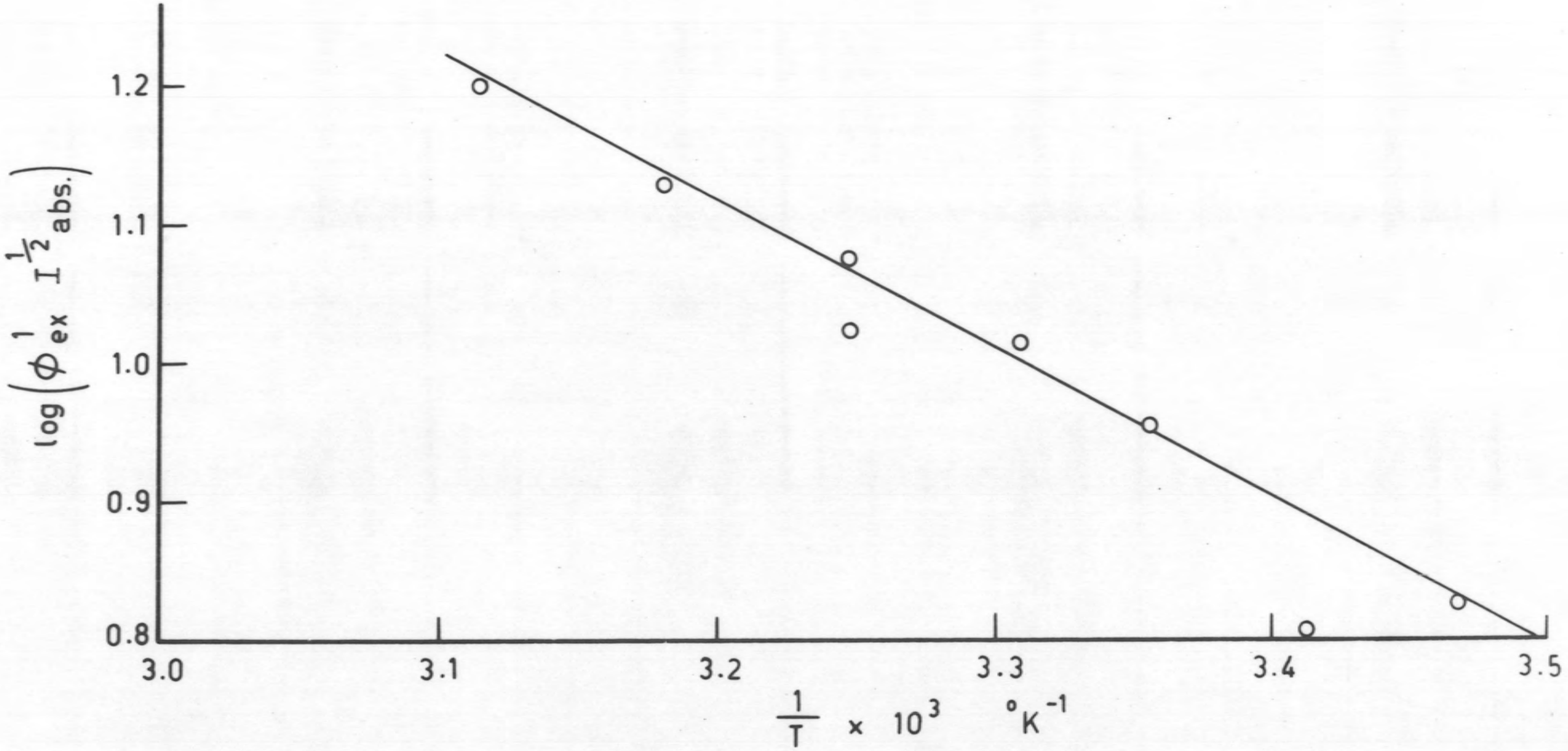


FIG. II · 12 Temperature Dependence.

$[Tl(III)] = 0.005$ $[Tl(1)] = 0.0051$ mole $l.^{-1}$

temperature plot obtained experimentally for a Tl(III) solution in the range 15-25°C. (There is only a small deviation from linearity, a 15% deviation at the lowest temperature, but considerably less at other values. It is considered that the error resulting from this assumption will be less than 5% at all temperatures and less in the range 25-40°C.) The quantum yield for exchange was otherwise calculated in the normal manner.

Fig. II.12 is a plot of log $\phi_{ex}^{1} I_{abs}^{\frac{1}{2}}$ against 1/T, which is a reasonable straight line. Now if the $\phi_{ex} I_{abs}^{\frac{1}{2}}$ values are converted to R_{ex} values by assuming I_{abs} has a constant value (25° value used), the slope of the graph may be fitted to the Arrhenius equation,

$$K_{ex} = Ae^{-\Delta G^{\neq}/RT},$$

where K_{ex} is the rate constant for exchange, $\Delta G^{\neq}$ is the activation energy, and A is a constant independent of temperature. Hence a value for $\Delta G^{\neq}$ may be calculated from the slope of the graph; and is found to be 5.0 ± 1 kcal mole^{-1}. $\phi_{ex}^{1} I_{abs}^{\frac{1}{2}}$ is plotted as this is the factor which should be independent of light intensity. Thus the activation energy calculated as described above should be independent of the increase in absorbed light intensity with increase in temperature. Actually as will be seen later, the correction is not exact, however the activation energy will not be affected by the change in light intensity with temperature by more than one kcal mole^{-1}. (The activation energy obtained by directly plotting log R_{ex} against $1/T$ is 7.3 kcal mole^{-1}.)

J. Dependence on the Wavelength of Irradiation

(a) Experimental.

The dependence on wavelength was studied with a 400 watt Osram xenon arc coupled to a Bausch and Lomb high intensity monochromator. The xenon arc was run off a stabilized D.C. power supply at a voltage of 10 volts and a current of 25 amps.

A silica lens system was used to focus the light from the xenon arc onto the entrance slit of the monochromator. According to information supplied by the manufacturer, the entrance and exit slits used in this experiment result in a 100 Å spread of wavelength at the exit, but with a maximum intensity at the dialled wavelength. A 1 cm silica spectrophotometer cell was accurately located in a constant position in the light beam, at a distance from the monochromator so that the cell was completely illuminated. However the light from the monochromator was not uniform in either intensity or wavelength across the cell face. An approximate diagram of the intensity and wavelength distribution is shown in Fig. II.13. The solid curve represents the distribution of absorbed light intensity across the light beam. The most intense absorption region thus would appear to fall at a wavelength lower than the wavelength dialled on the monochromator. However no allowance was made for this in the calculation, because of the difficulty of making any quantitative

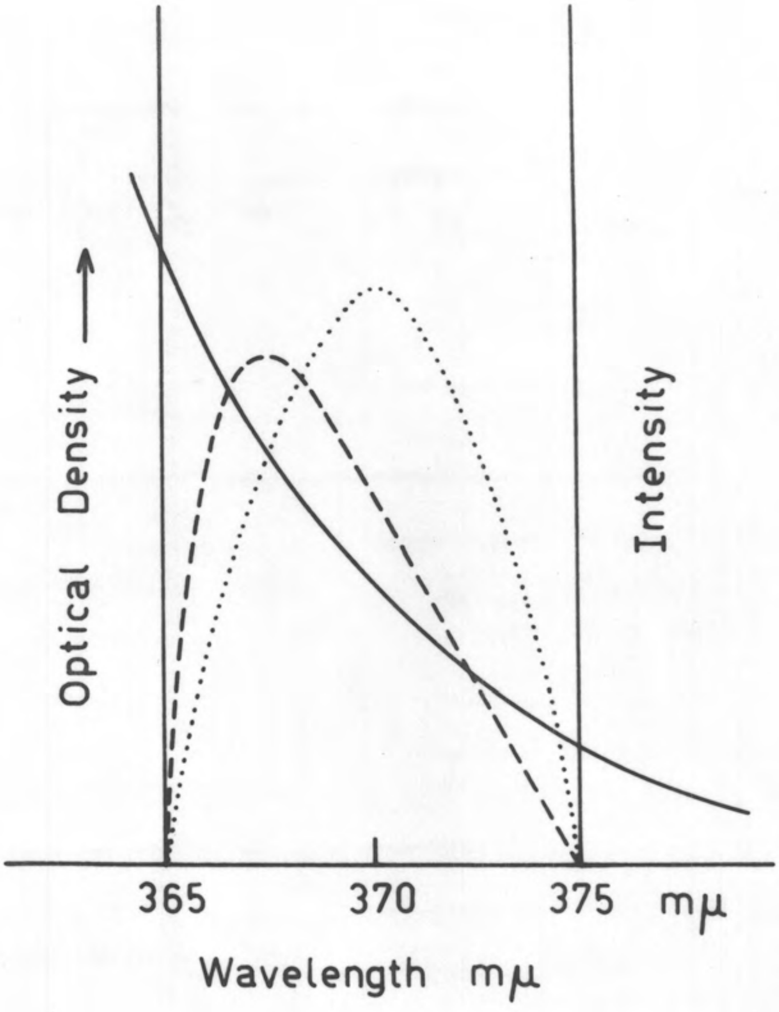


FIG. II·13 Distribution of Absorption Across the Cell.

——— Optical density of reactant solution.

········· Incident light intensity.

– – – – Absorbed light intensity

estimates of the error. There are two reasons for this.

(1) The output data for the monochromator supplied by the manufacturer presumably only applies for a uniform light source at the entrance slit. The source used in this experiment is not uniform in intensity.

(2) The cell is located inside the light beam which overlaps the cell to an unknown extent.

To determine the rate of reaction a 2 ml aliquot of reactant solution ($[Tl(III)] = .0214M$, $[Tl(I)] = .0224M$, $[HClO_4] = 1.10M$) was irradiated in the cell. After irradiation for time t, two samples were taken, separated and radioactively assayed. Samples were not taken at more than one time, as a change in the volume of solution in the cell would have altered the value of I_{abs} significantly. The half-time was determined from the usual log $(1 - F) - t$ plot assuming F the fraction of exchange to be zero at $t = 0$. The procedure was repeated twice at each wavelength with different times of irradiation. The runs were done in a thermostatted room which varied in temperature from 19 to 21°C.

The light intensity was determined with a 2 ml aliquot of ferrioxalate actinometer solution in the reaction cell. The small background of visible light was allowed for by actinometry with a soda glass filter in the light beam.

(b) Wavelength dependence - results.

Table II.13 shows the results obtained from a

Table II.13

Wavelength Dependence

$[Tl(III)] = .0214$; $[Tl(I)] = .0224$; $[HClO_4] = 1.10$ mole l^{-1}

Wavelength mμ	230	240	250	260	270
$I_o \times 10^6$ Einstein l^{-1} min^{-1}	1.96	2.84	4.80	4.45	7.11
$t_{\frac{1}{2}}$ min	440	275	130	100	130
	400	220	130	120	110
$R_{ex} \times 10^5$ mole l^{-1} min^{-1}	1.80	3.05	5.60	6.90	6.30
% abs. total	100	100	88.5	65.3	41.1
ϕ_{ex}	9.2	10.8	13.2	23.8	21.6
$\phi_{ex} I_{abs}^{\frac{1}{2}} \times 10^3$	12.9	17.9	26.4	40.5	37.0
% abs. Tl(III)	23.2	52	93	99	99.4
ϕ_{ex}^{1}	39.6	20.6	14.2	24.0	21.8
$\phi_{ex}^{1} I_{abs}^{\frac{1}{2}} \times 10^4$	267	251	282	406	371
% abs. $TlOH^{2+}$	6.3	33.0	65.5	52.3	30.6
ϕ_{ex}^{2}	146	32.6	17.9	29.8	29.0
$\phi_{ex}^{2} I_{abs}^{\frac{1}{2}} \times 10^4$	511	316	317	455	427

study of the variation of quantum yield with wavelength. The values of $t_{\frac{1}{2}}$ determined for the two irradiations are recorded with the longer irradiation second. The extinction coefficients in Table II.6 were used to calculate the % absorption by (a) all the species in solution, including Tl(I) ($\emptyset_{ex}$). (b) Tl(III) species only ($\emptyset_{ex}^{1}$). (c) $TlOH^{2+}$ only ($\emptyset_{ex}^{2}$). The values of % absorption and I_{abs} for these species are recorded in the table, together with the respective quantum yields for exchange.

Errors.

The errors in these results are of considerable magnitude for the following reasons:

(1) As discussed in the experimental section the distribution of intensity across the wavelength range is difficult to assess. The wavelengths for which calculations have been done is the wavelength dialled by the monochromator. Even assuming that the monochromator is accurate, the maximum intensity of absorbed light may fall above or below this value by up to 5 mμ. This is especially true where the % absorption is changing rapidly with wavelength. Thus it is possible that the optical density values used differ from the average value for the particular wavelength under consideration; but the magnitude of the wavelength error is not likely to be greater than 5 mμ. The error in the % absorption will therefore be less than the difference between the value used at wavelength λ, and the value at

$\lambda \pm 5$ mμ. From the figures in the table it may be seen that a maximum error of less than ± 15% is expected.

The error in some of the optical density values, especially at 230 mμ, may be considerable. However, this is not likely to be a major source of error even at 230 mμ.

(2) The actual fluctuations in light intensity may be considerable as there was some flicker in the light source. The random variation in the rate of exchange should also cover this source of error.

The random error in actinometry was ± 10%.

(3) Error in the rate of exchange. Significant random errors in the rate of exchange indicate an error of about ± 20%. Systematic errors in the calculation are negligible as compared to this value.

Thus the overall random error in the quantum yield is of the order of ± 50%.

K. Effect of Added Anions

The effect of adding another anion to the solution was tested experimentally. Table II.14 lists the results obtained with a solution .050 mole l^{-1} in Tl(I), .0051 mole l^{-1} in Tl(III), and 1.10 mole l^{-1} in $HClO_4$.

Table II.14

Additive	$t_{\frac{1}{2}}$ min	Optical Density	$R_{ex} \times 10^5$ mole l^{-1} min^{-1}	% abs. Tl(III)	ϕ_{ex}^{1}	$\phi_{ex}^{1} I_{abs}^{\frac{1}{2}}$
No additive	23	.255	13.7	33.1	12.3	41.0
10^{-3} NaCl	18	$.87_0$	17.5	80.4	6.5	33.7
10^{-3} Na_2SO_4	30 ± 5	.395	10.5	50.0	6.5	26.6

$I_o = 3.35 \times 10^{-5}$ Einstein l min^{-1}

The optical density of the reactant solutions were measured, but to establish meaningful quantum yields the relative optical densities of the species present, need to be known. It can safely be assumed however, from known stability constants, that complexing of Tl(I) will be negligible. Hence the optical density may be attributed to thallic species except for a contribution of .065 from Tl^+_{aq}. Quantum yields have been calculated on this basis.

L. Dependence on $HClO_4$ Concentration

Consideration was given to the possibility of useful results being determined from a study of the acid dependence of the quantum yield. Since varying the acid concentration varies the absorbed light intensity, the ratio of Tl(III) hydroxy and aquo species, and possibly the degree of hydrolysis of the chain carrier, quantitative interpretation of an acid dependence would not be possible.

However, to check for the possibility of unexpected large effects, an I_{abs} dependence was performed on a solution .4 mole l^{-1} in $HClO_4$ and .005 mole l^{-1} in both Tl(I) and Tl(III). The quantum yields were within a factor of two of the corresponding quantum yields at $[HClO_4]$ of 1.10 mole l^{-1}. This also established that the control over the acid strength was sufficient to reduce the error in quantum yield (due to error in acid concentration) to an insignificant amount.

Rotating sector measurements.

Two rotating sectors were used in this work. The first model was a large 90° sector which was used directly in the light beam. The second sector was a large disc with square one inch deep notches cut out from the circumfrence giving $^{2}/_{3}$ dark and $^{1}/_{3}$ light. The light beam was focussed with a 3" silica lens to a point at which the sector was located. Because of the inhomogeneity of the beam a point focus was, of course, not possible.

The 90° sector could be rotated up to 2,500 revs. min^{-1}, and the notched sector at 1,400 revs. min^{-1}. Under all conditions the quantum yield was within 10% of the quantum yield under continuous illumination. No change in rate of exchange was observed on increasing the speed of rotation to a maximum after an initial period at slow sector speeds. This indicates a very short lifetime for the chain carrier. No effect was observed for a light period of less than 5×10^{-3} sec, so that the lifetime must be less than this. A calculation assuming $\phi_{ex} \propto I_{abs}^{\frac{1}{2}}$, and making no allowance for penumbra effects, gave a value considerably larger than diffusion controlled rate constants for the termination rate constant.

SECTION II

CHAPTER 4: DISCUSSION

A. Mechanism of the Exchange Reaction

The quantum yield represents the number of reactions occurring per quantum of absorbed light. As one quantum will usually produce only one excited state or reactive species (dissociation of an excited state may produce more than one reactive fragment), quantum yields of less than one will usually be observed; unless the excited state can induce more than one reaction by a chain mechanism. Conversely, in this study quantum yields of up to thirty have been found, so that a chain mechanism must be invoked.

The next section attempts to find the simplest mechanism consistent with the kinetic data. As discussed in Section I, a chain mechanism for an exchange reaction must involve at least four reactions (not necessarily all independent).

(1) One initiation reaction.

(2) Two propagation reactions.

(3) One termination reaction.

Each of these stages is dealt with in detail in an attempt to find the most probable mechanism, consistent in broad terms with the kinetic data. Following this, the agreement between the experimental data and the proposed mechanism is discussed in detail.

(1) Initiation.

The initiation reaction or reactions in a chain mechanism produce the reactive species called the chain carrier, which induces reaction through the propagating steps.

Now, initiation in this photochemical reaction is induced by the absorption of a quantum of light. In the reactant solution there are three chromophores which absorb light and may produce a chain carrier. They are:

$\underline{Tl^{+}_{aq}}$. The single Tl(I) species, Tl^{+}_{aq}, absorbs a small proportion of the incident light at very high Tl(I) concentrations at 254 mμ. The Tl^{+}_{aq} absorption is considered to have no influence on the reaction (except indirectly by reducing the Tl(III) absorption). This conclusion is based on a consideration of the plateau region at high Tl(I) concentrations in the [Tl(I)] against ϕ_{ex} dependence. In the [Tl(I)] region of .05 to .15 mole l^{-1}, ϕ_{ex} is independent of Tl(I) concentration (see Table II.9). If Tl^{+}_{aq} absorption was producing chain carriers in significant concentration, ϕ_{ex} should increase with increasing [Tl(I)], as ϕ_{ex} is proportional to the chain carrier concentration. This conclusion is supported by a study of the dependence of ϕ_{ex} on wavelength of irradiation. If the Tl^{+}_{aq} absorption is considered to be creating chain carriers, the quantum yield calculated using this absorption should not decrease with decrease in wavelength, as observed experimentally (Table II.13).

<u>Tl(III)</u>. From the spectroscopic study of Waind and Rogers(4) it was concluded that there are only two chromophores in a solution of Tl(III) perchlorate in perchloric acid ($HClO_4$ > .5M). At 254 mμ

and 1.10M $HClO_4$, $TlOH^{2+}$ absorbs 82% of the light absorbed by thallium(III) and Tl^{3+}_{aq} absorbs the remaining 18%, even though $[TlOH^{2+}]$ is only 8% of the total [Tl(III)].

The Tl(III) absorption spectrum (Fig. II.1) is typical of charge-transfer bands for aquated cations, appearing in the far ultraviolet with a large oscillator strength. (Maximum extinction coefficients $> 10^4$ cm l mole^{-1}.) By analogy with other cations in high oxidation states (e.g. Fe(III), Co(III), Ce(IV)), the charge-transfer occurs from solvent (or ligand) to cation, producing an excited state with a reduced cation and an oxidized solvent molecule. For the $TlOH^{2+}$ species the absorption of a quantum may be represented by

$$h\nu + TlOH^{2+} \rightarrow \overset{*}{T}lOH^{2+}$$

or

$$h\nu + (Tl^{3+}OH^-) \rightarrow (Tl^{2+}OH)$$

where the brackets represent a solvent cage. Thus, on the assignation of this absorption band to charge-transfer, the first excited state for $TlOH^{2+}$ is expected to have a charge distribution shifted from that represented by $Tl^{3+}OH^-$ towards $Tl^{2+}OH$.

This excited state may decay to a lower energy state in several possible ways.

(a) By the reverse of the excitation process, i.e. back electron transfer to the ground state (or high vibrationally excited states of the ground electronic state). The energy of the absorbed quantum may be emitted as light (luminescence) or it may be transferred to the surrounding solvent molecules. If luminescent emission occurs, the lifetime of the excited state, calculated from the equation for spontaneous emission (see page 27) would be less than 10^{-7} sec. No luminescent inorganic charge-transfer excited states in aqueous solution have been reported in the literature. However no attempt to detect luminescence has been made in this study.

(b) The second possible fate of the ($\overset{*}{Tl}{}^{2+}OH$) excited state is dissociation into

$$\overset{*}{Tl}{}^{2+}OH \rightleftharpoons Tl^{2+}_{aq} + OH \qquad (1)$$

This is the most likely reaction by analogy with other similar charge-transfer excited states (see introduction). The potential energy minimum for the excited state may be expected to be small (i.e. the bonding is weak between Tl^{2+} and OH); so that dissociation will occur if the excited state is formed with only a small amount of repulsive energy in this vibrational mode.

The analogous excited state for the Tl^{3+}_{aq} species (which may be represented as ($Tl^{2+\ +}_{aq}$)), may also dissociate according to

$$(Tl^{2+\ +}_{aq}) \rightleftharpoons Tl^{2+}_{aq} + H_2O^{+} \rightarrow Tl^{2+}_{aq} + H^{+} + OH \qquad (1a)$$

yielding the same products. However the relative rates of forward and back reactions may be different for the two excited states; this will affect the quantum yield for the formation of Tl(II) via these reactions. The problem is discussed in more detail later.

(c) Other possible products of the decay of the charge-transfer excited state ($Tl^{2+}OH$), are electronically excited fragments such as

$Tl(II)^{\neq}$ and $OH^{\neq}$. Again the lifetime of these species is expected to be too short to be kinetically significant.

(d) The possibility of a dissociation process involving reaction with thallium(I) or (III) such as

$$(\overset{*}{T}l^{2+}OH) + Tl(I) \rightarrow 2Tl(II) + OH^-$$

has been considered. (See Appendix for derivation of appropriate rate expressions.) But, as the rate expressions do not fit the rate data any better than the simpler initiation reaction involving dissociation of the excited state, the mechanism is not considered further.

Thus the most likely initiation reaction is

$$Tl^{3+}OH^- + h\nu \rightleftarrows (\overset{*}{T}l^{2+}OH) \overset{\phi_1}{\rightleftarrows} Tl^{2+}_{aq} + OH \qquad (1)$$

and the analogous reaction for Tl^{3+}_{aq} excitation,

$$Tl^{3+}_{aq} + h\nu \rightleftarrows (Tl^{3+}_{aq}{}^{+}) \xrightarrow{\phi_1} Tl^{2+}_{aq} + OH + H^+ \qquad (1a)$$

where ϕ_1, the primary quantum yield is defined as the fraction of geminate pairs that escape both primary and secondary recombination. The observation that the quantum yield is not affected greatly by a large decrease in acid concentration; supports the hypothesis that $TlOH^{2+}$ is the main initiating chromophore. At the low acid concentration nearly all the light will be absorbed by this species.

From the treatment of Noyes of the probability of secondary recombination of geminate radical pairs, it is possible to speculate on the probable value of ϕ_1 for reaction (1), and the relative value of ϕ_1 for reactions (1) and (1a).

(ii) Secondary recombination.

Three factors control the efficiency of secondary recombination. (a) The probability of reaction per encounter (δ) of the geminate pair. The back reaction of (1) is expected to be very efficient, as it involves the reaction of a strong oxidant (OH), with a probable strong reductant (Tl(II)). It is quite likely that $\delta = 1$ for this reaction. Some rate constants for some similar reactions for comparison (taken from (60)) are:

$Fe^{2+} + OH$	3×10^{8} l mole^{-1} sec^{-1}
$Sn^{2+} + OH$	2×10^{9} "
$Ce^{3+} + OH$	2×10^{8} "

Noyes has shown that if $\delta < .1$, secondary recombination will be insignificant. The back reaction of (1a) is also probably very efficient.

(b) The separation distance of the geminate pair when they come to thermal equilibrium with the solvent.

(c) The probability of reencounter of the geminate pair after separation from a non-reactive encounter.

Quantitative calculation of these parameters and hence the probability of secondary recombination, using the Noyes equations, is not possible, as the difference in energy between $Tl^{3+}OH^{-}$ and $Tl^{2+}OH$ cannot be determined sufficiently accurately from any known data. The approximations in the Noyes theory would almost certainly not be justified in this system anyway. However, possibly some significance may be placed on differences between (1) and (1a). The difference in the energy between reactions (1) and (1a) can be shown to be equal to the energy of the acid dissociation reaction,

$$H^+ + TlOH^{2+}_{aq} \rightleftharpoons Tl^{3+}_{aq}$$

Using the van't Hoff equation and the values of the stability constants given by Waind and Rogers at 25 and 40°C, the enthalpy change for the reaction was calculated to be less than 2.6 kcal $mole^{-1}$. This value is insignificant compared to the approximations made in the Noyes calculation. Dainton et al(57) considered the analogous problem in the case of Fe^{3+}_{aq} and $Fe^{3+}OH^-$. They considered unjustified the assumption that the energy of hydration of the H^+ ion (in reaction (1a)) is converted to kinetic energy of the fragments. The H^+ is not completely hydrated until it is dissociated from the geminate Tl(II), and the energy of hydration will thus not be converted to kinetic energy. On this basis they justified the experimental observation that the primary quantum yield for the Fe^{3+}_{aq} species was less than for $Fe^{3+}OH^-$. They found $\phi_1 = .05$ at 254 mμ for Fe^{3+}_{aq} absorption as compared to $\phi_1 = .15$ at 313 mμ for $FeOH^{2+}$ absorption.

(iii) Primary recombination.

Very little is known of the possible extent of primary recombination in these systems. The lifetime of the species in the solvent cage is likely to be small (10^{-13} sec, Noyes), so that competing processes must be very rapid. Radiationless transitions to the ground state may compete with charge-transfer excited state dissociation.

Theoretically, then, the difficulties of calculating ϕ_1 are too great. However, considering the high probability of reaction per encounter (δ), recombination is likely to be significant.

Comparison to similar systems Fe(III) and Ce(IV), suggest that the primary quantum yield will be considerably less than 1, and perhaps of the order of .1 (see Table I.1 for values).

To complete the discussion of the probable initiation sequence, the influence of the reaction

$$\mathrm{OH} + \mathrm{Tl(I)} \rightarrow \mathrm{Tl(II)} + \mathrm{OH}^- \qquad (2)$$

needs to be considered. From radiation and photochemical studies it has been reported that the rate constant for this reaction is 9×10^9 l mole^{-1} sec^{-1} (60) which is very rapid and may be assumed to be diffusion controlled. (The rate constant was determined in .4M H_2SO_4.) This reaction will compete with the back reaction of (1),

$$\mathrm{Tl(II)} + \mathrm{OH} \rightarrow \mathrm{Tl(III)} + \mathrm{OH}^- \qquad (1)'$$

both with secondary and tertiary recombination. Reaction (2) is so rapid, that for radicals randomly distributed (i.e. those that escape secondary recombination), it will, because $[\mathrm{Tl(I)}] \gg [\mathrm{Tl(II)}]$, scavenge all the OH radicals. (Preventing tertiary recombination.)

Noyes(59) discussed the possibility of competition between secondary recombination and scavenging reactions. He derived an expression for the increased efficiency of scavenging (α), through competition with secondary recombination.

$$\alpha = 2a \frac{(\alpha)}{2\pi k_2'[s]} - \delta\ K_2 a^2[s]/\beta' + \ldots$$

According to Noyes the maximum value of a is 1.6×10^{-6} $\sec^{\frac{1}{2}}$, k_2' is the rate constant for the scavenging reaction (2) and [s] is the concentration of the scavenger [Tl(I)]. k_2' has been reported to be 9×10^9 l mole^{-1} $\sec^{-1}$ and for [Tl(I)] = .1M the increased scavenging efficiency is less than .2. Now if the probability of reaction per encounter (δ) is one for reaction (1), secondary recombination (β) may be significant, so that at this concentration scavenging by Tl(I) may be significantly competing with secondary recombination. However, the expression derived by Noyes assumes the products of scavenging are unreactive, i.e. they can no longer undergo recombination reactions. In the $TlOH^{2+}$ system, the OH radical is replaced by Tl(II) which also reacts very rapidly with Tl(II). Now if the reaction

$$Tl(II) + Tl(II) \rightarrow Tl(I) + OH \qquad (5)$$

is as efficient as the back reaction of (1), i.e. (1)', then reaction (2) will not effectively be competing with secondary recombination, as the rate of recombination of two Tl(II) radicals will be as great as the rate of recombination of Tl(II) with OH. The rate constant reported for reaction (5) of $2.3 \pm .8 \times 10^9$ l mole^{-1} $\sec^{-1}$ is close to diffusion controlled, as reaction (1)' is expected to be, so that secondary recombination may not be greatly reduced. All this argument attempts to show that the competition by reaction (2) with secondary recombination may significantly affect ϕ_1, but the variation of ϕ_1 with Tl(I) concentration due to this, will probably be insignificant; but certainly not affecting the primary quantum yield by more than 20%. This is supported by the lack of effect on ϕ_{ex} of increasing [Tl(I)] at high [Tl(I)]. In conclusion the initiation scheme may be schematically shown as

$$\mathrm{Tl}^{2+}\mathrm{OH}^- + h\nu \xrightarrow{\phi_1} \mathrm{Tl(II)} + \mathrm{OH} \qquad (1)$$

$$\mathrm{Tl(I)} + \mathrm{OH} \rightarrow \mathrm{Tl(II)} + \mathrm{OH}^- \qquad (2)$$

In the derivation of the rate expression it is necessary to assume that ϕ_1 is independent of reactant concentrations. In the light of the discussion on the last page this is probably a reasonable assumption.

2. Propagation.

For a complete exchange reaction, both thallous and thallic species must react with the chain carrier. If Tl(II) is the chain carrier two possible reactions are:

$$\mathrm{Tl}^{2+} + \overset{*}{\mathrm{T}}\mathrm{l(III)} \overset{K_3}{\rightleftharpoons} \overset{*}{\mathrm{T}}\mathrm{l(II)} + \mathrm{Tl(III)} \qquad (3)$$

$$\overset{*}{\mathrm{T}}\mathrm{l}^{2+} + \mathrm{Tl(I)} \overset{K_1}{\rightleftharpoons} \mathrm{Tl(II)} + \overset{*}{\mathrm{T}}\mathrm{l(I)} \qquad (4)$$

where the asterisk * indicates a labelled species. This reaction sequence satisfies the condition for chain propagating reactions, that reaction is induced without destruction of the chain carrier. The thallium(III) species involved is not specified, it may be either one or both of the Tl(III) species, Tl^{3+}_{aq} or TlOH^{2+}.
Other possible species that may act as chain carriers instead of Tl(II)

to be considered were:

(a) $(\mathrm{Tl}^{\neq}\mathrm{OH}^{2+})$- an excited TlOH^{2+} species. This chain carrier as a major contributor to the mechanism may be ruled out because the termination step would be a unimolecular decay to the ground state; which would yield a quantum yield independent of light intensity. This is contrary to the results.

(b) Electronically excited Tl(II). This possibility is improbable as the excitation would have to be transferred from one nucleus to another during electron transfer. (This, although unusual, is not obviously impossible.) As the chain carrier has to undergo a number of reactions (at least twice the chain length), reactions (3) and (4) must be extremely fast or the lifetime of the chain carrier must be long. Electronically excited states cannot have a lifetime greater than the lifetime for spontaneous emission which is 10^{-7} to 10^{-8} seconds for a highly allowed transitions. A possible excited Tl(II) excited state is the ^{2}P state with a ground state ^{2}S. The resulting transition would only be weakly forbidden, and hence would be expected to have a short lifetime. Cercek et al calculated a maximum molar extinction coefficient for Tl(II) of 5400, which would indicate an allowed transition. Thus the excited state of Tl(II) is not likely to have a long lifetime.

(c) Hydrolysed thallium(II) species. Possibly, but kinetically indistinguishable from Tl^{2+}_{aq}.

(d) Since the chain carrier must transfer the Tl^{204} label from Tl(III) to Tl(I), a non-thallium species is not capable of acting as a chain carrier.

3. Termination.

If Tl(II) is the chain carrier, the likely termination step is the disproportionation reaction,

$$\mathrm{Tl(II)} + \mathrm{Tl(III)} \rightarrow \mathrm{Tl(I)} + \mathrm{Tl(III)} \qquad (5)$$

As discussed under initiation all OH radicals are expected to be scavenged by Tl(I).

Overall mechanism.

The proposed mechanism is thus:

$$\text{Initiation} \qquad \mathrm{TlOH}^{2+} + h\nu \overset{\phi_1}{\rightleftarrows} \mathrm{Tl(II)} + \mathrm{OH} \qquad (1)$$

$$\mathrm{OH} + \mathrm{Tl(I)} \rightarrow \mathrm{Tl(II)} + \mathrm{OH}^- \qquad (2)$$

$$\text{Propagation} \quad \overset{*}{\mathrm{T}}\mathrm{l(III)} + \mathrm{Tl(II)} \overset{K_{III}}{\rightleftarrows} \mathrm{Tl(III)} = \overset{*}{\mathrm{T}}\mathrm{l(II)} \qquad (3)$$

$$\overset{*}{\mathrm{T}}\mathrm{l(II)} + \mathrm{Tl(I)} \overset{K_I}{\rightleftarrows} \mathrm{Tl(II)} + \overset{*}{\mathrm{T}}\mathrm{l(I)} \qquad (4)$$

$$\text{Termination} \quad \mathrm{Tl(II)} + \mathrm{Tl(II)} \xrightarrow{K_t} \mathrm{Tl(III)} + \mathrm{Tl(I)} \qquad (5)$$

where ϕ_1 is the quantum yield for Tl(II) and OH pairs that escape secondary and primary recombination, and K_{III}, K_I, and K_t are the rate constants for reactions (3), (4) and (5) respectively.

Before deriving an expression for the quantum yield of this reaction scheme the necessary assumptions and their validity require some discussion.

(1) It is assumed that ϕ_1, the primary quantum yield, is

independent of light intensity (I_{abs}). There is no apparent reason why this conventional assumption should not hold.

(2) It is assumed that ϕ_1 is also independent of both Tl(III) and Tl(I) concentrations. As described in the discussion of the initiation reaction a small dependence of ϕ_1 on Tl(I) concentration may exist due to the competition of reaction (2) with secondary recombination. But this is probably insignificant.

(3) The steady state assumption is applied to the concentration of active Tl(II). This approximation is valid as the concentration of active Tl(II) is small compared to active Tl(III) and Tl(I).

(4) It is assumed that the Tl(II) concentration is small compared to Tl(I) and Tl(III). This is valid.

The same kinetic expression is derived using

$$Tl^{3+}_{aq} + h\nu \xrightarrow{\phi_1} Tl(II) + H^+ + OH \qquad (1a)$$

as the initiation reaction. As, at this stage little can be said about the relative values of ϕ_1 for reaction (1) and (1a), both reactions must be considered.

The complete derivation of the following rate expression is given in the Appendix, together with derivations of some other rate expressions considered. For the above mechanism,

$$\phi_{ex} = \phi_1 \left\{ a + \frac{K_I[Tl(I)]\ K_{III}[Tl(III)]}{P} \left(\frac{1}{K_t I_{abs} \phi_1}\right)^{\frac{1}{2}} \right\}$$

where $P = K_{III}[Tl(III)] + K_I[Tl(I)] + 2(K_t I_{abs} \phi_1)^{\frac{1}{2}}$

and $a = (K_{III}[Tl(III)] + K_I[Tl(I)] + (K_t I_{abs}\phi_1)^{\frac{1}{2}})/P$.

For most conditions $K_{III}Tl(III) + K_I Tl(I)$ is $\gg 2(K_t I_{abs}\phi_1)^{\frac{1}{2}}$. Proof of this assumption for $\phi_{ex} \gg \phi_1$ is given in the Appendix. There are a few conditions where this assumption may lead to some error; these will be discussed in more detail in the appropriate place. With this assumption, which also leads to the approximation $a = 1$, the equation becomes,

$$\phi_{ex} - \phi_1 = \frac{K_I[Tl(I)]K_{III}[Tl(III)]}{K_I[Tl(I)] + K_{III}[Tl(III)]}\left(\frac{\phi_1}{K_t I_{abs}}\right)^{\frac{1}{2}} \qquad (i)$$

This may be rearranged to:

$$\frac{1}{\phi_{ex} - \phi_1} = \left\{\frac{K_t I_{abs}}{\phi_1}\right\}^{\frac{1}{2}} \left\{\frac{1}{K_{III}[Tl(III)]} + \frac{1}{K_I[Tl(I)]}\right\} \qquad (ii)$$

In this form the dependence of ϕ_{ex} on the experimental variables I_{abs}, $[Tl(I)]$, and $[Tl(III)]$ may be checked.

B. Comparison of Results and Mechanism

(a) Dependence of ϕ_{ex} on the rate of light absorption (I_{abs}).

The dependence of ϕ_{ex} on I_{abs} has been determined at four concentration ranges. The tables II.11 show the results obtained for Tl(III) absorption. From equation (ii) a plot of ϕ_{ex} against $I_{abs}^{-\frac{1}{2}}$ should be a straight line. However it was observed (for example, see Fig. II.14), that deviation from linearity occurs at low light intensities in all cases.

The deviation from linearity can be quantitatively measured

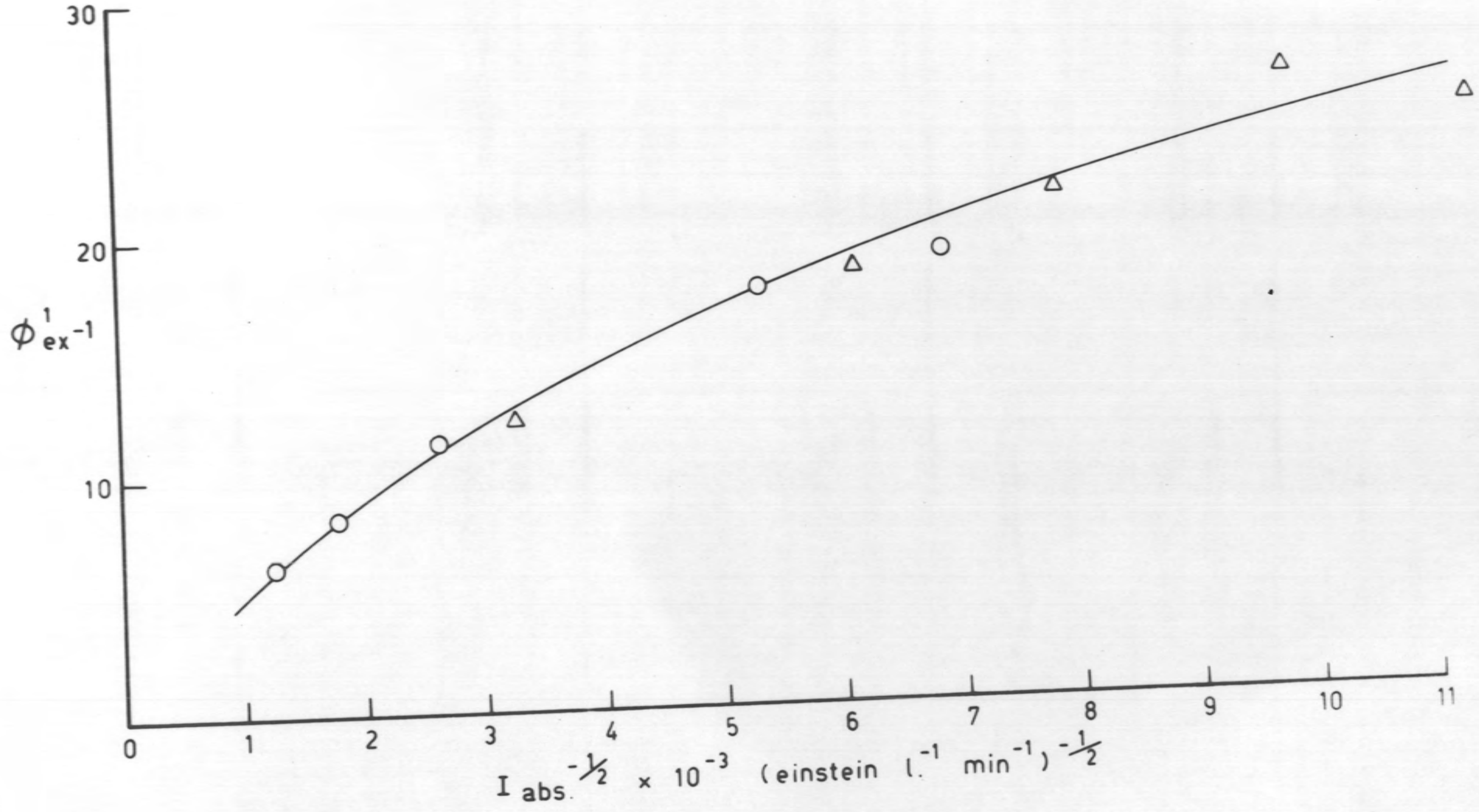


FIG. II·14 $I_{abs.}$ Dependence

$[Tl(I)] = 0.050$ $[Tl(III)] = 0.0051$ mole $l.^{-1}$

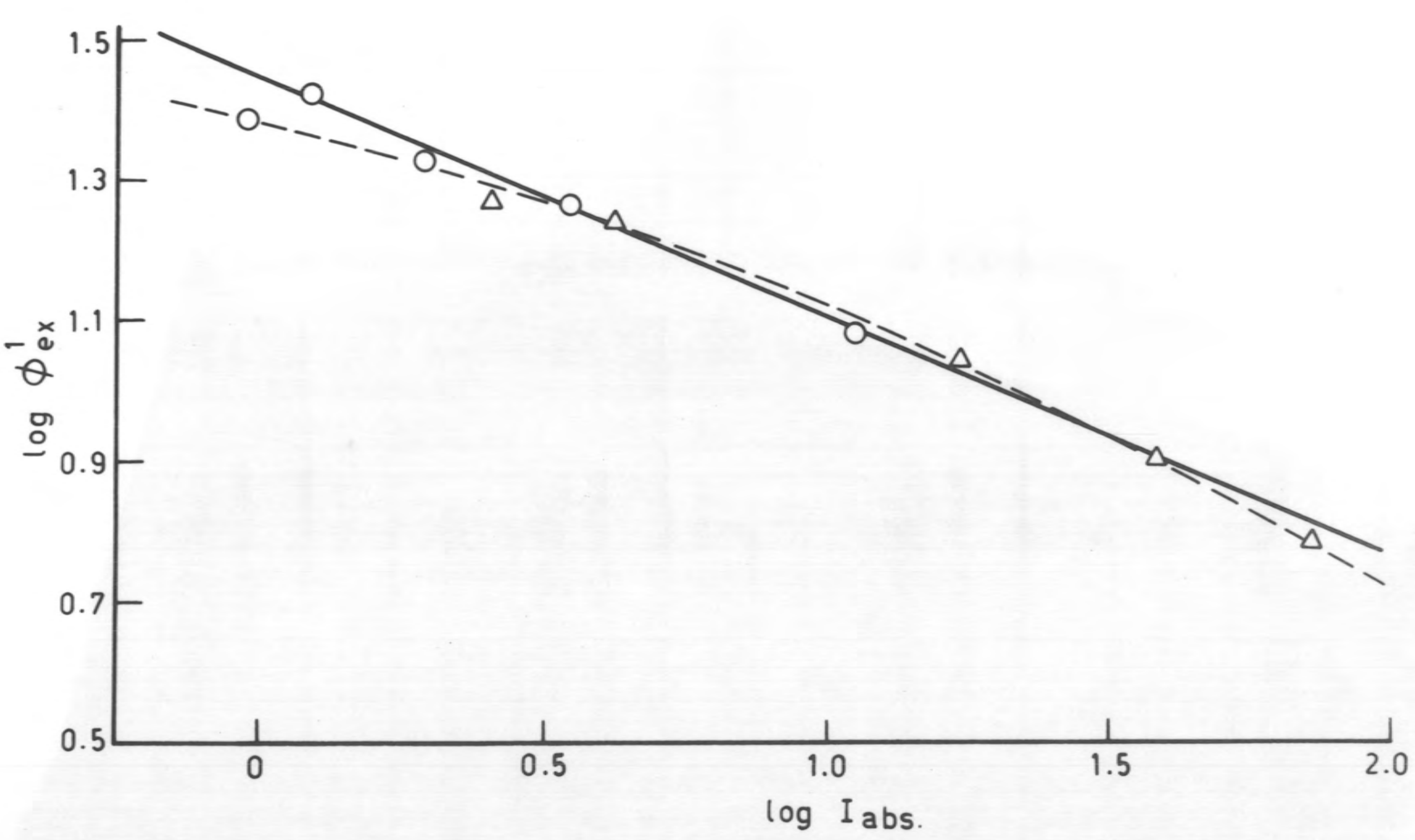


FIG. II·15 (a) $I_{abs.}$ Dependence

[Tl(1)] = 0.050 [Tl(III)] = 0.0051 mole l.$^{-1}$

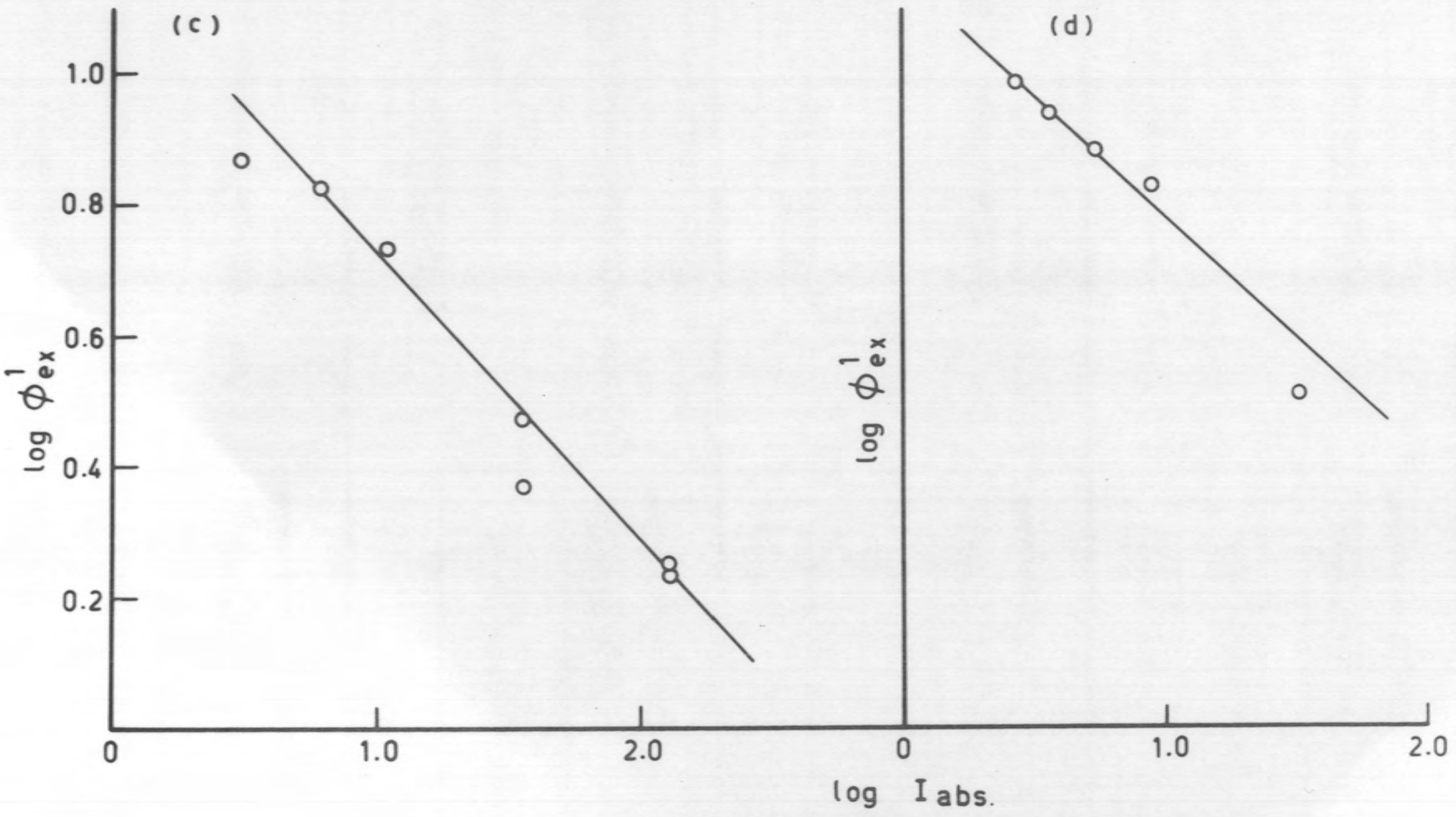


FIG. II·15 $I_{abs.}$ Dependence

(c) $[\mathrm{Tl(III)}] = 0.0412$
$[\mathrm{Tl(I)}] = 0.00315$

(d) $[\mathrm{Tl(III)}] = 0.040$
$[\mathrm{Tl(I)}] = 0.0051$

by plotting log $(\phi_{ex} - \phi_1)$ against log I_{abs}. As will be seen in theory later, these plots may be expected to be straight lines within experimental error. The slope of the lines is equal to the intensity exponent x in the empirical equation,

$$\phi_{ex} - \phi_1 = C\, I_{abs}^{\ x} \ .$$

The experimental results are plotted in Fig. II.15. The valuesof x obtained from these plots are shown in the right column of Table II.15. The first value is determined assuming $\phi_1 = 1$ and the second value assuming $\phi_1 \ll \phi_{ex}$. The error is determined graphically.

Table II.15

[Tl(I)] mole l^{-1}	[Tl(III)] mole l^{-1}	$\phi_1 \ll \phi_{ex}$ x	$\phi_1 = 1$ x
.05	.0051	−.34 ± .02	−.36 ± .02
.10	.0051	−.27 ± .05	
.0051	.04	−.37 ± .05	−.42 ± .05
.0032	.042	−.44 ± .03	−.59 ± .05

The results at each concentration range are worth considering in more detail individually.

(a) [Tl(I)] = .05 [Tl(III)] = .0051, mole l^{-1}

This solution was studied most extensively, over a hundred fold range of light intensities. The log $\phi_{ex} - \phi_1$ plots show good linearity, Fig. II.15(i).

(b) [Tl(I)] = .10 [Tl(III)] = .0051. mole l^{-1}

The individual scatter of points in this plot is very large, showing a large random variation. Two solutions were used in the study at this concentration. The solution prepared at an earlier stage, (solution 1) gave results up to 50% lower than the other solution, (solution 2). More care to avoid impurities was taken in the preparation of solution 2. Steps taken with solution 2 not taken with solution 1, include (i) recrystallization of the thallous carbonate starting material. (ii) Vacuum distillation of the perchloric acid solution. Also the thallium(III) in solution 2 was prepared from electrolysis of thallium(I), whereas the source of thallium(III) in solution 1 was thallic oxide. Another factor which may have affected the results is the length of storage of the solution; solution 1 having stood for a longer period than solution 2 before runs were performed.

The scatter of results clearly indicates the sensitivity of the reaction to impurities. Because of the large error, the value of the slope of the plot of log $\phi_{ex} - \phi_1$ against log I_{abs} is of little value. However, the plot of the points determined on solution 1, yields the result shown in the table.

(c) [Tl(I)] = .0051 [Tl(III)] = .040. mole l^{-1}

The plot of log $(\phi_{ex} - \phi_1)$ is not a good straight line. However, drawing a line of best fit yields the reasonable values obtained for the slope. Fig. II.11(c).

(d) [Tl(I)] = .00315 [Tl(III)] = .0412. mole l^{-1}

The actual values of the quantum yield are low at high light intensities, so that a large difference in value of the slope of the plot log $\phi_{ex} - \phi_1$ against log I_{abs} is found between plotting log $(\phi_{ex} - 1)$ and plotting log ϕ_{ex}. The value of $-.44 \pm .05$ obtained from the log ϕ_{ex} plot is a more reasonable value than the $-.59 \pm .05$ obtained from the log $\phi_{ex} - 1$ plot, on the grounds that $-.44$ is nearer that of the other concentrations. Values greater than .5 are also difficult to explain theoretically. This suggests that the assumption of $\phi_1 = 1$ is incorrect. However a ϕ_1 of .5 or less would give a reasonable value for the slope. This again supports the assumption that ϕ_1 is considerably less than one.

Note: The value of the exponent is independent of the fraction of light absorbed by each solution if $\phi_1 \ll \phi_{ex}$. Hence, the results are not affected by the assumption of Tl(III) absorption. But, when $\phi = 1$ is assumed, slightly different values will be obtained for x, dependent on the absorbing species. The results with $TlOH^{2+}$ absorption lie between the two values recorded in the table.

(b) Dependence of ϕ_{ex} on Tl(I) concentration.

The experimental results are shown in Table II.9 and Fig. II.9.

Now if ϕ_1 is assumed to be $\ll \phi_{ex}$, from equation (ii) a plot of $1/\phi_{ex}$ against $1/[Tl(I)]$ concentration should give a straight line of

$$\text{slope} = \frac{(K_t I_{abs})^{\frac{1}{2}}}{K_I \, \phi_1^{\frac{1}{2}}}$$

and intercept $\dfrac{(K_t I_{abs})^{\frac{1}{2}}}{\phi_1^{\frac{1}{2}} K_{III}[Tl(III)]}$

Hence the slope/intercept = $\dfrac{K_{III}[Tl(III)]}{K_I}$.

Fig. II.16 shows this plot to be a good straight line yielding a value of 1.6 ± .5 for K_{III}/K_I for total Tl(III) absorption, and 1.7 ± .5 for $TlOH^{2+}$ absorption only. (The error was determined visually from the graphs assuming ± 10% error in all points.)

Note: For the lowest values of the quantum yield for exchange the assumption that

$$K_{III}[Tl(III)] + K_I[Tl(I)] \gg 2(K_t I_{abs}\phi_1)^{\frac{1}{2}} \qquad \text{(iii)}$$

is not valid. However, the error introduced by the assumption is only just greater than the experimental error. At the lowest $\phi_{ex}^{\ 1}$ (1.91) calculation shows that (see Appendix) the left hand side is 5 times larger than the right side of (iii) when ϕ_1 is assumed = 1, and $10.5/\phi_1$ times larger when $\phi_1 \ll \phi_{ex}$ is assumed. Thus the error introduced by the assumption is at most, approximately 20%, i.e. the experimental value of the quantum yield is expected to be almost 20% lower than that predicted by equation (ii).

If $\phi_1 = 1$ is assumed and $1/\phi_{ex} - 1$ plotted against $1/[Tl(I)]$ for $TlOH^{2+}$ absorption, a straight line is obtained except for the point at the lowest [Tl(I)] concentration: which deviates 30% from the line (possibly due to the incorrect assumption discussed above). A

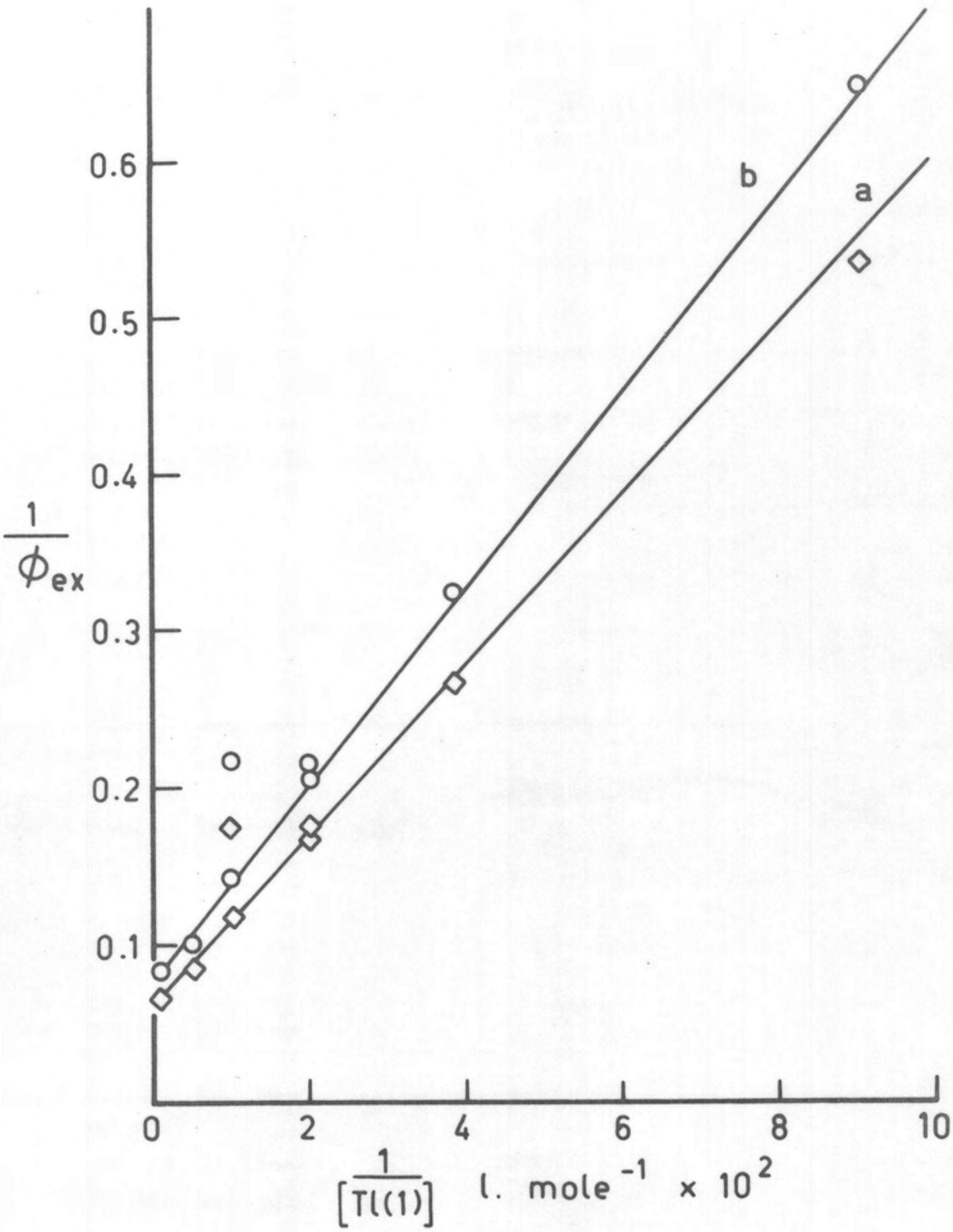


FIG. II·16 [Tl(1)] Dependence

$a = \frac{1}{\phi_{ex}^1}$ $b = \frac{1}{\phi_{ex}^2}$

value of $K_{III}/K_I = 2.5 \pm .5$ is obtained from this graph.

(c) Dependence of ϕ_{ex} on Tl(III) concentration.

The values in Table II.10 show the variation of ϕ_{ex} with [Tl(III)]. As I_{abs} varies with Tl(III) concentration, $(\phi_{ex} I_{abs}^{\frac{1}{2}})^{-1}$ is plotted against 1/[Tl(III)], which from equation (ii) should yield a straight line. Fig. II.17 shows the reasonable straight lines obtained. As ϕ_{ex} is not proportional to $I_{abs}^{-\frac{1}{2}}$ as predicted by equation (ii), particularly at low light intensities, the quantum yields at low Tl(III) concentration, where the light intensity is low, would be expected to be low.

The ratio of slope to intercept again yields values for the ratio of K_{III}/K_I. For Tl(III) absorption $K_{III}/K_I = 1.9 \pm .5$. For $TlOH^{2+}$ absorption $K_{III}/K_I = 2.0 \pm .5$. These are in good agreement with the values of 1.6 and 1.7 calculated from the [Tl(I)] dependence.

C. Linear Termination

At this stage it would seem necessary to develop an explanation for the difference between the observed intensity exponents and the anticipated value of .5. Irrespective of the propagation reactions, the value for the exponent x of less than .5 requires a mechanism involving both linear termination and quadratic termination. (It is conceivable that a complex initiation reaction sequence involving reaction of two excited species; would yield an overall mechanism

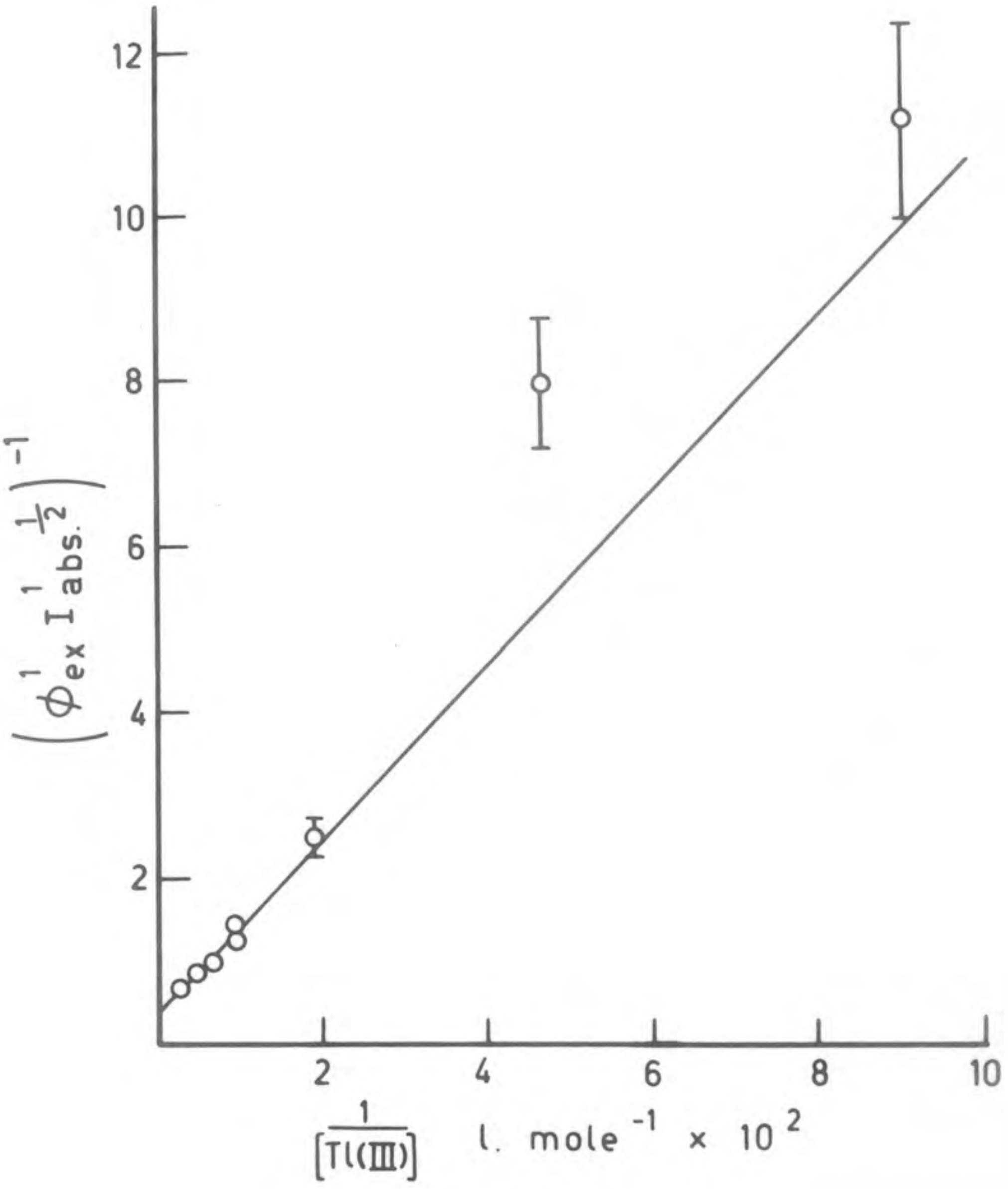


FIG. II·17 (a) [Tl(III)] Dependence
[Tl(III)] Absorption

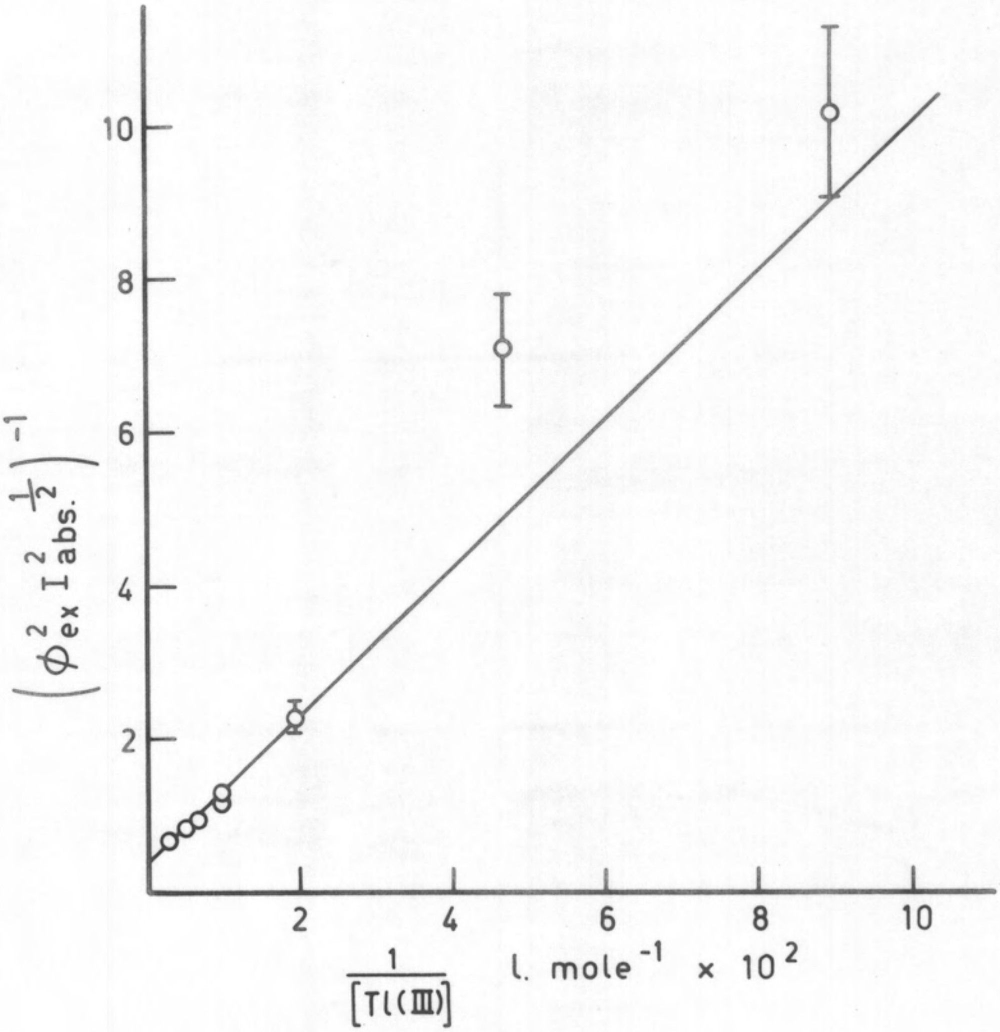


FIG. II·17(b) [Tl(III)] Dependence $TlOH^{2+}$ abs.

involving a mixed order dependence of quantum yield on I_{abs}. However any simple initiation process will not affect the dependence on light intensity. (See Appendix for derivation of rate expressions with unusual initiation reaction paths.) Thus it is considered that the initiation and propagation reactions postulated, are still the most probable reactions for these processes.

Possible linear termination reactions considered were:

(a) Termination by reaction of Tl(II) with solvent.

(i) Oxidation or reduction of solvent by Tl(II) is considered unlikely for two reasons. Firstly the pulse radiolysis studies of Cercek et al give good second order decay kinetics for Tl(II). Reaction with solvent would of course give first order kinetics. Secondly, Tl(II) is unlikely to oxidize water:

$$\mathrm{Tl(II)} + H_2O \rightarrow \mathrm{Tl(I)} + OH + H^+,$$

as the back reaction is known to be fast. Similarly for the reduction of water, the back reaction would probably be fast.

Either of these reactions would lead to net oxidation or reduction, if a stable product of the reaction with water is produced. As a check on this, the following experiments were carried out. The equilibrium ratio of activities was followed with time during a long irradiation of two reactant solutions. Irradiation of the solution for periods much longer than 10 times the half-time of exchange, enabled the assumption to be made that the ratio of activities equals the ratio of concentrations. Thus, as no change was observed in the activity ratio with time, an upper limit could be put on the change in concentration of the reactants, and hence on the quantum yields for net oxidation and reduction.

Table II.17

[Tl(III)]	[Tl(I)]	ϕ oxidation	ϕ reduction
.04	.003	$< .02$	$< .02$
.01	$< 1 \times 10^{-4}$	No information	$< .001$

The concentrations on the left hand side are the concentrations of reactant solution. Therefore, under these conditions net oxidation or reduction is considered negligible. However, if ϕ_1 is less than .1, a significant proportion of the Tl(II) may still be oxidized or reduced.

(ii) Tl(II) may react with the solvent to form a hydrolysed Tl(II) species. For this to be a termination reaction, the products of hydrolysis must be inert in the propagation reactions, and the hydrolysis must be a rate controlling step if the hydrolysed species also terminates through a bimolecular disproportionation. (If the bimolecular termination is more rapid than the hydrolysis, the termination will still be quadratic.) Both reactions are likely to be rapid, but if the hydrolysed Tl(II) species disproportionates at the same rate as the aquated Tl(II) (diffusion controlled), the hydrolysis reaction cannot be much faster than disproportionation.

The small effect of decreasing acid strength however, suggests that this is not an important mechanism. Also hydrolysis in 1.1M $HClO_4$ would be expected to be small for a divalent species.

(b) Another possible linear termination reaction is termination at the wall of the reaction vessel. However lack of any effect of stirring on the reaction rate, suggests that wall termination is not a significant feature.

(c) Termination by impurities.

Reactions such as

$$Tl(II) + X \rightarrow Tl(I) \text{ or } Tl(III) + X'$$

where X is any oxidizable (or reducible) material, organic or inorganic. It is possible that for an inorganic cation with two oxidation states, that the Tl(II) reacts with both oxidation states, reducing one and oxidizing the other. For example, Tl(II) has been reported(25) to react with both Fe(II) and Fe(III). That impurity effects are significant is shown by the scatter of results, particularly in the I_{abs} dependence at $[Tl(I)] = .1$ mole l^{-1}. Note that the lower quantum yields at this concentration, give a lower value for the intensity exponent, which supports the hypothesis that the quantum yields are reduced due to an increase in the rate of linear termination. However, reproducibility in most cases was surprisingly good for a reaction controlled by impurities.

In the next section an argument is developed to show that at high light intensities the effect of linear termination is small, and that it is only at the lowest light intensities that it dominates the reaction. In the appendix, an attempt was made to determine an explicit expression for the dependence of ϕ_{ex} on the variables of the system, when linear termination is competing with quadratic termination. It was found impossible to derive an explicit expression to directly test the experimental data. However the effect of linear termination can be tested indirectly. It was shown previously that

$$\phi_{ex} - \phi_1 = \frac{K_I[Tl(I)]\ K_{III}[Tl(III)]}{K_I[Tl(I) + K_{III}[Tl(III)]} \qquad [Tl(II)]$$

for a reaction involving the chain propagating reactions (3) and (4). For the two termination reactions,

$$Tl(II) + Tl(II) \xrightarrow{K_t} Tl(I) + Tl(III)$$
$$Tl(II) + \ ? \ \xrightarrow{K_2} Tl(I) \text{ or } Tl(III),$$

and assuming the same initiation reactions, the expression

$$2\ I_{abs}\phi_1 = 2\ K_t[Tl(II)]^2 + K_2[Tl(II)] \qquad (i)$$

may be deduced (assuming a steady state concentration of Tl(II)).

Now we consider the effect of variation of light intensity on the concentration of Tl(II), and hence on the quantum yield for exchange.

Let $\dfrac{I_{abs\ 2}}{I_{abs\ 1}} = \beta, \quad \dfrac{[Tl^{2+}]_2}{[Tl^{2+}]_1} = \alpha$

and let $\dfrac{K_t[Tl(II)]_1}{K_2} = 1$

That is at $[\mathrm{Tl(II)}]_1$, the rate of linear termination equals the rate of quadratic termination. Note that the rate of scavenging of Tl(II), due to quadratic termination, is twice that due to linear termination under this condition. Then,

$$\alpha = \frac{+1 \pm (1 + \delta\beta)^{\frac{1}{2}}}{2\beta} \qquad (i)$$

Some typical figures obtained from this equation are shown in Table II.18.

Table II.18

	β	α	Slope between points	x
1	10^2	$.073_2$	(1) and (3) = .562	.438
2	10	.250	(2) and (4) = .685	.315
3	1	1	(3) and (5) = .854	.146
4	10^{-1}	5.85		
5	10^{-2}	51.0		

Thus for an example, an increase of a factor of 10 in the light intensity (β = 10), increases the concentration of Tl(II) by a factor of 4, if the rate of linear termination equals the rate of quadratic termination at the lower light intensity.

Now since

$$\alpha = \frac{[\mathrm{Tl(II)}]_2}{[\mathrm{Tl(II)}]_1} = \frac{R_{ex2}}{R_{ex1}}$$

and $\beta = \frac{I_{abs2}}{I_{abs1}}$, a plot of log α against log β corresponds to a plot of log R_{ex} against log I_{abs}. The slope of the straight line drawn through any two points on this curve equals $1 - x$, where x is the exponent in the equation

$$\phi_{ex} = C\, I_{abs}^{-x} .$$

Some values of x determined in this way are shown in Table II.18.

By this technique, the value of α at the high and low intensity extremes of the experimental I_{abs} dependence may be calculated. Experimentally for the I_{abs} dependence at $[Tl(I)] = .05$ and $[Tl(III)] = .0051$, the exponent $-x$ was found to be $-.34$ or $-.36$. The values of α_1 and α_2 which give a slope corresponding to $x = .35$ from the equation

$$\frac{\log \alpha_1 - \log \alpha_2}{\log \beta_1 - \log \beta_2}$$

were found to be $\alpha_1 = .196$, $\alpha_2 = 3.78$ for $\beta_1/\beta_2 = 100$, corresponding to the hundred fold range of light intensities used experimentally. The theoretical curve is plotted on the same graph (Fig. II.15) as the experimental values. The deviation from the theoretical curve is less than the experimental error. The two values of α show that the ratio of the rates of linear termination to quadratic termination, varies from 3.78 at the lowest light intensities to .196 at the highest light intensities. Thus, at the high light intensities only $^1/_{10}$ of the Tl(II) is being scavenged by the linear termination reaction.

The question of most importance is how much does the linear termination affect the interpretation of the thallous and thallic concentration dependences.

(a) [Tl(I)] dependence-effect of linear termination.

The [Tl(I)] dependence is plotted at an I_{abs} value of 12×10^{-6} Einstein l^{-1} min^{-1}. At this value α for the point at [Tl(I)] = .05 is found from equation (1) to be $.89_0 \pm .1$ at $\beta = 1.2$. A second value of α may be calculated for $\beta = 1.2 \times 10^{10}$ (α_{10}), i.e. a 10^{10} increase in light intensity, at which stage linear termination may be considered negligible. Now, if α_{10} is corrected for light intensity back to $\beta = 1.2$, assuming pure quadratic termination (i.e. [Tl(II)] = $K\ I_{abs}^{\frac{1}{2}}$), a figure of .646 is obtained which may be compared to the value of $\alpha = .89_0$ obtained from equation (1). The ratio of these values is equal to the ratio of the Tl(II) concentration in a system without any linear termination, to the Tl(II) concentration in a system with the degree of linear termination experimentally observed. The ratio is 1.38 to 1, and thus an increase of approximately 40% in the quantum yield would be expected in the absence of linear termination.

This is nowhere near sufficient error to account for the turn-over in the Tl(I) dependence curve. Thus for example, if the rate at [Tl(I)] = .005M is considered correct, and a linear dependence of rate on [Tl(II)] assumed, then the expected quantum yield at [Tl(I)] = .05M is 45 instead of the observed value of 12.

The contention that the quantum yield reaches a region independent of Tl(I) concentration at high Tl(I) concentrations, mainly because of the competition between propagation reactions; and not due to the effects of linear termination, is based on this argument.

The effect of linear termination on the value of K_{III}/K_I.

The effect on the value of K_{III}/K_I will depend on whether linear termination is dependent on the concentration of reactants.

(i) If the degree of linear termination does not vary with the concentration of reactants, a constant correction to the quantum yield over the entire [Tl(I)] range would be needed, which would not affect the linearity of the plot or the value of K_{III}/K_I. (Some effect at low values of ϕ_{ex} when $\phi_{ex} - 1$ is plotted.) For the [Tl(III)] dependence, a larger correction to the lower values of ϕ_{ex} would need to be made because of the decreasing light intensity. Experimentally these values are found to be lower than expected from the $1/\phi_{ex}\ I_{abs}^{+\frac{1}{2}}$ against 1/[Tl(III)] plot. Overall the slope of this plot (and hence K_{III}/K_I) may be decreased but the correction would be less than 20%.

(ii) For completeness, the possible effect on K_{III}/K_I of linear termination varying with reactant concentration needs to be considered. From the calculations at [Tl(I)] = .05 mole l^{-1}, it was seen that in the absence of linear termination ϕ_{ex} would be expected to be 40%

higher. Assuming that the linear termination rate at [Tl(I)] = .15M is three times that at [Tl(I)] = .05M, the value of ϕ_{ex} would be expected to be 70% higher in the absence of linear termination. The intercept of the $1/[Tl(I)]$ against $1/\phi_{ex}$ graph is thus too high by 70%. The slope is also too high by a small amount (approximately 10%). Thus K_{III}/K_I will be too low by approximately 60%, (i.e. $K_{III}/K_I = 2.7 \pm .8$). The effect on the Tl(III) dependence will be smaller because of the lower concentrations and higher light intensities involved; the decreased slope and decreased intercept will compensate to some extent. Accurate predictions would depend on the assumptions made about the relationship of concentration to linear termination. However, the values of K_{III}/K_I obtained independently from the dependence of ϕ_{ex} on [Tl(I)] and [Tl(III)] are still in agreement within the large errors.

In conclusion, a value between 1.0 and 4.0 for K_{III}/K_I can be relied on despite the effects of linear termination.

Conclusions to this stage.

The results have been shown to be consistent with the mechanism given on page 134, with the addition of a linear termination reaction,

$$Tl(II) + X \rightarrow Tl(?) + X'$$

probably attributable to impurities. The possibility of misinterpretation of a complicated system such as this is always high, especially when unknown impurity effects may be present. Despite this, I feel the main features of the scheme do represent the true situation.

D. Calculation of Rate Constants and Activation Energies

Some more information on the nature of the reactions involved in the chain mechanism, may be deduced from the studies reported.

(a) If a value of ϕ_1 is known, absolute values for K_{III} and K_I may be computed. (If the value of K_t, the rate constant for the disproportionation of Tl(II), is taken as $2.3 \pm .8 \times 10^9$ l mole^{-1} sec^{-1}.)

The equation

$$\phi_{ex} - \phi_1 = \frac{K_{III}[Tl(III)]K_I[Tl(I)]}{K_{III}[Tl(III)] + K_I[Tl(I)]} \cdot \left\{\frac{\phi_1}{(K_t I_{abs})}\right\}^{\frac{1}{2}} ,$$

at high Tl(I) concentrations, may be approximated to

$$\phi_{ex} = \frac{K_{III}[Tl(III)]\phi_1^{\frac{1}{2}}}{(K_t I_{abs})^{\frac{1}{2}}}$$

ϕ_{ex} can be determined from the intercept of the $1/[Tl(I)]$ against $1/\phi_{ex}$ curve. A value of 17 ± 3 is obtained from Fig. II.16. Thus as $[Tl(III)] = .0051M$ and $I_{abs} = 12.0 \times 10^{-6}$ Einstein l^{-1} min^{-1}, then

$$\phi_1^{+\frac{1}{2}} K_{III} = 1.6 \times 10^7$$

$$\therefore K_{III} = (1.6 \pm .5) \times 10^7 \, \phi_1^{-\frac{1}{2}} \text{ l mole}^{-1} \text{ min}^{-1}$$

and from $K_{III}/K_I = 2$

$$K_I = (8 \pm 2) \times 10^6 \, \phi_1^{-\frac{1}{2}} \text{ l mole}^{-1} \text{ min}^{-1}.$$

Also $[Tl(II)] = \left\{\frac{I_{abs}\phi_1}{2K_t}\right\}^{\frac{1}{2}} = 6.6 \times 10^{-9} \, \phi_1^{\frac{1}{2}}$ mole l^{-1}.

It is interesting to compare these results to the theoretical predictions of the theories of Marcus and Hush. The calculation of the energy of activation by Marcus's theory involves the sum of three terms. The coulombic repulsion $\Delta G^{\neq}_{rep}$, the solvent reorganization term $\Delta G^{\neq}_{or}$, and a first coordination sphere reorganization term $\Delta G^{\neq}_{ir}$. For water at $25^{\circ}C$ (64)

$$\Delta G^{\neq}_{rep} = 4.22\ z_1 z_2/R \text{ kcal mole}^{-1},$$

where z_1, z_2 are the charge of the reacting ions and R is the distance between the centres of the reactants in the activated complex. This is assumed to be the sum of the ionic radii plus two water molecules. Similarly,

$$\Delta G^{\neq}_{or} = \frac{(\Delta z)^2 e^2}{4R} \left(\frac{1}{n^2} - \frac{1}{D^2}\right),$$

where n is the solvent refractive index and D is the static dielectric constant.

For water at $25^{\circ}C$,

$$\Delta G^{\neq}_{or} = 45.0\ (\Delta z)^2/R \text{ kcal mole}^{-1}.$$

The calculation of ΔG_{ir} from Marcus's equations, requires a knowledge of force constants for the metal to ligand bonds, and the equilibrium bond lengths for the two reacting ions. This information is not available for the thallium system. ΔG_{ir} must be a positive value so that the sum of $\Delta G^{\neq}_{or}$ and $\Delta G^{\neq}_{rep}$ will give a minimum value for $\Delta G^{\neq}$, the activation energy for the reaction. However ΔG_{ir} may be calculated from an equation derived by Hush,(63) applicable in the absence of crystal field effects.

$$\Delta G_{ir} = \frac{n\varepsilon\mu}{4(m - 2)} \left[\frac{1}{z(d_{ez})^2} + \frac{1}{(z - 1)(d_{ez - 1})^2}\right]$$

where $z\varepsilon$ is the charge on the ion, n is the number of water molecules coordinated to the ion, d_{ez} is the ion oxygen distance and μ is the dipole moment of water.

Hush calculated m = 7.7 for thallium. For H_2O at 25°C with d_{ez} in Å,

$$\Delta G_{ir} = 1.29 \times 10^2 \frac{n}{4(m - 2)} \left[\frac{1}{z(d_{ez})^2} + \frac{1}{(z - 1)(d_{ez - 1})^2}\right] \text{ kcal mole}^{-1}.$$

Equilibrium distance d_{ez} is the sum of the crystal radius, and the radius of a water molecule. n = 6 is assumed for the thallium reactions. This is probably too high for Tl(I), as the highest coordination number of Tl(I) observed with other ligands is 2. The values of $\Delta G^{\neq}_{ir}$ calculated may thus be high by a factor of 2.

Table II.19 lists the values of $\Delta G^{\neq}_{rep}$, $\Delta G^{\neq}_{o}$, ΔG_{ir} and $\Delta G^{\neq}$, the overall activation energy, for the reactions,

$$\overset{*}{\text{Tl}}(\text{I}) + \text{Tl}(\text{II}) \rightleftharpoons \overset{*}{\text{Tl}}(\text{II}) + \text{Tl}(\text{I}) \qquad (4)$$

$$\text{Tl}(\text{III}) + \overset{*}{\text{Tl}}(\text{II}) \rightleftharpoons \overset{*}{\text{Tl}}(\text{III}) + \text{Tl}(\text{II}) \qquad (3)$$

The radii used in the equations are the crystallographic radii plus the radius of one water molecule taken as 1.35 Å. The crystallographic radius of Tl(II) is of course not known, so two values are compared, one is close to the radius of Tl(I), and the other is the value calculated by Hush.(65) The actual values used were:

$$r_{Tl(I)} = 2.82\ \text{Å} \qquad r_{Tl(III)} = 2.30\ \text{Å}$$

$$r_{Tl(II)} = 2.75\ \text{Å} \text{ and } 2.50\ \text{Å}$$

Table II.19

Reaction	$r_{Tl(II)}$	$\Delta G^{\neq}_{rep}$	$\Delta G^{\neq}_{o}$	$\Delta G^{\neq}_{i}$	$\Delta G^{\neq}$	K
		kcal mole^{-1}				1 mole sec^{-1}
Tl(III)+Tl(II)	2.75	5.0	8.9	4.2	18.1	3.0×10^{-1}
"	2.50	5.3	9.4	4.9	19.6	2.4×10^{-2}
$TlOH^{2+}$+Tl(II)	2.50	3.5	9.4	5.9	18.8	
Tl(I)+Tl(II)	2.75	1.5	8.1	6.5	16.1	1.0×10
"	2.50	1.6	8.4	7.1	17.1	1.5

Now from the equation

$$K = \frac{kT}{n} e^{-\Delta G^{\neq}/RT}$$
$$= 6.1 \times 10^{12}\ e^{-\Delta G^{\neq}/RT}$$

(where K is the rate constant for the reaction and the other symbols have their usual significance), the rate constant for exchange may be calculated for the values of $\Delta G^{\neq}$ in Table II.19. The calculated rate constants are tabulated in the right column of II.19. These values may be compared to the experimental values of K_{III} and K_I.

$$K_{III} = 2.7 \times 10^{5}\ \phi_1^{-\frac{1}{2}} \quad \text{1 mole sec}^{-1}$$
$$K_I = 1.3 \times 10^{5}\ \phi_1^{-\frac{1}{2}} \quad \text{"}$$

The value of ϕ_1 is not known, but it most likely falls between .01 and 1 so that the absolute values of K_{III} and K_I probably lie within an order of magnitude of these values.

The agreement between experimental and calculated values is poor, especially for the reaction involving Tl(III). The suggestion that $TlOH^{2+}$ ions (rather than Tl^{3+}_{aq}), may play a significant role in the reaction despite their low concentration, is not supported by calculation (Table II.19). As the concentration of $TlOH^{2+}$ is only 7% of the total Tl(III) concentration, a large difference in activation energy (> 2 kcal mole^{-1}) would be necessary for $TlOH^{2+}$ reactions to be important.

Perhaps the most difficult fact to explain is that the rate constant for the Tl(III) reaction is greater than the rate constant for the Tl(I) reaction. On the grounds of calculations of the above type, and qualitative arguments, the rate constant for a reaction involving a triply charged and a doubly charged species, is expected to be much less than for a singly and a doubly charged species. For example, the ratio of rate constants for the two reactions

$$\mathrm{Fe(II) + Tl(II)} \xrightarrow{K_2} \mathrm{Fe(III) + Tl(I)} \qquad \text{(a)}$$

$$\mathrm{Fe(III) + Tl(II)} \xrightarrow{K_1} \mathrm{Fe(II) + Tl(III)}$$

has been reported by Ashurst and Higginson to be $K_2/K_1 = 27$. Possibly the two exchange reactions have different mechanisms. If one reaction has an inner-sphere mechanism, and not the other, the relative rates of reaction would be unpredictable. The Marcus and Hush equations are based on the assumptions of outer-sphere, adiabatic reactions, which may not be applicable to both reactions (or perhaps either).

(b) From the temperature dependence of the quantum yield for exchange, an upper limit to the activation energies of the two propagation reactions may be deduced. Two assumptions which appear to be reasonable need to be made.

(1) That ϕ_1 the primary quantum yield, does not decrease with temperature.

(2) That the rate of the termination reaction has a small temperature dependence.

The reported value of 2×10^9 l mole^{-1} sec^{-1} for the termination rate constant indicates that the reaction is close to diffusion controlled. The temperature dependence of diffusion controlled reactions is small (< 5 kcal mole^{-1}). In the equation below, ϕ_{ex} depends on $K_t^{-\frac{1}{2}}$, so that as

$$K_t = \text{const. } e^{-\Delta G^{\neq}/RT}$$

$$K_t^{\frac{1}{2}} = (\text{const.})^{\frac{1}{2}} e^{-\Delta G^{\neq}/2RT}$$

the effective temperature dependence of K_t will be a half of the actual activation energy. Hence the contribution to the overall temperature dependence of the termination reaction will be < 2.5 kcal mole^{-1}.

With these two assumptions it can be seen from the equation

$$\phi_{ex} - \phi_1 = \frac{K_I[Tl(I)]\ K_{III}[Tl(III)]}{K_I[Tl(I)] + K_{III}[Tl(III)]} \left\{\frac{\phi_1}{K_t I_{abs}}\right\}^{\frac{1}{2}},$$

that the temperature dependence of ϕ_{ex} is controlled mainly by the temperature dependence of K_I and K_{III}. The dependence of ϕ_{ex} on temperature was studied at $[Tl(I)] = [Tl(III)] = .005$ mole l^{-1}. An activation energy of 5 kcal mole^{-1} was found, after allowing for the increase in absorption with increase in temperature.

Two possibilities need to be considered:

(1) If K_{III}/K_I remains unaltered with temperature, then an increase in ϕ_{ex} of a factor of 2 corresponds to an increase in both K_I and K_{III} of a factor of 2. Thus, if K_t and ϕ_1 are independent of temperature, the activation energy for K_I and K_{III} will be the same as for the quantum yield, i.e. 5 kcal mole^{-1}. Allowing for 5.0 kcal mole^{-1} activation energy in the termination reaction, then the activation energy for K_I and K_{III} will be less than 7.5 kcal mole^{-1}.

(2) If the ratio of K_{III}/K_I varies greatly in the range of temperatures studied, that is the activation energies for the corresponding reactions are very different, a non-linear activation energy plot would be expected. Secondly, it is not unreasonable to assume that neither activation energy will be very much less than 7.5 kcal mole^{-1}, so the conclusion might be reached that both activation energies lie in the range 6-10 kcal mole^{-1}. (It may be definitely stated that either one or both of these reactions has an activation less than 7.5 kcal mole^{-1}.)

Note that the activation energies are smaller than predicted by the Marcus-Hush calculations. These values, tabulated below have been calculated from

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

where $\Delta H^{\neq}$ is the enthalpy of activation and $\Delta S^{\neq}$ is the entropy of activation calculable from$^{(64)}$

$$\Delta S^{\neq} = -\left(\frac{19.4\ z_1 z_2 + 9.4}{R}\right) \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Table II.21

Reaction	$r_{Tl(II)}$	$\Delta G^{\neq}$ kcal mole^{-1}	$\Delta S^{\neq}$ cal deg^{-1} mole^{-1}	$\Delta H^{\neq}$ kcal mole^{-1}
Tl(III)+Tl(II)	2.50	19.6	-24.2	12.4
Tl(I)+Tl(II)	2.50	17.1	-16.7	12.1

It is interesting to speculate on the reasons why these exchange reactions are so much faster than predicted by the calculations. The Marcus-Hush theories are not very successful in predictions of activation energies for transition metal cation exchange reactions, so they are not expected to be any more precise in the thallium system. However, it is possible that the unusual electronic structure of the Tl(II) species, and its consequent instability has some effect on the reaction rate.

(c) The results in the presence of added sodium sulphate and chloride, indicate that the mechanism is basically unaltered even though the absorbing species is different. The usual interpretation of the change in absorption spectrum with anions such as these, is to assume that charge-transfer is occurring from the anion (associated with the cation) to the cation. On this basis, the initiation reaction in the presence of Cl^- would be:

$$TlCl^{2+} + h\nu \rightleftarrows Tl^{2+} + Cl\ .$$

Similarly with $SO_4^{''}$, the initiation reaction is probably,

$$TlSO_4^{\ +} + h\nu \rightleftarrows Tl^{2+} + SO_4^{\ -}.$$

(At the concentrations used - anion concentration much less than Tl(III) concentration - no significant amount of Tl(III) associated with two anions is expected.)

The similarity of the quantum yields in the solutions containing Cl^-, $SO_4^{''}$ and ClO_4^-, (all within a factor of 2) implies that the primary quantum yield is also similar (within a factor of 4 as ϕ_{ex} $\phi_1^{\frac{1}{2}}$). This result is perhaps a little surprising. In terms of the Noyes model, the separation distance of the fragments when they come to thermal equilibrium with the solvent, would be expected to be quite different for two such diverse species as SO_4^- and Cl. However, it is possible that a separation distance is small in all cases; and as the probability of reaction per encounter is probably one for all the systems, recombination is relatively constant. The small separation distance may be attributed to only a small fraction of the total energy being converted to kinetic energy of the fragments.

Similar remarks may be directed at explaining the small effect of decreasing wavelength on the quantum yield. The expected increase in quantum yield with increasing energy of the absorbed quantum is not observed (see Table II.13). The few studies of the wavelength dependence of quantum yields of similar compounds in charge-transfer bands (Section I, Ref. 29), would suggest that the quantum yields do have a region where they are only slightly dependent on wavelength. For example, $Fe(C_2O_4)^{3-}$ exhibits quantum yields of 1.25 at 254 mμ and 1.11 at 436 mμ, for the production of Fe(II).

The maximum primary quantum yield may not be reached because of primary recombination, rather than secondary recombination. Primary recombination would be predicted to be less sensitive to the wavelength of irradiation. In the systems mentioned, the probability of reaction of the fragments per encounter may be small, so that primary recombination must be important.

Further study.

Some further useful work might be done in the following areas.

(a) Obviously, a determination of the primary quantum yield ϕ_1, would be of value in establishing more concrete values for the rate constants. In principle ϕ_1 might be determined by scavenging all the Tl(II) species, with species reactive to Tl(II), and determining the rate of change of concentration of either the scavenger or the thallium reactants or products. However in practice, the problem of finding a suitable scavenger has proved insurmountable, since the scavenger (1) must react rapidly with Tl(II), but neither it or its reaction product can react with Tl(I), Tl(III) orTl(II). (2) Must not absorb light appreciably at 254 mμ. The latter point may be overcome by working at very low concentrations of scavenger, and using microanalytical techniques.

(b) The possibility of producing Tl(II) and trapping it in a solid matrix (probably ice), may be used for looking at the E.S.R., and ultraviolet spectra of this species. The ultraviolet spectrum would be of particular interest, for comparison with the γ-produced Tl(II) spectrum.

SECTION II

CHAPTER 5: APPENDIX

A. Derivation of Rate Expressions

The following rate expressions are derived with only one general assumption; that the steady state assumption may be applied to the concentration of active chain carriers. To illustrate the general technique, a relatively simple chain reaction is derived in full. We consider a chain reaction involving exchange between two species A and B.

$$\overset{*}{A} + B \rightarrow A + \overset{*}{B}$$

where, for example, $\overset{*}{A}$ and B may be $Tl^{+} + Tl^{3+}$ or $PtCl_6^{2-}$ and Cl^{-}. A chain reaction must involve three stages; initiation, propagation, and termination.

(a) Initiation.

The initiation step must produce a chain carrier C. A typical photoinitiation is

$$A + h\nu \xrightarrow{\phi_1} C + X$$

where X may be any species formed by photodecomposition of A. ϕ_1 is the quantum yield for the formation of C. In the terminology of Noyes it is the fraction of CX pairs that escape both primary and secondary recombination. ϕ_1 should be constant under the following conditions:

(i) At constant wavelength.

(ii) If the rate of scavenging by the solvent is > 10^7 mole/litre/sec.

(b) Chain propagation.

The essential requirement for C to act as a chain carrier is that C must be capable of exchanging with both A and B at a rate faster than its rate of destruction, as in the sequence

$$C + \overset{*}{A} \rightleftharpoons A + \overset{*}{C}$$

$$\overset{*}{C} + B \rightleftharpoons C + \overset{*}{B}$$

(c) Termination.

The simplest termination step is the reverse of initiation:

$$C + X \rightarrow A$$

This gives the overall mechanism as:

$$\begin{array}{ll} A + h\nu \rightarrow C + X & \phi_1 \\ C + \overset{*}{A} \rightleftharpoons \overset{*}{C} + A & K_1 \\ \overset{*}{C} + B \rightleftharpoons \overset{*}{B} + C & K_2 \\ C + X \rightarrow A & K_t \end{array}$$

The net photodecomposition of A or B is assumed to proceed at a negligible rate as compared to the rate of exchange. Let the concentration of the chemical species A, B, C and X be a, b, c and x respectively, and the concentrations of isotopically labelled A, B, and C be α, β and γ at a stated time t.

Then $\frac{d\alpha}{dt} = -I_{abs}\emptyset_1 \frac{\alpha}{a} + K_1 ac\frac{\gamma}{c} - K_1 ac\frac{\alpha}{a} + K_t xc\frac{\gamma}{c}$ (1)

and $\frac{d\beta}{dt} = K_2 bc.\frac{\gamma}{c} - K_2 bc\frac{\beta}{b}$ (2)

where I_{abs} is the absorbed light intensity. Assuming in accordance with the steady state hypothesis, that the rate of loss of activity in A equals the rate of gain of activity in B,

i.e. $\frac{d\alpha}{dt} = -\frac{d\beta}{dt}$ and $\frac{d\gamma}{dt} = 0$.

$$\text{Hence } \gamma = \frac{(I_{abs}\emptyset_1 \frac{\alpha}{a} + K_1 ac\frac{\alpha}{a} + K_2 bc\frac{\beta}{b})}{K_1 a + K_2 b + K_t x} \tag{3}$$

Substituting for γ in (2), we obtain

$$\frac{d\beta}{dt} = P\alpha + Q\beta \tag{4}$$

where

$$P = \left\{\frac{K_2 b}{D}\right\}\left\{\frac{I_{abs}\emptyset_1 + K_1 c}{a}\right\}$$

$$Q = K_2 c\left\{\frac{K_2 b - 1}{D}\right\}$$

and

$$D = K_1 a + K_2 b + K_t c$$

Now

$$\alpha = (1 + \frac{a}{b})\ \beta_\infty - \beta \tag{5}$$

from mass balance

where β_∞ equals β at time ∞.

Thus

$$\frac{d\beta}{dt} = P(1 + \frac{a}{b})\ \beta_\infty + (Q - P)\beta \tag{6}$$

It can be shown that the coefficient of β and β_o are equal and opposite, hence $\frac{d\beta}{dt}$ may be written,

$$\frac{d\beta}{dt} = P(1 + \frac{a}{b})(\beta_{\infty} - \beta) \qquad (7)$$

For any exchange reaction with isotopic labelling present at tracer concentration, i.e. at concentration negligible compared to total concentration of reacting species, the rate of exchange, R_{ex}, is:

$$R_{ex} = \frac{d\beta}{dt}\,\frac{ab}{a + b}\,\frac{1}{(\beta_{\infty} - \beta)} \qquad (8)$$

which is a form of the well known McKay equation. The derivation involves two assumptions. (1) That no two active species exchange, i.e. that exchange only occurs between active and inactive or inactive and inactive species. This is valid at a concentration of active species much less than the concentration of inactive species. (2) That the activity remains in two forms, that of either of the two reactants. Thus in the thallium system it is necessary to assume that the concentration of Tl(II) is negligible compared to Tl(I) and Tl(III) concentrations. This is also implicit in the steady state assumption. Substitution in (8) using (7) yields:

$$R_{ex} = \frac{K_1 a . K_2 b}{D} .c + \frac{I_{abs}\phi_1 . K_2 b}{D} \qquad (9)$$

Since $\frac{dc}{dt} = 0$ and $c = x$,

then $K_t c^2 = I_{abs}\phi_1$. (10)

Substitution for c in (9) gives the expression

$$R_{ex} = \frac{K_1 a . K_2 b}{K_1 a + K_2 b + (K_t I_{abs}\phi_1)^{\frac{1}{2}}} \left\{\frac{\phi_1 I_{abs}}{K_t}\right\}^{\frac{1}{2}} + \frac{K_2 a . \phi_1 I_{abs}}{K_1 a + K_2 b + (K_t I_{abs}\phi_1)^{\frac{1}{2}}}$$

The quantum yield for exchange ϕ_{ex} is defined as R_{ex}/I_{abs}.

Hence:

$$\phi_{ex} = \frac{K_1a.K_2b}{K_1a + K_2b + (K_tI_{abs}\phi_1)^{\frac{1}{2}}}\left\{\frac{\phi_1}{K_tI_{abs}}\right\}^{\frac{1}{2}} + \frac{K_2b\phi_1}{K_1a + K_2b + (K_tI_{abs}\phi_1)^{\frac{1}{2}}}$$

Several features of interest should be noted:

(a) The second term in the expression is always less than ϕ_1. It represents the rate of exchange in the absence of the first propagation step in the mechanism. This term may therefore be neglected if $\phi_{ex} \gg \phi_1$. (ϕ_1 must, by definition, be less than one.)

(b) If $K_1a + K_2b \gg (K_tI_{abs}\phi_1)^{\frac{1}{2}}$, then the first term is proportional to $I_{abs}^{-\frac{1}{2}}$. This proportionality is a feature of reactions where the fragments of photoinitiation react together in the chain termination reaction.

A number of expressions have been derived using the above treatment. The mechanism for the exchange is shown, followed by the complete expression for the quantum yield. Approximate expressions which may be of interest are then deduced.

B. Non-Chain Mechanism

As an illustration the expression for a non-chain mechanism is derived, e.g.

$$Tl^{3+}OH^- + h\nu \xrightarrow{\phi_1} Tl^{3+} + OH$$

$$Tl^{2+} + \overset{*}{T}l^+ \overset{K_1}{\rightleftarrows} \overset{*}{T}l^{2+} + Tl^+ \qquad (1)$$

$$\overset{*}{T}l^{2+} + OH \xrightarrow[K_t]{} \overset{*}{T}l^{3+} + OH^- \qquad (t)$$

Note: As with all the following expressions (unless otherwise noted), this gives an overall reaction equivalent to the electron exchange reaction

$$\overset{*}{\mathrm{Tl}}^{3+} + \mathrm{Tl}^{+} \rightleftarrows \mathrm{Tl}^{+} + \overset{*}{\mathrm{Tl}}^{3+}.$$

The kinetic mechanism yields the expression,

$$\phi_{ex} = \frac{\phi_1 \ K_1 [\mathrm{Tl}^+]}{K_1 [\mathrm{Tl}^+] + K_t} .$$

As $K_1 [\mathrm{Tl}^+] + K_t$ is always $> K_1 [\mathrm{Tl}^+]$, this expression for ϕ_{ex} is always $< \phi_1 < 1$. Hence a non-chain mechanism of this type cannot give quantum yields for exchange greater than one; contrary to the data for both the thallium and the platinum systems.

Note: It is possible to imagine a non-chain mechanism that has a quantum yield greater than one, but not greater than two or three.

C. Chain Mechanisms with Linear Termination

Example: Mechanism B(i)

Initiation $\mathrm{Tl}^{3+}\mathrm{OH}^- + h\nu \xrightarrow{\phi_1} \mathrm{Tl}^{2+}\mathrm{OH}$

Propagation $\mathrm{Tl}^{2+}\mathrm{OH} + \overset{*}{\mathrm{Tl}}^{+} \overset{K_I}{\rightleftarrows} \overset{*}{\mathrm{Tl}}^{2+}\mathrm{OH} + \mathrm{Tl}^{+}$ (1)

$\overset{*}{\mathrm{Tl}}^{2+}\mathrm{OH} + \mathrm{Tl}^{3+} \overset{K_{III}}{\rightleftarrows} \overset{*}{\mathrm{Tl}}^{3+} + \mathrm{Tl}^{2+}\mathrm{OH}$ (2)

Termination $\mathrm{Tl}^{2+}\mathrm{OH} \xrightarrow{K_t} \mathrm{Tl}^{3+}\mathrm{OH}^-$ (t)

The distinguishing feature of this mechanism is that the rate of destruction of chain carrier ($\mathrm{Tl}^{2+}\mathrm{OH}$) is proportional to its concentration, i.e.,

$$\frac{d[\mathrm{Tl}^{2+}\mathrm{OH}]}{dt} \propto [\mathrm{Tl}^{2+}\mathrm{OH}] .$$

This feature results in ϕ_{ex} being independent of light intensity (I_{abs}).

$$\phi_{ex} = \frac{K_I[Tl^+].K_{III}[Tl^{3+}]}{(K_I[Tl^+] + K_{III}[Tl^{3+}] + K_t)} \frac{\phi_1}{K_t} + \frac{K_I[Tl^+]\ \phi_1}{K_I[Tl^+] + K_{III}[Tl^{3+}] + K_t} \tag{I}$$

Approximations.

(1) For $\phi_{ex} \gg 1$ the second term is negligible. It can be shown by the following argument that K_t must always be less than

$$K_I[Tl^+] + K_{III}[Tl^{3+}] \text{ for } \phi_{ex} > 1.$$

Separating the first term into the product,

$$\phi_{ex} = \frac{K_I[Tl^+]}{K_I[Tl^+] + K_{III}[Tl^{3+}] + K_t} \cdot \frac{K_{III}[Tl^{3+}]\ \phi_1}{K_t}$$

It can easily be seen that the first term is always less than one, so for $\phi_{ex} > 1$,

$$\frac{K_{III}[Tl^{3+}]}{K_t} \text{ must be} > 1,$$

and since $\phi_1 < 1$, K_t must be less than $K_{III}[Tl^{3+}]$ and therefore

$$K_t < K_I[Tl^+] + K_{III}[Tl^{3+}].$$

Thus,

$$\phi_{ex} = \frac{K_I[Tl^+]\ K_{III}[Tl^{3+}]}{K_I[Tl^+] + K_{III}[Tl^{3+}]} \cdot \frac{\phi_1}{K_t} \tag{II}$$

Mechanisms of this type are possibly easier to imagine for the platinum system. For example,

$$\text{Initiation} \qquad \mathrm{Pt(IV)} + h\nu \xrightarrow{\phi_1} \overset{\neq}{\mathrm{Pt}}\mathrm{(IV)} \quad (\neq \text{ Excited } \mathrm{Pt(IV)})$$

$$\text{Propagation} \qquad \overset{\neq}{\mathrm{Pt}}\mathrm{(IV)} + \overset{*}{\mathrm{Cl}}^- \overset{K_1}{\rightleftarrows} \overset{*\neq}{\mathrm{Pt}}\mathrm{(IV)} + \mathrm{Cl}^-$$

$$\overset{*\neq}{\mathrm{Pt}}\mathrm{(IV)} + \mathrm{Pt(IV)} \overset{K_2}{\rightleftarrows} \overset{\neq}{\mathrm{Pt}}\mathrm{(IV)} + \overset{*}{\mathrm{Pt}}\mathrm{(IV)}$$

$$\overset{\neq}{\mathrm{Pt}}\mathrm{(IV)} \xrightarrow{K_t} \mathrm{Pt(IV)}$$

This gives the analogous expression to (II),

$$\phi_{ex} = \frac{K_1[\mathrm{Pt(IV)}].K_2[\mathrm{Cl}^-]}{K_1[\mathrm{Pt(IV)}] + K_2[\mathrm{Cl}^-]} \cdot \frac{\phi_1}{K_t}$$

Mechanism B(ii)

Other possible ways of achieving linear termination are

(i) termination at the vessel wall,

(ii) termination with an impurity of constant concentration, i.e. concentration not significantly lowered by reaction with chain carrier.

For example,

$$\text{Initiation} \qquad \mathrm{Tl}^{3+}\mathrm{OH}^- + h\nu \xrightarrow{\phi_1} \mathrm{Tl}^{2+} + \mathrm{OH}$$

$$\text{Propagation} \qquad \mathrm{Tl}^{2+} + \overset{*}{\mathrm{Tl}}{}^{3+} \overset{K_{III}}{\rightleftarrows} \mathrm{Tl}^{3+} + \overset{*}{\mathrm{Tl}}{}^{2+}$$

$$\overset{*}{\mathrm{Tl}}{}^{2+} + \mathrm{Tl}^{+} \overset{K_{I}}{\rightleftarrows} \overset{*}{\mathrm{Tl}}{}^{+} + \mathrm{Tl}^{3+}$$

$$\text{Termination} \qquad \mathrm{Tl}^{2+} + \text{Wall} \xrightarrow{K_t} \mathrm{Tl}^{3+}$$

which yields the same expression (I) as in B(i)

D. Chain Reaction with Quadratic Termination

D1. The simplest chain mechanism with quadratic termination was derived in the initial pages of this chapter.

Initiation $\quad \mathrm{Tl}^{3+}\mathrm{OH}^- + h\nu \xrightarrow{\phi_1} \mathrm{Tl}^{2+} + \mathrm{OH}$

Propagation $\quad \overset{*}{\mathrm{T}}\mathrm{l}^{3+} + \mathrm{Tl}^{2+} \overset{K_{III}}{\rightleftharpoons} \mathrm{Tl}^{3+} + \overset{*}{\mathrm{T}}\mathrm{l}^{2+}$

$\qquad \overset{*}{\mathrm{T}}\mathrm{l}^{2+} + \mathrm{Tl}^{+} \overset{K_{I}}{\rightleftharpoons} \mathrm{Tl}^{2+} + \overset{*}{\mathrm{T}}\mathrm{l}^{+}$

Termination $\quad \mathrm{Tl}^{2+} + \mathrm{OH} \xrightarrow{K_t} \mathrm{Tl}^{3+} + \mathrm{OH}^-$

which yields the expression,

$$\phi_{ex} = \frac{K_I[\mathrm{Tl}^+]\,K_{III}[\mathrm{Tl}^{3+}]}{D}\left\{\frac{\phi_1}{I_{abs}K_t}\right\}^{\frac{1}{2}} + \frac{K_I[\mathrm{Tl}^+]\phi_1}{D}$$

Where $\quad D = K_{III}[\mathrm{Tl}^{3+}] + K_I[\mathrm{Tl}^+] + (K_t I_{abs}\phi_1)^{\frac{1}{2}}$

The distinguishing feature of quadratic termination is the dependence of ϕ_{ex} on I_{abs} ($\phi_{ex} \propto I_{abs}^{-\frac{1}{2}}$).

Approximations.

(i) For $\phi_{ex} >> 1$: (a) The second term is negligible.

(b) $K_{III}[\mathrm{Tl}^{3+}] + K_I[\mathrm{Tl}^+] > (K_t\phi_1 I_{abs})^{\frac{1}{2}}$

Considering the first term only in ϕ_{ex}, as $K_{III}[\mathrm{Tl}^{3+}]/D$ is always less than 1, for ϕ_{ex} to be > 1,

$$K_I[\mathrm{Tl}^+]\left\{\frac{\phi_1}{K_t I_{abs}}\right\}^{\frac{1}{2}} \text{ must be} > 1.$$

Hence $\quad K_I[\mathrm{Tl}^+]\phi_1^{\frac{1}{2}} > (K_t I_{abs})^{\frac{1}{2}}$.

As ϕ_1 is < 1 $\quad K_I[\mathrm{Tl}^+] > (K_t I_{abs})^{\frac{1}{2}}$

and $\quad K_I[Tl^+] > (K_t I_{abs} \phi_1)^{\frac{1}{2}}$

and since $K_{III}[Tl^{3+}]$ is positive,

$$K_I[Tl^+] + K_{III}[Tl^{3+}] > (K_t I_{abs} \phi_1)^{\frac{1}{2}}.$$

Hence,

$$\phi_{ex} = \frac{K_{III}[Tl^{3+}].K_I[Tl^+]}{K_{III}[Tl^{3+} + K_I[Tl^+]} \left\{\frac{\phi_1}{K_t.I_{abs}}\right\}^{\frac{1}{2}} \quad .$$

(c) If $K_I[Tl^+] \gg K_{III}[Tl^{3+}]$

$$\phi_{ex} = K_{III}[Tl^{3+}] \; . \left\{\frac{\phi_1}{K_t I_{abs}}\right\}^{\frac{1}{2}} \quad .$$

Mechanism D2.

Variation in termination reactions.

Termination $\quad Tl^+ + OH \rightarrow Tl^{2+} + OH^-$

$$Tl^{2+} + Tl^{2+} \overset{K_t}{\rightarrow} Tl^{3+} + Tl^+$$

With the same initiation and propagation reactions as in Mechanism D1.

$$\phi_{ex} = \phi_1 \left\{\frac{K_I[Tl^+].K_{III}[Tl^{3+}]}{P} \left(\frac{1}{K_t I_{abs} \phi_1}\right)^{\frac{1}{2}} + \frac{K_{III}[Tl^{3+}] + K_I[Tl^+] + (K_t I_{abs} \phi_1)^{\frac{1}{2}}}{P}\right\}$$

where $P = K_{III}[Tl^{3+}] + K_I[Tl^+] + 2(K_t I_{abs} \phi_1)^{\frac{1}{2}}$

Approximations.

(i) For $\phi_{ex} \gg 1$ the same expression as in D1 is obtained.

$$\phi_{ex} = \frac{K_{III}[Tl^{3+}].K_I[Tl^+]}{K_{III}[Tl^{3+}] + K_I[Tl^+]} \left\{\frac{\phi_1}{K_t I_{abs}}\right\}^{\frac{1}{2}}$$

Mechanism D3.

A combination of D1 and D2 termination reactions does not yield a simple expression; as the steady state concentration of chain carrier (Tl^{2+}) is expressed in a cubic equation; which cannot be solved simply.

With the same propagation reactions and

$$Tl^{3+}OH^- + h\nu \xrightarrow{\phi_1} Tl^{3+} + OH$$

$$OH + Tl^+ \xrightarrow{K_6} Tl^{2+} + OH^-$$

$$Tl^{2+} + OH \xrightarrow{K_{t1}} Tl^{3+} + OH^-$$

$$Tl^{2+} + Tl^{2+} \xrightarrow{K_{t2}} Tl^{3+} + Tl^+$$

$$\phi_{ex} = \frac{K_{III}[Tl^{3+}].K_I[Tl^+]}{q} . [Tl^{2+}] + T_1 + T_2$$

where T_1 and T_2 are terms < 1, q is an expression similar to P and equal to P for $\phi_{ex} > 1$, and $[Tl^{2+}]$ is the concentration of Tl^{2+} which in theory may be obtained from the equation (derived from steady state concentration of Tl^{2+}).

$$I_{abs}\phi_1 = \frac{K_{t1}K_{t2}[Tl^{2+}]^3}{K_6[Tl^+]} + K_{t2}[Tl^{2+}]^2 \qquad (i)$$

This equation reduces to

$$I_{abs}\phi_1 = K_{t2}[Tl^{2+}]^2$$

if $K_6[Tl^+]$ is much larger than the numerator; which corresponds to mechanism D3 above. This applies when $K_6[Tl^+] \gg K_{t1}[Tl^{2+}]$. As $[Tl^+]$ is much greater than $[Tl^{2+}]$, this is a reasonable assumption in practice. However the alternative $K_{t1}[Tl^{2+}] > K_6[Tl^+]$ is more complex as this leads to net reduction. However ignoring for the moment the mathematical complications arising from net reduction; (i) reduces to $I_{abs}\,\phi_1 = K_{t1}K_{t2}[Tl^{2+}]^3/K_6[Tl^+]$ and $\phi_{ex} \propto I_{abs}^{-2/3}$. As no results show a dependence of ϕ_{ex} on I_{abs} of power less than $-\frac{1}{2}$, this mechanism is regarded as unsuitable.

Mechanism D4.

Mixed linear termination and quadratic termination.

Initiation $$Tl^{3+}OH^- + h\nu \xrightarrow{\phi_1} Tl^{2+} + OH$$

$$OH + Tl^+ \xrightarrow{K_6} Tl^{2+} + OH^-$$

Termination $$Tl^{2+} + Tl^{2+} \xrightarrow{K_{t1}} Tl^{3+} + Tl^+ \qquad t_1$$

$$Tl^{2+} + ? \xrightarrow{K_{t2}} Tl^{3+}?\ \text{or}\ Tl^+? \qquad t_2$$

The same basic kinetic expression as in D3 results for $\phi_{ex} > 1$.

$$\phi_{ex} = \frac{K_{III}[Tl^{3+}].K_I[Tl^+]}{K_{III}[Tl^{3+}] + K_I[Tl^+]} \cdot [Tl^{2+}]$$

From steady state concentration of Tl^{2+} and OH

$$2I_{abs}\phi_1 = 2K_{t1}[Tl^{2+}]^2 + K_{t2}[Tl^{2+}] \qquad I$$

and hence $$[Tl^{2+}] = \frac{-K_{t2}}{4K_{t1}} + \frac{(K_{t2}^{\ 2} - 16I_{abs}\phi_1K_{t1})^{\frac{1}{2}}}{4K_{t1}}$$

This expression which controls the variation of ϕ_{ex} with I_{abs} is independent of the concentration of any reactant species, so that the dependence of ϕ_{ex} on I_{abs} would be expected to be independent of the concentration of reactants. However if we alter the second termination reaction t_2 to

$$Tl^{2+} + M \xrightarrow{K_{t2}} ?$$

where M is an impurity whose concentration is proportional to $[Tl^+]$, then analogously to equation 1

$$2I_{abs}\phi_1 = 2K_{t1}[Tl^{2+}]^2 + K_{t2}[Tl^{2+}][Tl^+],$$

where K_{t2} is now actually $K_{t2}[M]/[Tl^+]$, which is a constant. Now $\phi_{ex} \propto I_{abs}^{-\frac{1}{2}}$ when $K_{t2}[Tl^+] > K_{t1}[Tl^{2+}]$, i.e. when the rate of t_2 is insignificant compared to t_1, and $\phi_{ex} \propto I_{abs}^{\,0}$ when $K_{t2}[Tl^+] < K_{t1}[Tl^{2+}]$. Presumably some mixed order will occur when the two termination steps are comparable.

Note: At high light intensities (high $[Tl^{2+}]$) the first termination reaction will become more significant, hence ϕ_{ex} will tend towards an $I_{abs}^{-\frac{1}{2}}$ dependence at high light intensities and $I_{abs}^{\,0}$ at low light intensities.

Mechanism D5.

Possible variation in initiation reactions.

Kinetically different initiation reactions are difficult to imagine. However improbable initiation reactions such as

$$Tl^{3+}OH^- + h\nu \underset{k_r}{\overset{\phi_1}{\rightleftharpoons}} (\overset{\neq}{TlOH})^{2+}$$

$$(\overset{\neq}{\mathrm{TlOH}})^{2+} + \mathrm{Tl}^{+} \xrightarrow{k_i} 2\mathrm{Tl}^{2+} + \mathrm{OH}^{-} \qquad (i)$$

do give a different dependence on I_{abs}. Where $(\overset{\neq}{\mathrm{TlOH}})^{2+}$ is any excited species. From these initiation steps and

$$\mathrm{Tl}^{2+} + \mathrm{Tl}^{2+} \xrightarrow{K_t} \mathrm{Tl}^{+} + \mathrm{Tl}^{3+}$$

as termination reaction:

$$[\mathrm{Tl}^{2+}] = \left\{\frac{k_i[\mathrm{Tl}^{+}]}{k_r + k_i[\mathrm{Tl}^{+}]} \times \frac{I_{abs}\phi_1}{K_t}\right\}^{\frac{1}{2}}$$

Thus as before $\phi_{ex} \propto$ const. $[\mathrm{Tl}^{2+}]/I_{abs}$ for $\phi_{ex} > 1$, $\phi_{ex} \propto I_{abs}^{-\frac{1}{2}}$. An analogous expression is obtained by replacing Tl^{+} by Tl^{3+} in equation (i).

E. Proof of Assumption $K_I[\mathrm{Tl(I)}] + K_{III}[\mathrm{Tl(III)}] \gg 2(K_t I_{abs}\phi_1)^{\frac{1}{2}}$

For the $[\mathrm{Tl(I)}$ dependence,

$$\phi_{ex} = 1.91 \text{ at } [\mathrm{Tl(I)}] = .0011,\ [\mathrm{Tl(III)}] = .005 \text{ mole } l^{-1}.$$

If $K_{III}/K_I = 2$ is assumed

$$\frac{K_I[\mathrm{Tl(III)}]}{K_I[\mathrm{Tl(I)}] + K_{III}[\mathrm{Tl(III)}]} = \frac{1}{1.1} \quad \text{since} \quad \frac{K_I[\mathrm{Tl(I)}]}{K_{III}[\mathrm{Tl(III)}]} = \frac{1}{10}\,.$$

Now making the assumption

$$\phi_{ex} - \phi_1 = \frac{K_I[\mathrm{Tl(III)}]}{K_I[\mathrm{Tl(I)}] + K_{III}[\mathrm{Tl(III)}]} \cdot \frac{K_{III}[\mathrm{Tl(III)}]\phi_1^{\frac{1}{2}}}{(K_t I_{abs})^{\frac{1}{2}}}$$

Assuming $\phi_1 = 1$

$$1.91 - 1 = \frac{1}{1.1} \cdot \frac{K_I[\mathrm{Tl(I)}]}{(K_t I_{abs})^{\frac{1}{2}}}$$

Hence $K_I[Tl(I)] = .91 \times 1.1\ (K_t I_{abs})^{\frac{1}{2}}$,

and hence

$$K_I[Tl(I)] + K_{III}[Tl(III)] = 10\ (K_t I_{abs})^{\frac{1}{2}}$$
$$= 5.0 \ .\ 2\ .\ (K_t I_{abs})^{\frac{1}{2}}$$

F. Correction for Non-Uniform Absorption

An error may arise as a consequence of the dependence of the quantum yield on light intensity in reactant solutions of high optical density. The error arises because the average quantum yield, as measured by the total rate of reaction divided by the total rate of light absorption, is not the same as the average of the quantum yields in each infinitely small element of space. The problem has been discussed by Leighton and Noyes.(52)

If the quantum yield may be expressed by

$$\phi_{ex} = C\ I_{abs}^{-\frac{1}{2}} \qquad (1)$$

where C is independent of I_{abs}, the quantum measured experimentally will be,

$$\phi_{ex}^{exp} = \frac{\int_0^l R_{ex} \cdot dx}{\int_0^l dl} = \frac{1}{l}\int_0^l C\ I_{abs}^{+\frac{1}{2}} . dl \qquad (2)$$

where x is the distance from the front face of the reaction cell and l is the length of the cell. I_{abs}, R_{ex}, apply to the local values in the element dx.

Substituting $$I_{abs} = \frac{-dI}{dx} = 2.303\ a\ I_o\ 10^{-ax} \qquad (3)$$

(where - al = optical density of the reactant solution), and integrating we obtain

$$\phi_{ex}^{exp} = \frac{2C}{(2.303\ a\ I_o)^{\frac{1}{2}}(1 + 10^{-al/2})} \qquad (4)$$

The main assumptions made in this calculation are:

1. The diffusion of chain carriers from one element of volume to another is negligible.
2. Absorption follows the simple Beer's law equation,

   $$I = I_o\ 10^{-al}$$

   where I_o is the incident light intensity.

At low optical densities, equation (4) reduces to equation (1). Equation (1) would correspond to the experimental quantum yield, if absorption was uniform through the cell. The ratio of equation (1) to (4) may be used as a correction to allow for this phenomenon. The ratio is:

$$\alpha = \phi_{ex}/\phi_{ex}^{exp} = \frac{l^{\frac{1}{2}}}{2}(2.303a)^{\frac{1}{2}}\ \frac{(1 + 10^{-al/2})}{(1 - 10^{-al})^{\frac{1}{2}}}$$

The optical density of the most concentrated Tl(III) solution is 1.56, at which $\alpha = 1.13$. Thus a maximum error of 13% may arise from this source, the experimental quantum yield will be apparently low by this factor. In an I_{abs} dependence study at constant concentration, the correction factor a will be constant (i.e. independent of light intensity). Two factors will tend to reduce a.

1. The observation that ϕ_{ex} varies as $I_{abs}^{-(.3 - .4)}$ rather than $I_{abs}^{.5}$ will probably reduce a, but since direct integration of $\phi_{ex} \propto I_{abs}^{-.3}$ expression is not justified, no quantitative estimate of the difference can be determined.

2. If diffusion of the chain carriers becomes important, in contradiction to assumption 1, then a will be smaller.

Thus, although the maximum possible error is 13%, it is likely to be less. The error does not affect the linearity or the slope of the reciprocal concentration plots, nor does it affect the slope of the I_{abs} dependence graphs, so the consequences of this source of error have been neglected for the thallium study.

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SECTION III

THE ULTRAVIOLET LIGHT INDUCED CHLORIDE EXCHANGE REACTION BETWEEN *trans* $Pt(en)_2Cl_2^{2+}$ ION AND CHLORIDE ION

SECTION III

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Summary

Ultraviolet light has been found to induce an exchange between free chloride ion and complexed chloride ion in *trans* $Pt(en)_2Cl_2^{2+}$ in aqueous solution. A quantitative study of the reaction mechanism has shown that the reaction is a chain process, probably involving a Pt(III) species as chain carrier. A comparatively slow net photolysis reaction was also observed to occur. Mechanisms for the photolysis and exchange reactions are postulated and compared to the experimental data.

The first chapter is a survey of some of the literature relevant to the study.

SECTION III

CHAPTER 1: INTRODUCTION

A. Thermal Reactions of Pt(IV) Complexes

The thermal substitution reactions of Pt(IV) complexes were recently reviewed by Basolo and Pearson.(10) Other reviews may be found in standard texts on inorganic kinetics.

These reactions (including exchange, hydrolysis, isomerization) of Pt(IV) complexes may be divided into two groups, (1) the hexahalide ions, (2) halo-amine complexes.

1. The hexahalide ions show reactions which are very sensitive to impurities, reductants catalysing the reaction, and oxidants inhibiting the reaction. Included amongst the chemists who have studied these reactions are Põe and Vaidya(1), Davidson and Jamieson(5), Dreyer(18), Blasius et al(3), Taube(4), Grinberg(4c), and Nikolawa(4b). A mechanism involving a more labile Pt(III) species has been proposed, but the incomplete inhibitive effect of oxidants suggests a second mechanism may be operating. An alternative explanation of catalysis by Pt(II) ions was discarded by Põe and Vaidya because the catalytic effects of added Pt(II) compounds were too small. Dreyer, however, considered that the chloride exchange reaction proceeds via a Pt(II) - Pt(IV) intermediate.

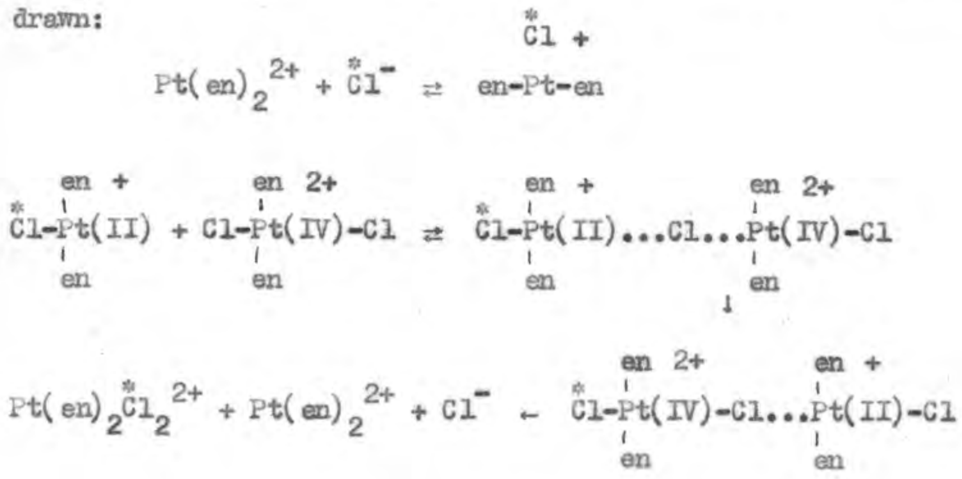
2. The exchange reactions of mixed amine and halide complexes, in particular the chloro complexes such as $Pt(en)_2Cl_2^{2+}$, exhibit unusual properties. A large body of kinetic data on these reactions

was discussed by Basolo et al$^{(5b)}$. See Table III.1 for some typical rate data.

The reactions are extremely slow in the absence of Pt(II) compounds, and have been shown to follow a rate law involving a first order dependence on Pt(II) concentration.

$$\text{Rate of exchange} = k[Pt(IV)][Pt(II)][X^-]$$

This led Basolo et al to propose a mechanism involving chlorine atom transfer between Pt(II) and Pt(IV) in a complex intermediate. For example, for <u>trans</u> $Pt(en)_2Cl_2^{2+}$ - Cl^- exchange, the mechanism may be drawn:



$$Pt(en)_2^{2+} + \overset{*}{Cl}^- \rightleftharpoons \overset{\overset{*}{Cl}\ +}{\text{en-Pt-en}}$$

$$\overset{*}{Cl}\text{-}\underset{en}{\overset{en\ +}{Pt}}(II) + Cl\text{-}\underset{en}{\overset{en\ 2+}{Pt}}(IV)\text{-}Cl \rightleftharpoons \overset{*}{Cl}\text{-}\underset{en}{\overset{en\ +}{Pt}}(II)\ldots Cl\ldots\underset{en}{\overset{en\ 2+}{Pt}}(IV)\text{-}Cl$$

$$\downarrow$$

$$Pt(en)_2\overset{*}{Cl}_2^{2+} + Pt(en)_2^{2+} + Cl^- \leftarrow \overset{*}{Cl}\text{-}\underset{en}{\overset{en\ 2+}{Pt}}(IV)\text{-}Cl\ldots\underset{en}{\overset{en\ +}{Pt}}(II)\text{-}Cl$$

The mechanism predicts that electron exchange between Pt(II) and Pt(IV) will occur at the same rate as chloride exchange. This was shown to be so experimentally.$^{(9)}$ The mechanism provides an adequate explanation of most of the results on Pt(IV) substitution reactions involving Pt(II) catalysis.

However, the chloride exchange of **<u>cis</u>** $Pt(en)_2Cl_2^{2+}$ was found$^{(8)}$ to proceed without isomerization as predicted by the mechanism above.

Table III.1

Reaction	Rate mole l^{-1} sec^{-1}		Temperature °C	Ref.
trans $Pt(en)_2Cl_2{}^{2+}$ - Cl^-	6.0×10^1	$[Pt(en)_2Cl_2{}^{2+}][Pt(en)_2{}^{2+}][Cl^-]$	30	9b
	3.9×10^1	"	20	9b
	1.5×10	"	25	7, 9a
cis $Pt(en)_2Cl_2{}^{2+}$ - Cl^-	6.0×10	$[Pt(en)_2Cl_2{}^{2+}][Pt(en)_2{}^{2+}][Cl^-]$	30	8
trans $Pt(en)_2Br_2{}^{2+}$ - Cl^-	6.04×10	$[Pt(en)_2Br_2{}^{2+}][Pt(en)_2{}^{2+}][Cl^-]$	30	7
trans $Pt(NH_3)_4Cl_2{}^{2+}$ - Br^-	1.08×10^2	$[Pt(NH_3)_4Cl_2{}^{2+}][Pt(NH_3)_4{}^{2+}][Br^-]$	25	15
trans $Pt(NH_3)_4Cl_2{}^{2+}$ - Cl^-	4×10^2	$[Pt(NH_3)_4Cl_2{}^{2+}][Pt(NH_3)_4{}^{2+}][Cl^-]$	25	11
trans $Pt(NH_3)_4Br_2{}^{2+}$ - Cl^-	4.2×10^3	$[Pt(NH_3)_4Br_2{}^{2+}][Pt(NH_3)_4{}^{2+}][Cl^-]$	25	15
$Pt(NH_3)_5Cl^{3+} + Cl^-$ $\rightarrow Pt(NH_3)_4Cl_2{}^{2+}$	6.5×10^{-4}	$[Pt(NH_3)_5Cl^{3+}][Pt(NH_3)_4{}^{2+}][Cl^-]$	25	6

Johnson, who studied the reaction, found that the reaction followed the same rate law with the same rate constant as the trans complex, but was forced to postulate direct chloride exchange in the Pt(II) - Pt(IV) complex because isomerization did not occur. However there is some doubt(27) that Johnson actually prepared the cis isomer. Basolo et al(14) also studied the substitution of trans $Pt(en)_2Cl_2^{2+}$ by several anions, including Br^-, CNS^-, CN^-, and OH^-. All these anions substitute for chloride in the complex, presumably through an analogous mechanism to the exchange reaction.

In the presence of acid, no hydrolysis of the chloroamines occurs on heating at elevated temperatures for several days, even when Pt(II) is added. The base hydrolysis of several Pt(IV) chloroamine complexes was investigated by Johnson et al(13), who found big differences in characteristics between the complexes. They suggested a bridge mechanism for the hydrolysis of trans $Pt(NH_3)_4Cl_2^{2+}$, and direct substitution by OH^- for cis $Pt(NH_3)_4Cl_2^{2+}$, and $Pt(NH_3)_5Cl^{3+}$. Trans $Pt(en)_2Cl_2^{2+}$, and trans $Pt(en)_2ClOH^{2+}$ were found to reduce to Pt(II) on heating in base (in the presence of Pt(II)), but trans $Pt(en)_2(OH)^{2+}$ was stable in base. For the reduction the authors proposed an intermediate bridged through the amine, followed by oxidation of the amine and reduction of the metal. Trans $Pt(NH_3)_4Cl_2^{2+}$ also reduces to some extent on heating with base.

B. Photochemical Reactions

The unusual characteristics of the thermal reactions of Pt(IV) complexes, have led to the prediction of several complex reaction paths. The photochemical reactions also exhibit unusual features - the exchange reactions of the hexahalide complexes are chain reactions, and the quantum yields observed for both hydrolysis and exchange reactions, are independent of the wavelength of irradiation. The reported data for the photochemical reactions are considered in detail in this section. Table III.2 summarises some of these data.

In 1954 Rich and Taube(16) reported that the rate of exchange of chloride ion with Pt(IV) Cl_6^{2-} ion in water, was extremely photosensitive. Since then, several other Pt(IV) halide exchange and substitution reactions have been shown to be photosensitive, and quantitative studies published. Adamson(17) studied the photochemical exchange of Br^- ion with $PtBr_6^{2-}$, Dreyer(18) reported on the analogous chloride exchange, and the substitution of $PtCl_6^{2-}$ by Br^-. Recently Balzani et al(19) studied the photochemical hydrolysis of $PtBr_6^{2-}$.

Rich and Taube postulated a mechanism involving Pt(III) as a chain carrier.

$$PtCl_6^{2-} + h\nu \rightleftarrows PtCl_5^{2-} + Cl$$

$$PtCl_5^{2-} + \overset{*}{Cl}^- \rightleftarrows Pt\overset{*}{Cl}_5^{2-} + Cl^-$$

$$Pt\overset{*}{Cl}_5^{2-} + PtCl_6^{2-} \rightleftarrows PtCl_5^{2-} + Pt\overset{*}{Cl}_6^{2-}$$

Adamson, in a quantitative study of the hexabromide exchange, reported a chain mechanism which followed the kinetic expression,

Table III.2

Reaction	Quantum Yields	λ	Comments	Effect of Impurities	Decomposition	Ref.
$PtBr_6^{2-} - Br^-$ exchange	$\phi = \alpha[PtBr_6^{2-}]I_{abs}^{-\frac{1}{2}}$	360	Chain Reaction	allyl chloride, acetone - no effect	$\phi < .1$ hydrolysis or reduction	17
$PtCl_6^{2-} - Cl^-$ exchange	$\phi \; \alpha \; k[Cl^-]$ k cmall $\phi \; \alpha \; I_{abs}^{x}$ x not const.	546 436 366 320-230	Chain Reaction $\phi_{max} = 1000$	Br_2 $10^{-5}M$ stops reaction		18a
$PtCl_6^{2-}/Br^-$ substitution	No quantitative results	578 436 366	Chain Reaction	$Br_2 > 10^{-6}M$ inhibits reaction		18b
$PtBr_6^{2-}/H_2O$ hydrolysis	ϕ constant = .5 ± .1 Independent of I_{abs} " " $[PtBr_6^{2-}]$ Reduced by $[Br^-]$	313 365 433 530	Reversible aquation reaction	H_2O_2 no effect ($10^{-4}M$) hydroquinone some effect	No reduction No reaction $[Br^-] > .1$ mole l^{-1}	19

$$\phi = k[PtBr_6^{2-}]I_{abs}^{-\frac{1}{2}}$$

where I_{abs} is the rate of light absorption. He also noted that the quantum yields were independent of the wavelength of irradiation. The analogous mechanism to the chloride exchange mechanism above was consistent with his results. Up to this stage there was little serious consideration given to other possible mechanisms. However, Dreyer(18a) and then Adamson(21) in a later paper postulated different mechanisms.

Dreyer et al made a quantitative study of the effect of light on the $PtCl_6^{2-}/Cl^-$ exchange and the $PtCl_6^{2-}/Br^-$ substitution reaction. They also reported large quantum yields indicating a chain reaction, but found the dependence of quantum yield on the kinetic variables to be more complex. The following results have been extracted from their paper on the chloride exchange reaction.

(a) The quantum yield shows little dependence on the wavelength of irradiation. (546, 436, 366, and 320...230 mμ were the wavelengths of irradiation.)

(b) The dependence of quantum yield on light intensity was fitted to the expression

$$\log R \propto I_{abs}$$

where I_{abs} was given in units of cal mole^{-1} min^{-1}. This leads to a complex dependence on I_{abs}, when I_{abs} is in units of Einstein l^{-1} min^{-1}.

(c) The dependence of quantum yield on chloride ion concentration was found to be complex, varying with wavelength of irradiation. However, at 564 mμ, and 436 mμ, a straight line was fitted to the results.

$$\text{Rate of Exchange} = a + b\ [Cl^-]$$

In general, the quantum yield was shown to be much less than linearly dependent on chloride concentration.

It seems that these authors discard Pt(III) as a chain carrier, in favour of a mechanism involving photocatalysis of exchange in the Pt(II) - Pt(IV) complex postulated as an intermediate in the thermal exchange.

In a brief note, Adamson et al(21) reported that they had failed to find the expected Br atom in flash photolysis studies of $PtBr_6^{2-}$. This, plus the observation that hydroquinone stopped the formation of products, led them to postulate that a Pt(II) species is formed by photolysis.

$$PtBr_6^{2-} + h\nu \rightarrow \overset{\neq}{PtBr_4}{}^{2-} + Br_2$$

The excited Pt(II) species was then predicted to act as the chain carrier in the exchange reaction.

Balzani(9) et al also reported a study of the photolysis of $PtBr_6^{2-}$. They observed that hydroquinone drastically altered the absorption spectrum of Pt(IV), suggesting misinterpretation by Adamson. Balzani et al did not study the exchange reaction, but determined quantum yields for the hydrolysis of $PtBr_6^{2-}$ at low Br^- concentrations. The quantum yield (.5 ± .1) was again found to be independent of wavelength, irrespective of whether irradiation occurred in the d-d or charge-transfer bands. On this fact they concluded that at all wavelengths the same excited state is formed, with nearly unitary efficiency by internal conversion or intersystem crossing from other excited states. They suggested the triplet state ($^3T_{2g}$) as the most likely excited state.

On the exchange reactions they commented,

(a) "the exchange is scarcely reproducible"

(b) "thus it appears that no relation exists between hydrolysis and exchange processes".

Several other reactions of Pt(IV) have been reported by Grinberg and other Russian$^{(20)}$ workers to be photosensitive. Among these are the rate of aquation of $PtCl_4(NH_3)_2$, and hydrolysis and reduction of $PtCl_2\{(NO_2).(NH_3)\}_2$ complexes. Chernyaev commented on the latter reaction: "On account of the high sensitivity of halogen to light, absorption by a complex leads first to weakening and rupture of the Pt-halogen bond, which in turn causes the acceleration of at least two independent processes, namely the hydrolysis and reduction of Pt(IV) to Pt(II)".

The present study of the exchange between $Pt(en)_2Cl_2{}^{2+}$ with Cl^-, has shown it to be a chain reaction also, but the kinetic characteristics are considerably different to the hexabromide system. The study was instigated to try and determine the chain carriers and mechanism of these unusual reactions. It was also of interest to compare the photochemical reactions of diammine complexes to the hexahalide complexes as their thermal reactions show different characteristics.

The trans diammine complex was chosen because of its stability, ease of preparation, and slow thermal exchange rates. It also has the important property of large separation of the d-d and charge-transfer bands.

C. Absorption Spectra of Pt(IV) Complexes

Fig. III.1 depicts the absorption spectrum of trans $Pt(en)_2Cl_2^{2+}$, which may be regarded as typical of Pt(IV) complex absorption spectrum. As in most transition metal complexes, the bands may be divided into two groups; at shorter wavelengths the high intensity charge-transfer bands, and at longer wavelengths the less intense d-d absorption bands.

Jørgenson(22) has successfully interpreted the charge-transfer bands of the hexahalide complexes in terms of the molecular orbital model discussed in Section I. On this basis, the lowest energy charge-transfer transition is assigned to a transition from a ligand π to a metal d orbital (γ_3). The short wavelength band of the $Pt(en)_2Cl_2^{2+}$ spectrum (λ_{max} = 207 mμ, $\epsilon_{max} = 3 \times 10^4$ l mole^{-1} cm^{-1}) is considered to be a charge-transfer band because of the large extinction coefficient; and by analogy to the hexahalides may be assigned to a $\pi - \gamma_3$ transition. The lower symmetry of this complex raises the question as to which ligand π orbital is being referred to, if indeed it is meaningful to refer to a π orbital of a particular ligand rather than a molecular orbital involving the whole complex.

In terms of charge-transfer theory, the band would probably be assigned to a transition from the most easily oxidizable ligand (in this case probably chloride ion) to the metal ion.

The d-d bands of transition metal complexes have been well interpreted.(23) Two term series referred to as strong field and weak field configurations arise for each electronic configuration. Pt(IV) complexes exhibit one of the highest ligand field splittings of any metal ion, so that the strong field configuration may be assumed to apply to Pt(IV) complexes.

The strong field term series for an octahedral d_6 ion is $^1A_{1g}$, $^3T_{1g}$, $^3T_{2g}$, $^1T_{2g}$, $^1T_{1g}$, $^5T_{2g}$, ^5E_g. Thus in octahedral symmetry two moderate intensity bands $^1T_{2g} \leftarrow {}^1A_{1g}$, and $^1T_{1g} \leftarrow {}^1A_{1g}$ might be expected. The two moderate intensity absorption bands of $Pt(en)_2Cl_2^{2+}$ (λ_{max} = 263 mμ, ϵ_{max} = 950, and λ_{max} = 332 mμ and ϵ_{max} = 105) may be assigned to these transitions, although the lower symmetry of the molecule reduces the certainty of the assignation. Similarly, the low intensity band (λ_{max} = 380 mμ, $\epsilon_{max} \sim 20$) may be assigned to a spin forbidden transition from the singlet ground state $^1A_{1g}$ to either of the low-lying triplets $^3T_{1g}$ and $^3T_{2g}$. (Consideration was given to the possibility that this band was due to traces of a yellow impurity. However a batch of complex recrystallized several times and white in appearance still had the same absorption band.)

Cotton and Harris(24) performed some molecular orbital calculations on the hexachlorides of Re(IV), Os(IV), Ir(IV), and Pt(IV), determining

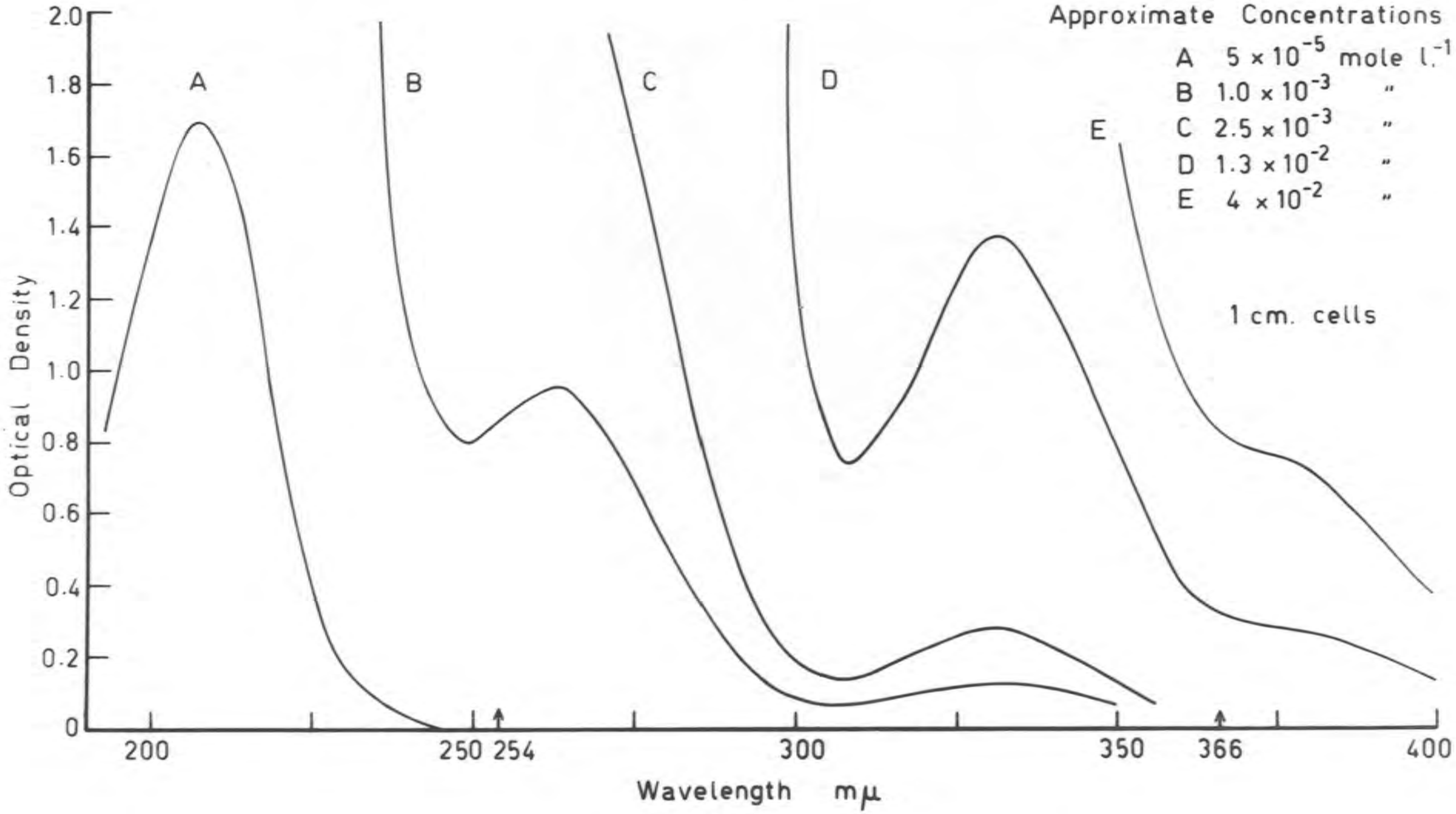


FIG. III·1 Absorption Spectra of $[PtEn_2Cl_2](ClO_4)_2$ in H_2O.

values for the ligand field splitting (Δ), the energy of d-d transitions and the energy of the charge-transfer $t_{2u} \rightarrow t_{2g}$ transition. The agreement obtained between calculated experimental values was considered to be satisfactory. Their calculations indicate about 80% metal character in the t_{2g} orbital for $PtCl_6^{2-}$.

SECTION III

CHAPTER 2: PLATINUM EXPERIMENTAL

A. Preparation of Reactants

Deionized water, distilled from $KMnO_4$ and then from $K_2Cr_2O_7$ was used throughout the study.

a. Trans $[Pt(en)_2Cl_2]Cl_2$.

The complex, trans $[Pt(en)_2Cl_2]Cl_2$ was prepared by the method of Basolo et al(30) from Na_2PtCl_6 and $(NH_4)_2PtCl_6$. The Na_2PtCl_6 was of unknown purity but the $(NH_4)_2PtCl_6$ was of "Specpure" quality. In early preparations KCl was added so that the precipitate of K_2PtCl_6 could be used as an indicator in the SO_2 reduction. In later preparations, KCl was used as an external indicator. Analysis of the first batch of product yielded the following figures:

C	N	Cl	H	Pt
10.06%	11.20%	29.2%	4.28%	39.40%
	11.27%			

which corresponds to

	4.00	3.82	3.94	20.5	.97
calc.	4.00	4.00	4.00	16.0	1.0

The complex was shown to contain some water of hydration. Vacuum drying at approximately 100°C resulted in loss of weight corresponding to approximately 1.7 water molecules per mole. The complex returned to its original weight on exposure to the atmosphere. This explains the high % H in the complex, and the low %, but correct ratios of the other elements. The complex has been reported to be hydrated by Schleicher,(31) and Chiu and Doyle(27) reported that the complex was monohydrated.

Cl, N, C and H analysis were done by the Microanalytical Service connected with the University of Melbourne and C.S.I.R.O. Platinum analysis was performed by decomposing a known weight of complex to Pt metal over a bunsen burner. The use of very small weights resulted in a fairly large error.

b. Preparation of the perchlorate salt - $[Pt(en)_2Cl_2](ClO_4)_2$.

$[Pt(en)_2Cl_2](ClO_4)_2$ was prepared from the chloride salt by dissolution of the complex in dilute $HClO_4$ acid (2M A.R. May and Baker). The volume was reduced by evaporation under vacuum (max. temp. 70°C). The resulting solution and precipitate was mixed with approximately 5 times the volume of alcohol, filtered, washed with alcohol, and dried under vacuum. Analysis of all batches of the perchlorate for chloride by potentiometric titration with $AgNO_3$ (after base hydrolysis) gave correct figures (within ½%). The perchlorate salt has no water of crystallization. Platinum analysis by decomposition was not possible because of the explosive nature of decomposition. The infrared(8) and ultraviolet absorption(32) spectra were in accord with the reported spectra.

c. Preparation of Cl^{36} labelled complex.

Cl^{36} labelled perchlorate was prepared by heating a solution of either the inactive chloride or the perchlorate salt with active HCl^{36} for approximately 4 hours on a water bath at approximately 90°C; when exchange was shown to be complete. The perchlorate salt was separated by vacuum distillation as above. A 2N solution of HCl^{36} (500 μc/g) was supplied by the A.A.E.C.

B. Purity and Spectra

The absorption maxima in the spectra of the chloride and perchlorate complexes have the same wavelength and molar extinction coefficients as reported by Basolo(30) and Pöe.(32) The complexes were pale yellow to white, the perchlorate complex being lighter in colour than the chloride. Several recrystallizations of a small amount of compound from aqueous $HClO_4$ acid gave an apparently white compound. The compound still showed all the characteristic peaks of the complexes.

In a kinetic study, impurities that affect the rate of reaction are a source of concern. It is impossible to prove absolutely that an impurity effect is not present; however if batches prepared from different purity sources yield the same results, some degree of confidence may be felt that impurity levels are not affecting the rate of reaction. All batches used in this study gave consistent results even though prepared from considerably different quality material.

C. Stereochemistry

The method of preparation outlined above has been reported to lead to the formation of the trans complex.(28,30) However, there was some indication that the conversion of trans to cis had occurred in the last stage of the preparation of the perchlorate complex, so verification of the stereochemistry of the complex was sought.

Johnson(8) reported the infrared spectra of the cis and trans complexes in the region 700 to 4000 cm^{-1}, and used the differences in these spectra as a criterion to distinguish between the cis and trans isomers. However, no significant differences were discovered between the cis and trans spectra in his thesis.

Chiu and Doyle(27) recently reported the infrared spectra of cis and trans chloride complexes. They commented that it was doubtful whether Johnson prepared the cis isomer, as the rate constant for exchange reported by Johnson for his complex was the same as that reported for the trans complex. The I.R. spectrum of the complex chloride may be compared to the reported spectra of Chiu and Doyle in Fig. III.2 (KBr disc). The spectrum is more closely comparable to the trans spectrum of Chiu and Doyle, except perhaps for the peak at 760 mμ which is absent in the spectrum prepared for this study.

One batch of the perchlorate salt was prepared without heating, by precipitation with $HClO_4$, from a saturated solution of the chloride salt. The infrared spectrum in the region 400 cm^{-1} to 1000 cm^{-1}, showed no significant differences to the spectrum of the reactant complexes.

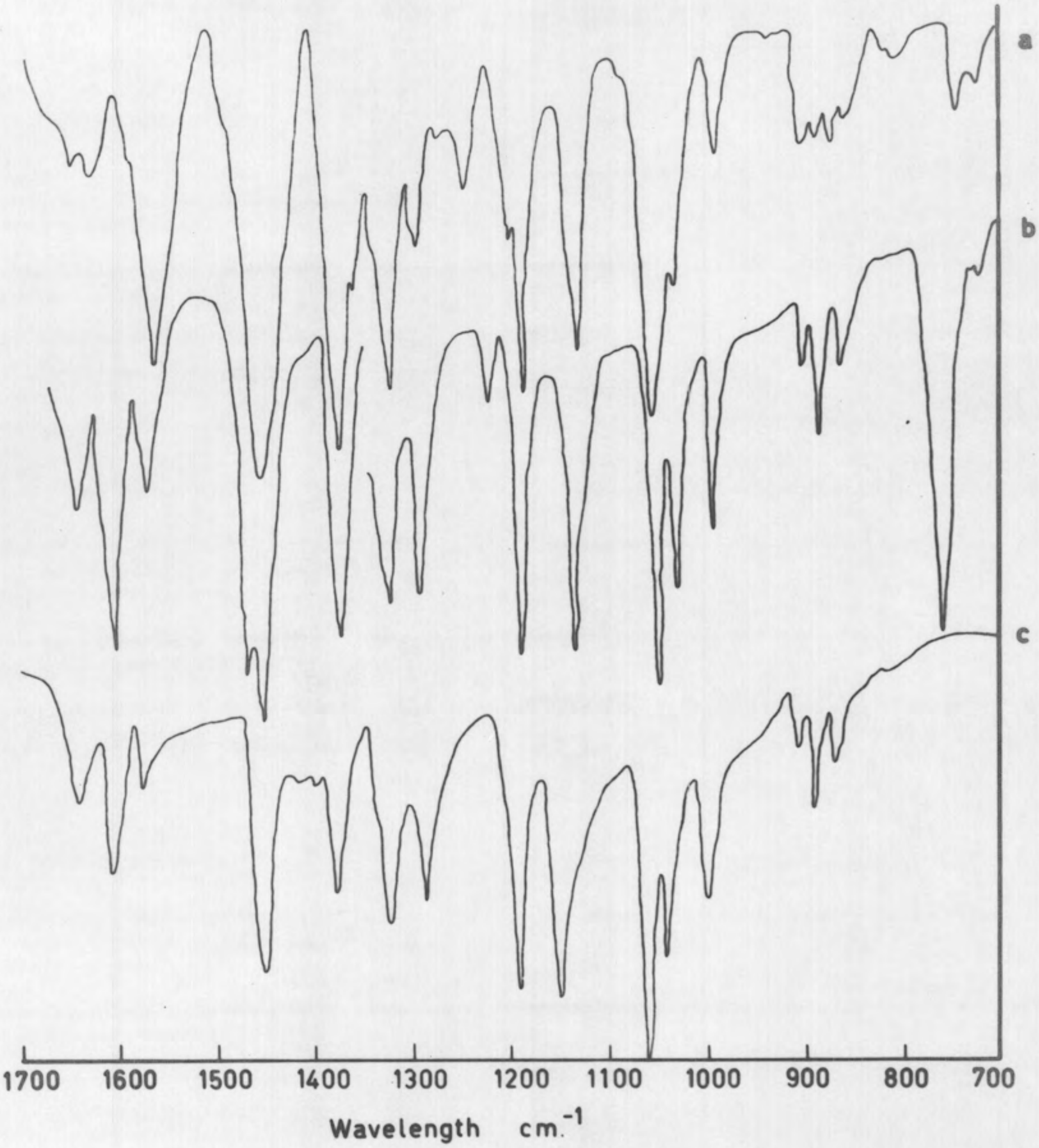


FIG. III·2 Infrared Spectra of $[PtEn_2Cl_2]Cl_2$

a. Chiu & Doyle — cis
b. " " — trans
c. This Study

In an attempt to further establish the identity of the complex, x-ray powder photographs were taken of the reactant complex, and the complex mentioned above. Johnson(8) reported data on the powder photographs of <u>cis</u> and <u>trans</u> perchlorates. There are significant differences between the data he reported. A powder photograph of the perchlorate used in the present study, was obtained using a Philips x-ray diffraction tube with CuKα radiation, with a circular camera, (11.483 cm diameter). The photograph is shown in Fig. III.3.

From the photograph the distance between the corresponding lines was measured. This distance was converted to interplanar spacings (d) using a table of values.(33) Density of the lines was determined visually by assigning a value of 1.0 to the most dense lines and .1 to the least dense. The values obtained by this technique are listed in Table III.3, together with the analogous values reported by Johnson.

Table III.3

Powder Photographs of $[Pt(en)_2Cl_2](ClO_4)_2$.

	This Study				Cis			Trans	
	Sample 2		Sample 1						
	d	dens	d	dens	d	d	dens	d	dens
						15.996	.3	16.113	1.0
1	9.18	1.0	9.25	1.0	9.18_5	9.263	1.0	8.999	.2
2	5.91	.8	5.98	.8	6.11	6.045	.5,.7	8.125	.1
3	4.69	.5	4.67	.5	4.71_5	4.741	.4	5.956	.4
4	4.38	1.0	4.38	.9	4.42	4.440	.8	4.741	.5

(contd.)

Table III.3 (contd.)

	This Study				Cis			Trans	
	Sample 2		Sample 1						
	d	dens	d	dens	d	d	dens	d	dens
5	4.21	.4	4.19	.2	4.25	4.259	.4	4.423	.9
6	3.154	.4	3.15	.4	3.20	3.211	.5	4.251	.5
7	3.064	.2	3.045	.1	3.02	3.048	.2	3.087	.1
8	2.974	.1	2.97	.2	2.70_5	2.710	.4,.3	2.846	.3
9	2.659	.2	2.64	.3	2.516	2.513	.2	2.516	.1
10	2.569	.1			2.356	2.353	.2,.1		
11	2.470	.1			2.235	2.238	.3		
12	2.424	.1			2.119	2.118	.3,.2		
13	2.296	.1			2.032	2.039	.2		
14	2.192	.2			1.922	1.922	.3,.2		
15	1.909	.8							

Cis and trans values quoted from Johnson, G.L.(8) Ph.D. Thesis.

Sample 1 is the reactant complex. Sample 2 is the perchlorate prepared at room temperature from the chloride as discussed in the section on the infrared spectrum. The two patterns are identical, but do not correspond with the results reported by Johnson for either the cis or the trans complex, although more similarity is observed to the cis data. In view of the doubt about the stereochemistry

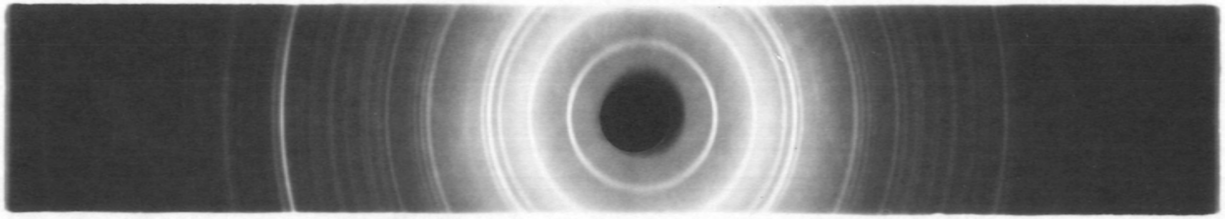


FIG. III·3 Powder Photograph.

of the Johnson complexes, this is quite inconclusive evidence.

Despite the powder photograph dilemma, the complex studied in this thesis is probably the trans isomer. Previous workers(8, 34,30,27) have established that the chloride salt prepared by the method used in this study is the trans isomer. The only stage where my preparation differed from their method, was in the preparation of the perchlorate from the chloride. The correspondence of the infrared spectrum and powder photographs of the perchlorate prepared at room temperature and elevated temperatures, eliminates the possibility of isomerization in this stage. The slow rates of substitution of these complexes, makes it improbable that isomerization takes place rapidly at room temperature. An N.M.R. study in sulphuric acid, would definitely establish the absence of large amounts of the cis complex.

D. Kinetic Runs

The same experimental apparatus was used for the platinum study as for the thallium study, except that a glass tube was used to bubble N_2 or A through the reaction mixture in the cell. Oxygen-free N_2 was passed through a bubbler containing distilled water and immersed in the water bath at the reaction temperature. (This brought the gas to bath temperature and saturated it with water at that temperature.) Other small differences in technique from those used in the thallium study include:

(i) The cell was filled with a 5 ml aliquot.

(ii) The cell position was altered from the thallium system.

(iii) The lowest intensity position was achieved with a filter of dilute $K_2Cr_2O_7$.

Separation of free chloride from complexed chloride.

Two separation methods were tested.

(a) Precipitation of chloride as Hg_2Cl_2 proved to be unsatisfactory because of large zero time exchange.

(b) The method adopted for this study was precipitation of free chloride as AgCl, followed by filtration on a small sinter glass filter. The filtrate was collected in a 25 ml standard flask. The AgCl precipitate was dissolved in NH_3 and collected in a second 25 ml standard flask. Thus both precipitate and filtrate were obtained as aqueous samples and assayed in liquid Geiger tube. The detailed experimental technique used was:- To 2 ml .1N $AgNO_3$ $^1/_3$ ml of reaction mixture was added, followed by $^1/_3$ ml and .2N HCl. This was filtered through 1 cm diameter porosity 4 filter (arranged as described for the thallium systems) and washed with approximately .02N $AgNO_3$. The precipitate was dissolved in 5N NH_3 and then washed with water direct into the standard flask. The filter arrangement was a smaller version of the arrangement used for the thallium system.

The method is extremely good as:

(a) Separation on a sample of $^1/_3$ ml was reproducible to within ± 1%.

(b) Zero time separation with active free Cl^- is less than 1%. Zero time separation with active complex Cl^- is less than 3%. Thus the ratio of active free Cl^-/active complex Cl^- as determined experimentally, is accurate to within ± 3%.

(c) The solutions are stable for more than one hour.

Exchange runs.

Reactant solution was prepared just prior to the run, and 5 ml of the solution was pipetted into the reaction vessel (previously rinsed with reactant solution). The vessel was located in the correct position for irradiation, the bubbler inserted, and the solution degassed for $1/2$ to $3/4$ hour. The run was started by the removal of a shutter from the light beam. (Light warmed up for more than one hour.) Aliquots of ca. $1/3$ ml were taken at the required times and separated. In short runs the shutter was replaced during removal of the sample.

Reduction studies.

The same technique was used to study the rate of reduction; although much longer irradiation times were required. A solution brought to exchange equilibrium in an exchange run, or thermally by standing, was irradiated and the change in the equilibrium ratio of free chloride to bound chloride followed with time.

Light intensity.

The light intensity was determined at 254 mμ in the same manner as in the thallium exchange study. In most reaction mixtures at this wavelength the optical density of the reactant solutions was greater than 2, so that almost all the incident light was absorbed. A correction was made for those few samples where transmission of light was significant. At 366 mμ the incident light intensity was calculated directly from ferrioxalate actinometry.

SECTION III

CHAPTER 3: RESULTS

A. Preliminary Work

The following features of the reaction were established in the preliminary work on the system.

(a) The rate of exchange in the dark has a half-time of more than 1000 hours. (The thermal exchange is catalysed by visible light.)

(b) The rate of exchange under the influence of light is greatly accelerated, but shows good McKay plots with an induction period. (See Fig. III.43.)

(c) Some net decomposition occurs on photolysis, at a rate three orders of magnitude slower than the rate of exchange. This was shown by an increase in the percentage of free chloride in the reaction mixture with time.

(d) The effect of O_2 on the rate of reaction was studied in several experiments.

(i) The rate of reaction in solutions either in equilibrium with air or with bubbled O_2 was approximately one half the rate of the reaction of solutions bubbled with N_2 (for more than a half hour) before irradiation. Fig. III.4A shows the effect graphically.

(ii) A run with N_2 from a Cr(II) scrubbing tower showed the same rate as runs bubbled with N_2 from the cylinders (within ± 3%).

(iii) Bubbling rate was shown to have an insignificant effect.

It was concluded from this work that O_2 only affects the rate

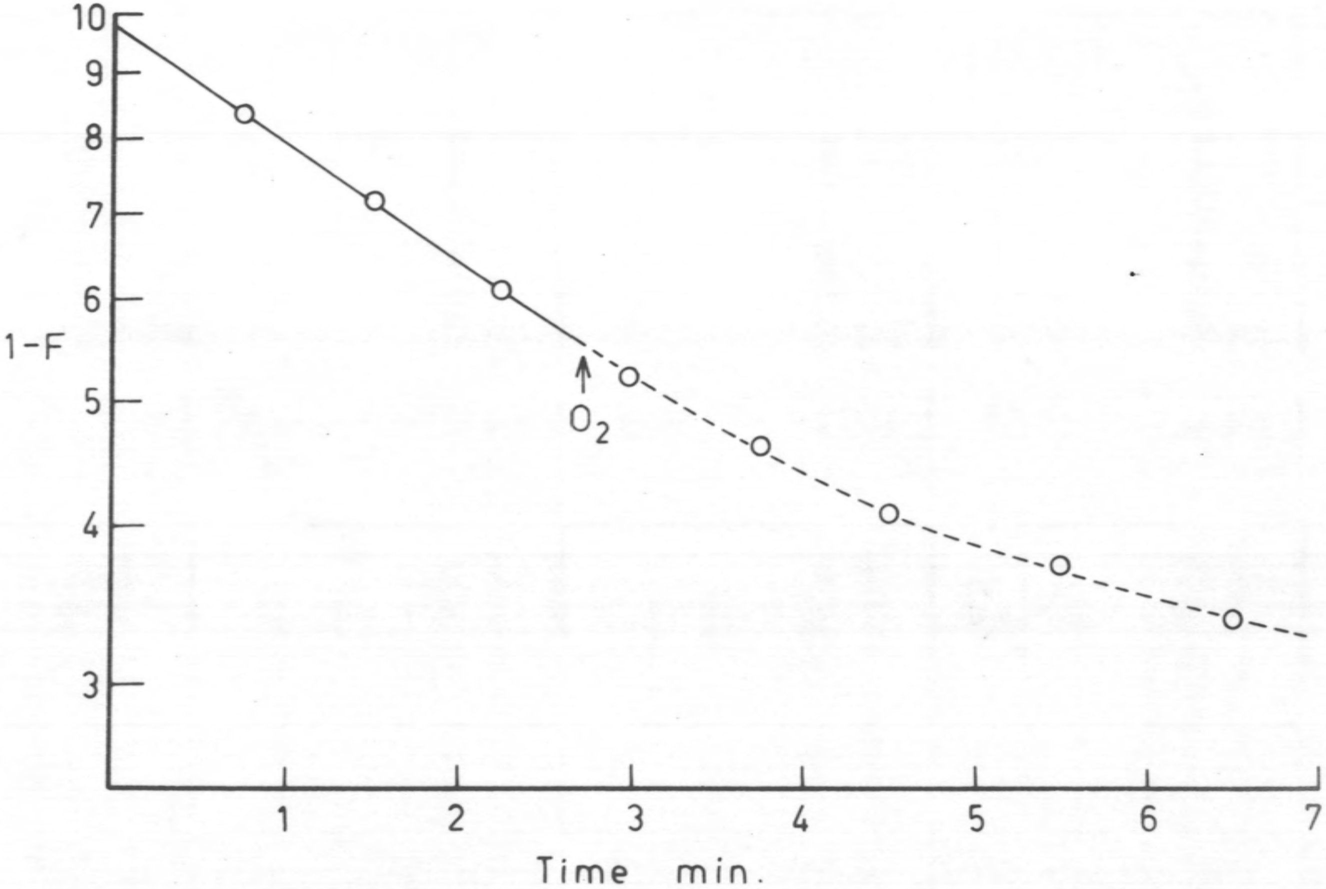


FIG. III·4A Effect of O_2 on the Rate of Exchange.

—— N_2

- - - O_2

significantly when in high concentrations. Hence all runs were bubbled with N_2 or A for more than a half hour, before the run was started.

Ionic strength and acidity.

The approximate effect of ionic strength on the rate of reaction was determined so that the measure of control over ionic strength necessary could be determined.

Run 15 with no $NaClO_4$ gave a half-time of 9.0 ± .4 minutes.
Run 16 with .211M $NaClO_4$ gave a half-time of 2.0 ± .5 minutes.
Run 17 with .147M $HClO_4$ gave a half-time of 1.4 ± .2 minutes.
These results were taken to show that perchloric acid had the same order of magnitude effect as sodium perchlorate. The observation that the two sources of perchlorate ions both affect the rate to the same degree is an indication that their impurity level is not affecting the reaction significantly.

Induction period.

An induction period was observed with all runs not specially treated. As in the thallium study, this induction period is attributed to small traces of organic impurities. It was shown by removing the induction period that it did not affect the observed half-time of the reaction. Pre-irradiation of a solution without platinum complex for more than one hour, followed by direct addition of complex to the cell gave a rate plot without an induction period but with a slope consistent with runs with an induction period. The induction period may be attributed to the reaction of chain carrier with impurities (probably organic matter) with the consequent destruction of the impurities. If this reaction is affecting the later stages of the reaction, the rate of the reaction would be expected to increase with time, resulting in curvature in the rate plots. No such curvature in the rate plots was observed.

Rate of exchange.

The rate of exchange was determined from a McKay plot. A typical log (1 - F) against time curve is shown in Fig. III.4B. Unlike the thallium reaction, F the fraction of exchange was calculated as A_t/A_∞ where A_t is the fraction of activity in one form at time t and A_∞ is the same fraction calculated for infinite time. A typical set of figures for the run plotted in Fig. III.4 is given in Table III.4.

Quantum yield for exchange.

The quantum yield for exchange ϕ_{ex} was calculated from the equation

$$\phi_{ex} = \frac{R_{ex}}{I_{abs}}$$

where R_{ex} is the rate of exchange (in units of mole l^{-1} min^{-1}), and I_{abs} is the absorbed light intensity (in Einstein l^{-1} min^{-1}).

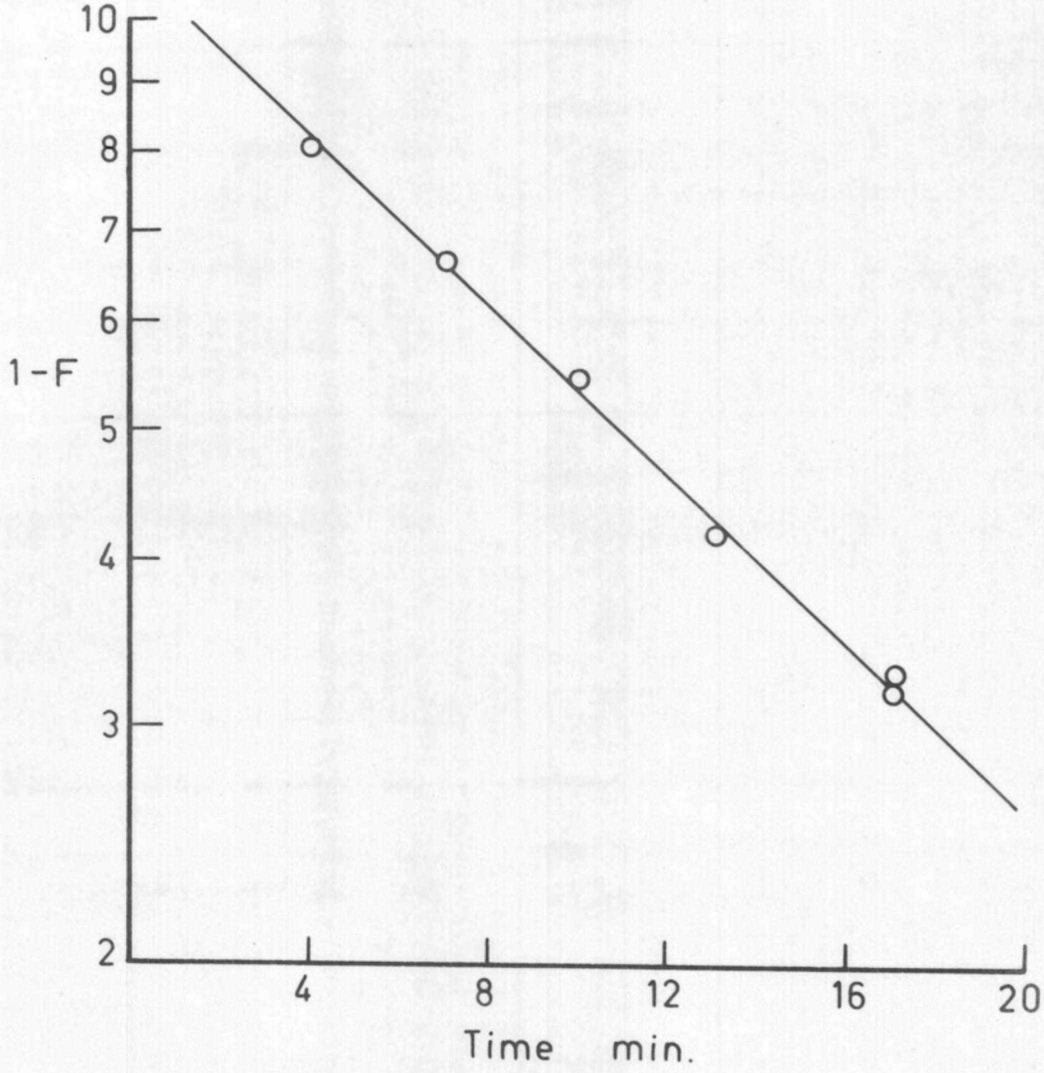


FIG. III·4B Typical Rate Plot

Table III.4

Typical Rate Data.

Time min.	Activity in Complex counts $\min^{-1}$ A_1	Activity in free Cl^- counts $\min^{-1}$ A_2	$\frac{A_1^*}{A_1^* + A_2^*} = A_t$	$F = \frac{A_t}{A_\infty}$
4	96	479	142	.199
7	168	492	239	.334
10	200	392	326	.455
13	251	342	417	.584
17	347	363	488	.681
17	316	340	480	.671

Notes: 1. A_1^* and A_2^* are A_1 and A_2 corrected for background activity.

2. F is the fraction of exchange.

3. A_∞ is calculated from the expression $\frac{2a}{2a + b}$ where a is the concentration of $Pt(en)_2Cl_2^{2+}$ and b is the concentration of free chloride ion.

Errors.

The two main sources of error in the quantum yield are:

1. In the determination of the half-time from the McKay rate plot. A random error due to this, of less than ± 5% (determined graphically). Other systematic errors due to concentration errors

± 2% (the active HCl was diluted using a .1 ml micro pipette, with an accuracy of ± 1%), separation errors ± 2%, timing errors, errors in temperature etc., result in an overall error of the order of ± 10% in the rate of exchange.

2. As discussed in Section II, the random error in I_{abs}, the absorbed light intensity is of the order of ± 3%, so that an overall random error of ± 8% in the quantum yield is expected. Random impurity effects may however increase this error. The scatter of results indicate that the random error in the measurements is at least ± 10%. Total systematic errors are of the order of ± 10%, so that the overall error is approximately ± 20%.

B. Dependence on Complex Concentration

The dependence of the quantum yield for exchange on the concentration of $[Pt(en)_2Cl_2](ClO_4)_2$ is shown in Table III.5 and Fig. III.5. Because of the high optical densities a correction is necessary for the effects of non-uniform intensity. Values of α, the correction factor, (defined and derived in the appendix of Section I) - calculated for the reactant solutions are listed in the right hand column of Table III.5. The optical densities used in this calculation were determined with the assumption that the extinction coefficient of the reactant at 254 mμ is 850 cm l mole^{-1}.

The three runs marked with an asterisk were performed at a lower light intensity. Both the uncorrected values and the values corrected for light intensity by the equation $\phi_{ex} \propto I_{abs}^{-.37}$ are plotted.

Table III.5

Dependence of Quantum Yield on Complex Concentration.

Complex Concentration mole l^{-1} x 10^3	$t_{\frac{1}{2}}$ min	R_{ex} mole $l^{-1}min^{-1}$ x 10^4	ϕ_{ex}	ϕ_{ex} corrected	a
*1.02_5	17	.423	9.75	10.1	1.04
2.0	7.2	1.28	20.3	23.4	1.15
2.56	7.0	1.42	22.5	27.8	1.23_5
2.66	7.3	1.38	21.9	27.4	1.25_0
2.78	6.2	1.68	27.6	35.0	1.27
2.88	6.4	1.61	25.6	32.9	1.28_5
2.93	6.9	1.50	23.8	30.7	1.29
*2.96	8.4	1.23	24.6	32.0	1.30
*5.28	7.5	1.55	31.0	49.5	1.60
7.73	4.9	2.50	39.7	77.0	1.94

25°C $[NaClO_4]$ = .211 mole l^{-1} $[HCl] = 2 \times 10^{-3}$ mole l^{-1}

$I_{abs} = 6.30 \times 10^{-6}$ Einstein l^{-1} min^{-1}

* $I_{abs} = 5.0 \times 10^{-6}$ " " "

C. Dependence of Quantum Yield for Exchange on the Concentration of Hydrochloric Acid

Table III.6 and Fig. III.6 illustrate the results. All the

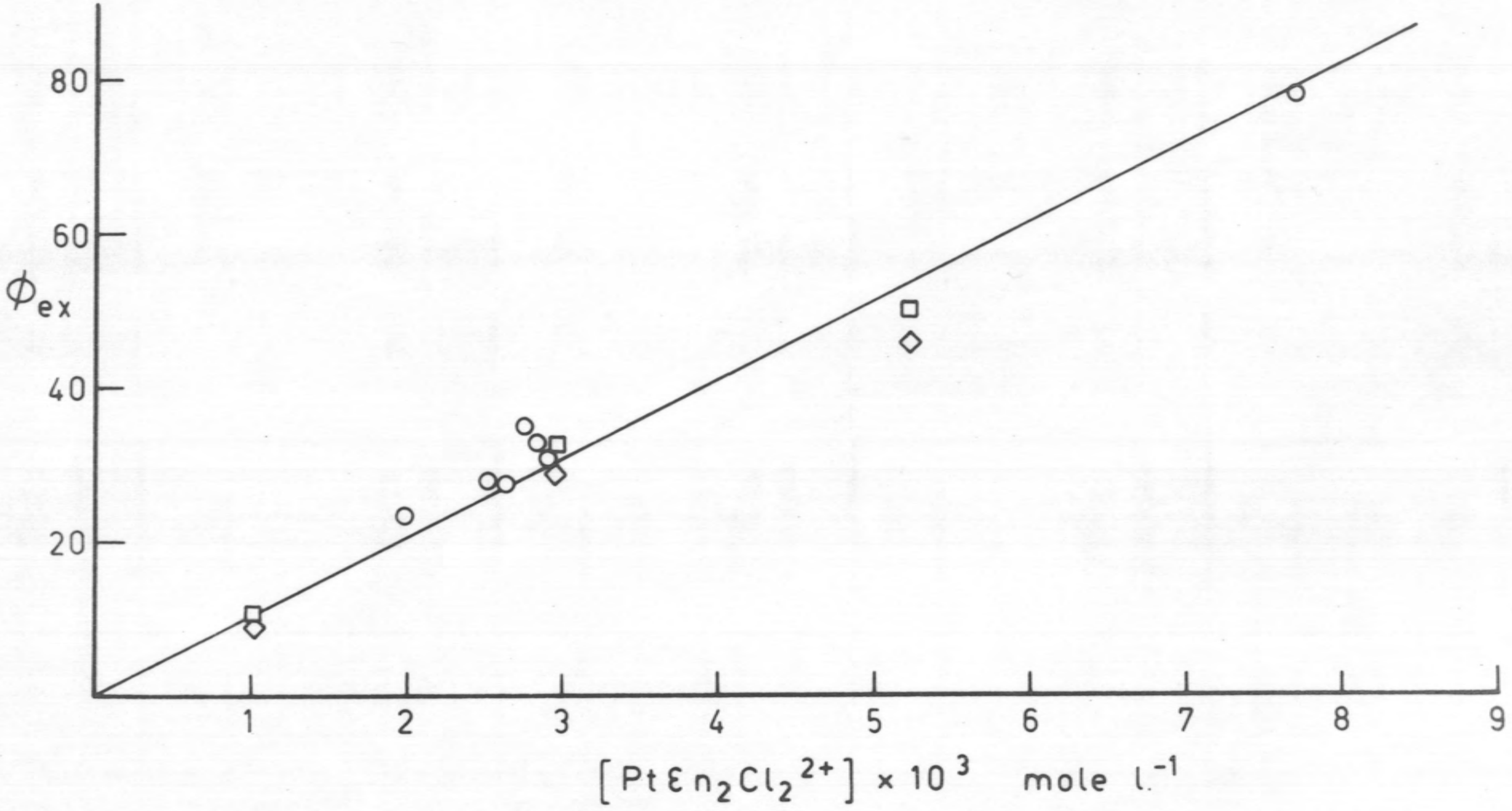


FIG. III·5 Dependence on Complex Concentration.

figures have been corrected to a constant $Pt(en)_2Cl_2^{2+}$ concentration of 2.70×10^{-3} mole l^{-1} (from the $Pt(en)_2Cl_2^{2+}$ dependence plot).

The last run in Table III.6 was done at a NaCl concentration of 10.0×10^{-3} mole l^{-1}, and $I_{abs} = 5.0 \times 10^{-3}$ mole l^{-1}. The quantum yield plotted is corrected to the I_{abs} value of the other points. The quantum yield is within experimental error of the quantum yield expected in the presence of HCl of the same concentration.

Table III.6

Dependence of Quantum Yield on Chloride Ion Concentration.

HCl Conc. mole $l^{-1} \times 10^3$	$Pt(en)_2Cl_2^{2+}$ conc. mole $l^{-1} \times 10^3$	Rate of Exchange mole l^{-1} $\times 10^4$	Quantum Yield	Quantum Yield Corrected to Pt(IV) conc. of 2.70×10^{-3} mole l^{-1}
2.0	2.70	From Fig. 1 Pt(IV) dep.	22.5	22.5
3.28	2.60	1.37	21.7_5	22.0_5
4.55	2.56	1.24	19.7	20.1_6
5.19	2.66	.719	11.4	11.5
7.73	2.74	.98	15.5_8	15.4_4
10.23	2.65	.654	10.3_8	10.5_5
11.6	3.06	.651	10.3_2	9.1_2
15.4_6	2.74	.330	5.24	5.11
[NaCl] = 10.0	3.08	8.03	16.1	12.7

$[Pt(en)_2Cl_2^{2+}] = 2.70 \times 10^{-3}$ mole l^{-1}; $I_{abs} = 6.30 \times 10^{-6}$ Einstein l^{-1} min^{-1}

$[NaClO_4]$ = .2N mole l^{-1}

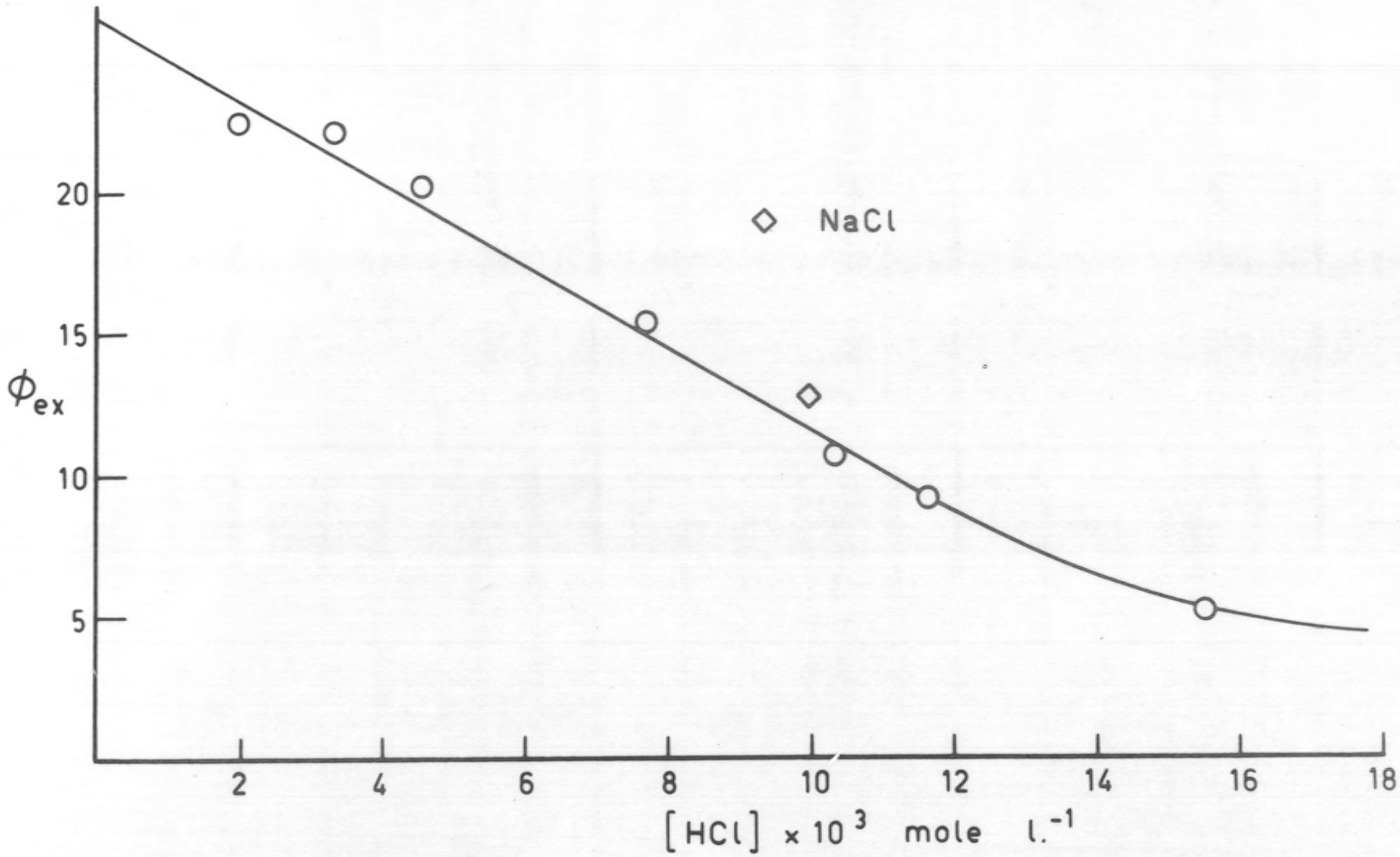


FIG. III·6 Dependence on HCl Concentration.

D. Dependence of Quantum Yield on Light Intensity

Fig. III.7 and Table III.7 show the experimental data on this variable. Again quantum yields are corrected to a $[Pt(en)_2Cl_2^{2+}]$ of 2.70 mole l^{-1}. The graph in Fig. III.7 of log ϕ_{ex} against log I_{abs}, yields a straight line approximated by the equation

$$\phi_{ex} = k\ I_{abs}^{-.37 \pm .04}$$

where k is a constant.

Table III.7

Dependence of Quantum Yield on Light Intensity

$[Pt(en)_2Cl_2^{2+}]$ mole l^{-1} min^{-1} x 10^3	Half-time of Exchange $t_{\frac{1}{2}}$ min	Rate of Exchange R_{ex} mole l^{-1} min^{-1} x 10^4	Absorbed Light Intensity I_{abs} Einstein l^{-1} min^{-1} x 10^6	Quantum Yield	Quantum Yield Corrected to Pt(IV) conc. 2.70 x 10^{-3} mole l^{-1}
2.80	2.0 ± .1	5.11	37.5	13.6_5	13.32
2.71	3.71 ± .3	2.73	14.12	19.3	19.2
2.70	From Graph 1 - (Pt(IV) Dependence		6.30	23.0	23.0
2.54	9.6 ± .6	1.07	3.46	29.9	30.4
2.69	12.0 ± .5	.843	2.38	35.4	35.4

$[HCl] = 2.0 \times 10^{-3}$ mole l^{-1}; $[NaClO_4] = .211$ mole l^{-1}; 25°C.

E. Exchange Quantum Yields at 366 mμ

One accurate exchange run was performed with light of wavelength 366 mμ. The light source was a high pressure mercury arc, with

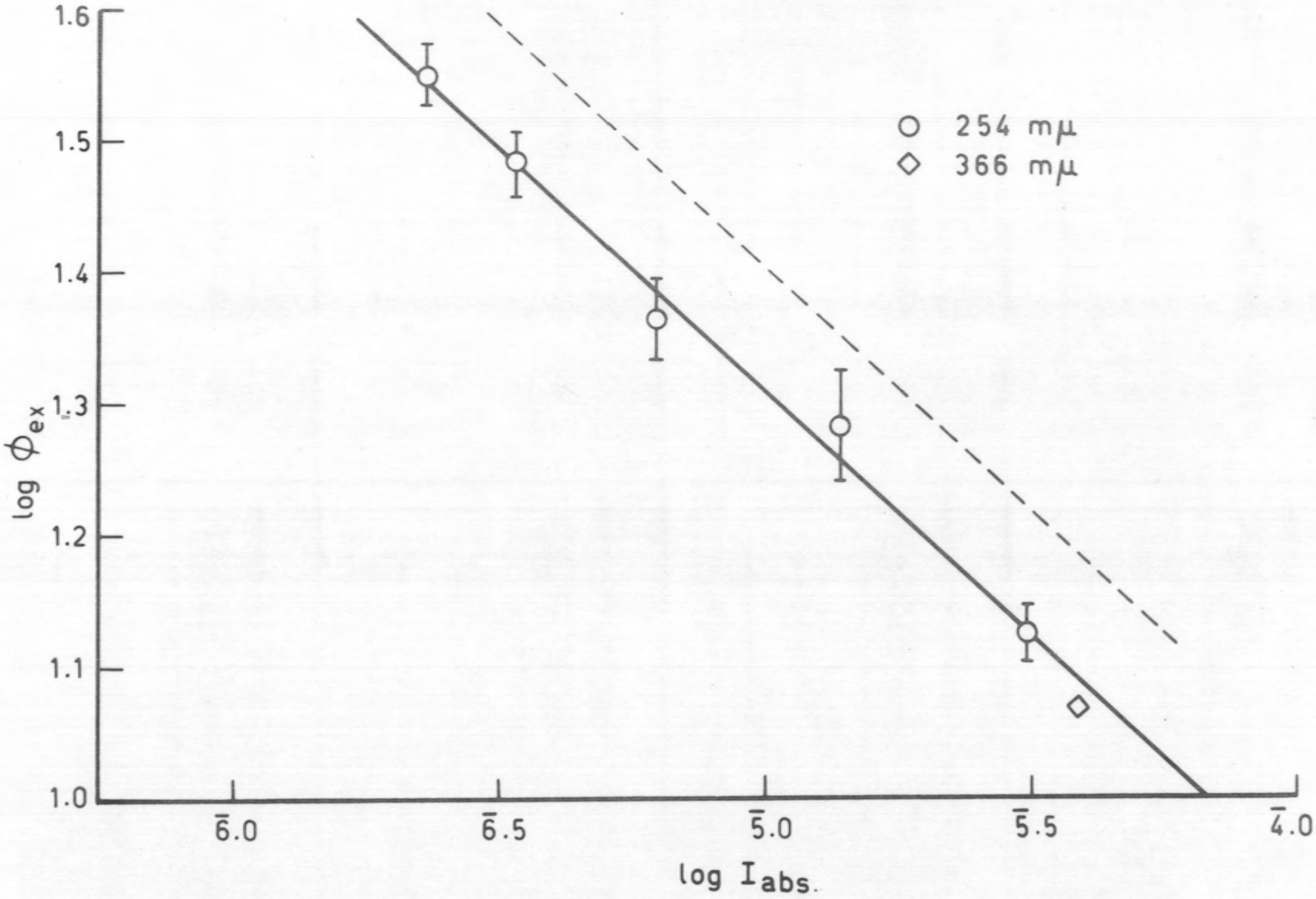


FIG. III·7 Dependence on Light Intensity.

appropriate filters to isolate the 366 mμ line. In all other respects the experimental arrangement was the same. (The apparatus was that used by Stirling.$^{(35)}$) The relevant data for the exchange reaction at this wavelength is listed below.

$[Pt(en)_2Cl_2^{2+}]$ mole l^{-1}	$t_{\frac{1}{2}}$ min	R_{ex} mole l^{-1} min^{-1}	I_o Einstein l^{-1} min^{-1}	I_{abs} (ε = 24)	ϕ_{ex}
3.04×10^{-3}	2.3 ± .2	4.55×10^{-4}	2.54×10^{-4}	3.92×10^{-5}	11.6

If this quantum yield is corrected to $Pt(en)_2Cl_2^{2+}$ concentration of 2.70×10^{-3} mole l^{-1} and plotted on Fig. III.7, the quantum yield represented by a square is obtained, which is within experimental error of the graph at 254 mμ. However, if the correction factor for non-uniform absorption is applied to the results at 254 mμ, the upper dotted line is obtained. (No correction at 366 mμ is necessary.) The quantum yield at 366 mμ may thus be lower by approximately 30%, which is still within experimental error.

F. Net Photolytic Reaction

As reported previously, irreversible changes in the rates of complexed to free chloride are observed after long periods of irradiation. The solutions exhibit a half-time for exchange of less than 10 minutes, so the free chloride may be considered to be in equilibrium with the complexed chloride at times greater than one hour. The first sample in the photolysis runs was taken in all cases at times greater than six half-times for exchange.

The method of calculation of the quantum yields ϕ_{ph} was as follows: If the $Pt(en)_2Cl_2^{2+}$ concentration is a before irradiation and x at time t; and the free chloride concentration is b at time t = 0, then at

time	$[Pt(en)_2Cl_2^{2+}]$	$[Cl^-]$	θ
0	a	b	$2a/2a + b$
t	x	$2(a-x)+b$	$2x/2a + b$

where θ is the ratio of complexed chloride to free chloride, which is assumed to be equal to the ratio determined experimentally. From the experimental values of θ, a-x, the change in $[Pt(en)_2Cl_2^{2+}]$, may be calculated, assuming that the product of photolysis does not contain bound chloride ion (i.e. Cl^- not precipitated as AgCl). This change in complex concentration was plotted against time. (Example, Fig. III.8) From the slope of the plots obtained, the rate of change of $[Pt(en)_2Cl_2^{2+}]$ may be calculated, and consequently, the quantum yield for photolysis. (The non-zero intercept in the graphs may be attributed to experimental error in separation of the complexed and free chloride, in concentrations, and in the radio-assay.) The results are listed in Table III.8.

From the results it may be concluded that within the fairly large errors, the quantum yield is independent of

1. Light intensity (Range $6 \times 10^{-6} - 1.5 \times 10^{-4}$ Einstein l^{-1} min^{-1}).
2. Chloride concentration (0 to 2×10^{-3} mole l^{-1}).
3. Wavelength (254 mμ and 366 mμ).

Table III.8

	$[Cl^-]$ mole l^{-1} x 10^3	$[Pt(en)_2Cl_2{}^{2+}]$ mole l^{-1} x 10^{+3}	Rate mole l^{-1} min^{-1} x 10	I_{abs} Einstein $l^{-1}min^{-1}$	ϕ_{ph}
At	254 mμ				
4	2.0	5.04	$1.30 \pm 1 \times 10^{-7}$	6.30×10^{-6}	$.0206 \pm .002$
3	2.0	5.30	$3.6 \pm .3 \times 10^{-6}$	1.45×10^{-4}	$.025 \pm .004$
2	<.1	35	$3.2 \pm .5 \times 10^{-6}$	1.37×10^{-4}	$.023 \pm .01$
x	<.1	16	$2.9 \pm .5 \times 10^{-6}$	1.3×10^{-4}	$.023 \pm .01$
At	366 mμ				
	2.0	3.04	$9.8 \pm .3 \times 10^{-7}$	3.9×10^{-5}	$.027 \pm .05$

25°C; $[NaClO_4] = .211$ mole l^{-1}

Notes: 1. The solutions were bubbled with N_2 as in the exchange runs.

2. The irradiations were taken to a maximum of 30% release of bound chloride.

The absorption of the products of reduction is small up to this stage.

Qualitative observations on the photolysis products.

Reducing products are formed by the photolysis, since acid $KMnO_4$ is reduced rapidly by the photolysed solution, but not by the non-irradiated solution. Attempts to determine the concentration of reducing species by titration with acid $KMnO_4$ failed, as reproducibility could not be obtained between samples. However, in all cases a sufficient concentration of reductant was observed to account for the release of the complexed chloride by reduction of Pt(IV) to Pt(II).

The ultraviolet spectrum of a photolysed solution showed increased absorption in the 350 to 400 mμ region, but no new peaks were observed. The presence of aldehydes was sought by a spot test with Schiff's reagent. (Freshly prepared, rosanaline hydrochloride in water bubbled with SO_2.) A reactant solution irradiated for 20 hours, the last four without N_2 bubbling, gave a positive Schiff's test (magenta colour). The same solution, after bubbling for an hour with N_2, gave no response to the Schiff's test. Negative responses to the test from the unirradiated solution and separately, a solution of $Pt(en)_2^{2+}$, were also observed. It was concluded that a volatile aldehyde was formed by irradiation. However, it is difficult to prove that the aldehyde is a direct product of photolysis of the reactant, rather than a product of secondary photolysis of the products of the primary photolysis.

No H_2O_2 was detected with titanium sulphate after 20 hours irradiation.

These observations are consistent with the oxidation of ethylenediamine by electron transfer reaction from ethylenediamine to Pt(IV). A similar example is the photoreduction of $Co(en)_3^{3+}$ in acid solution. Moeller and Klein(26) reported the formation of Co(II), NH_3, en, and HCHO, following irradiation at 254 mμ.

An alternative explanation is the photodecomposition of Pt(II), which probably occurs by analogy to the decomposition of $Pt(II)(gly)_2$, reported by Balzani et al(25) (gly = glycine). These authors reported a black precipitate soluble in HCl on long irradiation at 254 mμ. A black precipitate was also observed on long irradiation (> 40 hours) of $Pt(en)_2Cl_2^{2+}$.

It was observed that solid $Pt(en)_2Cl_2^{2+}$ salts change colour under the influence of visible light to a bright orange. Qualitatively this could be explained by the formation of Pt(II) by photolysis; the colour arising from a Pt(II) - Pt(IV) complex.

G. Effect of Additives on the Exchange

Small amounts of several compounds have been added to the reaction mixture and the effect on the rate of reaction observed. The results are summarized in Table III.9. The tests were performed under the following reaction conditions:

$$[Pt(en)_2Cl_2^{2+}] = 2.5 \times 10^{-3} \text{ mole } l^{-1}$$
$$[HCl] = 2.0 \times 10^{-3} \text{ mole } l^{-1}$$
$$[NaClO_4] = 2.11 \times 10^{-1} \quad \text{"}$$
$$I_{abs} = 6.30 \times 10^{-6} \text{ Einstein } l^{-1} \text{ min}^{-1}$$
$$\text{Temp.} = 25.0^{\circ}\text{C.}$$

Table III.9

Additive	Concentration	Effect
Br_2	$< 5 \times 10^{-5}$ mole l^{-1}	Stops reaction
H_2O_2	$< 4 \times 10^{-4}$ "	No effect
Cl_2	$< 5 \times 10^{-4}$ "	Stops reaction

H. Rotating Sector Measurements

One run was performed with a 90° sector operating in the unfocussed light beam. Only a small effect on the rate of exchange was observed. As in the thallium study, accurate quantitative estimation of the termination rate constant (s) is not possible, but approximate calculations suggest that the termination rate is close to diffusion controlled.

SECTION III

CHAPTER 4: DISCUSSION

A. Nature of Reactant Solutions

As in the thallium study, it is necessary to begin the discussion with a summary of the nature of species in the reactant mixtures. As mentioned in the results, the reactant complex has the empirical formula $[Pt(en)_2Cl_2](ClO_4)_2$, and is probably the <u>trans</u> complex. Complexes of this type dissociate into ions in solution, in this case into $Pt(en)_2Cl_2^{2+}$ and ClO_4^- ions. This is supported by the fact that the U.V. spectra of $[Pt(en)_2Cl_2]Cl_2$ and the perchlorate salt are identical.

As discussed in the introduction, <u>trans</u> $Pt(en)_2Cl_2^{2+}$ in acid does not hydrolyse in days at high temperatures, so that at lower temperatures undetectable amounts of aquo or hydroxy species will be present.

Pōe(32) reported the appearance of a new absorption band at 242 mμ in solutions of high chloride concentration. This new band was attributed to association of chloride ion with the $Pt(en)_2Cl_2^{2+}$ ion, in the second coordination sphere. From the linear increase in intensity of the band with increasing chloride concentration up to .5 mole l^{-1}, they determined the association constant k_a,

$$k_a = \frac{[Pt(en)_2Cl_2^{2+}.Cl^-]}{[Pt(en)_2Cl_2^{2+}][Cl^-]}$$

to be less than .1 l $mole^{-1}$. The maximum extinction coefficient for the ion pair was reported to be greater than 8000 cm^{-1} 1 $mole^{-1}$. Thus in the reactant solutions in this study, the maximum concentration of ion pair is 10^{-5} mole l^{-1}, less than 1% of the non-ion paired complex concentration. (In a solution 5×10^{-3}M in chloride, the ion pair concentration is less than 10^{-6}M.) Also light absorption by the ion pair is considerably less than 1% of the total absorption. Hence, the concentration of ion pair is considered to be insignificant.

Association of perchlorate ions with the complex can confidently be expected to be small. The effect of perchlorate ion ($NaClO_4$ and $HClO_4$) on the charge-transfer peak at 207 mμ was found to be negligible up to perchlorate concentration of 1.5 mole l^{-1}.

B. Mechanism of the Exchange Reaction: Qualitative Considerations

The photochemically induced chloride exchange between trans-$Pt(en)_2Cl_2^{2+}$ ion and free Cl^- ion has been shown to be a chain reaction. The most important species in a chain reaction is the chain carrier, so the next section is devoted to a discussion of the possible chain carriers in this system.

A few general properties of the chain carrier may be defined without reference to any particular mechanism.

(a) The chain carrier must exchange chloride ion with both reactants, that is $Pt(en)_2Cl_2^{2+}$ and Cl^- ion, without being destroyed in the reaction. Therefore it must contain chlorine in some form.

(b) The chain carrier must be produced through absorption of light by the Pt(IV) complex, and must be produced with constant quantum yield independent of the wavelength of the band of irradiation.

(c) The chain carrier must be destroyed to a large extent in a quadratic termination step. The dependence of the quantum yield on light intensity, necessitates a termination mechanism involving mainly quadratic, but with some linear termination.

(d) The effect of impurities may be assumed to be due to the reaction of chain carrier with the impurity.

The chain carrier involved in this reaction and the analogous chain reactions of the hexahalides, has been variously postulated as one of four species. An examination of the results in this thesis and those reported elsewhere, enables a distinction to be made between these possible chain carriers. In this discussion it has been assumed that all the reported chain reactions involve a similar chain carrier. This is done on the basis that it is improbable that these reactions will occur by greatly different mechanisms. The four possible chain carriers that have been considered are discussed below.

1. Adamson$^{(17)}$ suggested that a Pt(II) species in an excited state may act as a chain carrier in the $\mathrm{PtBr_6}^{2-}$ - Br^- exchange reaction. (Where the reaction is not photochemically induced, it will be referred to as a thermal reaction.) The reaction scheme proposed was

$$\mathrm{PtBr_6}^{2-} + h\nu \rightleftharpoons \overset{\neq}{\mathrm{P}}\mathrm{tBr_4}^{2-} + \mathrm{Br_2} \qquad (1)$$

$$\overset{\neq}{\mathrm{P}}\mathrm{tBr}^{2-} + \overset{*}{\mathrm{B}}\mathrm{r}^- \rightleftharpoons \overset{\neq}{\mathrm{P}}\mathrm{t}\overset{*}{\mathrm{B}}\mathrm{r_4}^{2-} + \mathrm{Br}^- \qquad (2)$$

$$\overset{\neq}{\mathrm{P}}\mathrm{t}\overset{*}{\mathrm{B}}\mathrm{r_4}^{2-} + \mathrm{PtBr_6}^{2-} \rightleftharpoons \overset{\neq}{\mathrm{P}}\mathrm{tBr_4}^{2-} + \mathrm{Pt}\overset{*}{\mathrm{B}}\mathrm{r_6}^{2-} \qquad (3)$$

It is considered that an excited Pt(II) as a chain carrier is unlikely on the following grounds.

(a) The initiation reaction (1) is unique, no similar example of this type has been reported.

(b) One of the main points which led Adamson to postulate Pt(II), was the inhibitive effect of hydroquinone on the hydrolysis reaction. Balzani et al suggest that this conclusion was incorrect as the hydroquinone interacts with the Pt(IV) ground state.

(c) Exchange reactions of the type of reaction (3), are suggested to be electron transfer reactions, so that the photochemical excitation of the Pt(II) species must be transferred during the electron transfer. Again, no reports of similar energy transfer have been noted in the literature.

2. Pt(IV) excited state. Balzani et al suggested a Pt(IV) d-d excited state as an intermediate in the hydrolysis of $PtBr_6^{2-}$. If this excited state were the chain carrier in the exchange reactions, the following reaction sequence might be imagined.

$$PtBr_6^{2-} + h\nu \rightleftharpoons \overset{\neq}{PtBr}_6^{2-} \qquad (1)$$

$$\overset{\neq}{PtBr}_6^{2-} + \overset{*}{Br}^{-} \rightleftharpoons \overset{\neq}{Pt}\overset{*}{Br}_6 + Br^{-} \qquad (2)$$

$$\overset{\neq}{Pt}\overset{*}{Br}_6^{2-} + PtBr_6^{2-} \rightleftharpoons Pt\overset{*}{Br}_6^{2-} + \overset{\neq}{PtBr}_6^{2-} \qquad (3)$$

$$\overset{\neq}{PtBr}_6^{2-} + \overset{\neq}{PtBr}_6^{2-} \rightarrow PtBr_6^{2-} + PtBr_6^{2-} \qquad (4)$$

Again this mechanism may be criticised on several grounds.

(a) The termination step (4), necessary because of the light intensity dependence, is an improbable reaction. If the excited state is a triplet state, the two triplet states are reacting to produce at least one ion in the ground state. However, triplet-triplet annihilation is known in organic systems, so it is not inconceivable for the platinum complexes.

(b) As in the previous case, the exchange reaction (3) involves the transfer of the triplet energy of the $\overset{\neq}{\mathrm{PtBr}}_6{}^{2-}$ to another $\mathrm{PtBr}_6{}^{2-}$. No similar examples have been reported for inorganic complexes. (Most closely related example is energy transfer from ligand to metal in lathanides.)

(c) The effect of impurities on the reaction is not consistent with a Pt(IV) chain carrier. Oxidants such as Br_2, Cl_2, and organic impurities are not likely to rapidly affect Pt(IV), even in an excited state.

3. Chlorine atom or (bromine atom). The mechanism here would be

$$\mathrm{Pt(en)_2Cl_2}^{2+} + h\nu \rightleftharpoons \mathrm{Pt(en)_2Cl}^{2+} + \mathrm{Cl} \qquad (1)$$

$$\mathrm{Cl} + \overset{*}{\mathrm{Cl}}{}^- \rightleftharpoons \overset{*}{\mathrm{Cl}} + \mathrm{Cl}^- \qquad (2)$$

$$\overset{*}{\mathrm{Cl}} + \mathrm{Pt(en)_2Cl_2}^{2+} \rightleftharpoons \mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}_2^{2+} + \mathrm{Cl} \qquad (3)$$

(a) This mechanism is more reasonable than the previous two, but again reactions similar to reaction (3) have not been reported in inorganic complexes.

(b) Adamson added allyl alcohol to the $\mathrm{PtBr}_6{}^{2-}$ system, and deduced from its lack of effect that Br atoms were not involved as a chain carrier in the reaction. Again in the flash photolysis of $PtBr_6^{2-}$ Adamson found no evidence for Br atoms. He gives no indication of the upper limits of his detection method, so that it is possible that he failed to detect small concentrations.

(c) The effect of Cl_2 in stopping the reaction is not consistent with a chlorine atom mechanism, as the reaction of a chlorine atom with Cl_2 would not destroy the chlorine atom chain carrier.

Dreyer reported that the photochemical substitution of $PtCl_6^{2-}$ by Br^- was a chain reaction. This requires a mechanism similar to

$$PtCl_6^{2-} + h\nu \rightarrow PtCl_5^{2-} + Cl \qquad (1)$$

$$Cl + Br^- \rightarrow Br + Cl^- \qquad (2)$$

$$Br + PtCl_6^{2-} \rightarrow PtCl_5Br^{2-} + Cl \qquad (3)$$

Reaction (3) may be energetically unfavourable, and hence would probably be too slow to act as a chain propagation reaction. (Rate constant greater than 10^3 l mole^{-1} sec^{-1} required.)

4. Pt(III) chain carrier. A mechanism involving Pt(III) would be

$$Pt(en)_2Cl_2^{2+} + h\nu \rightleftarrows Pt(en)_2Cl^{2+} + Cl \qquad (1)$$

$$Pt(en)_2Cl^{2+} + \overset{*}{Cl}^- \rightleftarrows Pt(en)_2\overset{*}{Cl}^{2+} + Cl^- \qquad (2)$$

$$Pt(en)_2\overset{*}{Cl}^{2+} + Pt(en)_2Cl_2^{2+} \rightleftarrows Pt(en)_2Cl^{2+} + Pt(en)_2\overset{*}{Cl}_2^{2+} \qquad (3)$$

I consider this to be the most probable chain carrier in the exchange reactions. Reaction (3) is probably an electron transfer electron, possibly involving simultaneous transfer of a chlorine atom. Hence, both it and reaction (2), a simple substitution reaction, are related to common reactions.

The criticism above that no Br atoms were detected in the flash photolysis of $PtBr_6^{2-}$, throws some doubt on reaction (1). An alternative to the formation of Cl or Br atoms is electron transfer from the solvent to the platinum complex. A further alternative in the diamine complexes is electron transfer from the diammine to the platinum. This possibility will be discussed in more detail in the next section.

In all other aspects, Pt(III) as a chain carrier accords qualitatively with the experimental data.

(i) Oxidants would be expected to react readily with the unstable oxidation state Pt(III), thus explaining the inhibitive effect of these compounds.

(ii) The termination reaction (-1) (the back reaction of (1)), has the correct form to yield a quadratic dependence on light intensity.

(iii) The effect of increase in ionic strength is consistent with (1), a rate controlling step involving two like-charged ions.(29)

$$2.303 \log \left\{\frac{K_{\mu}}{K_{\partial}}\right\} = z_1 \cdot z_2 \quad \mu^{\frac{1}{2}}$$

(iv) The rotating sector measurements, indicating a very rapid termination step, are consistent with a termination step involving Pt(III) and the other product of initiation (Cl for example).

Reactions of this type between two reactive species would be expected to be fast.

Two other intermediates which were considered are:

1. Platinum(II). The known rate of catalysis of the exchange reactions by Pt(II) is too slow for Pt(II) to be considered as a chain carrier. From reference (9b) for the trans $Pt(en)_2Cl_2^{2+}$-Cl^- exchange, the rate of exchange $R_{ex} = 3 \times 10^2\ [Cl^-][Pt(IV)][Pt(II)]$ mole l^{-1} min^{-1}. Taking typical values for this study of $[Cl^-] = 2 \times 10^{-3}$, $[Pt(IV)] = 3 \times 10^{-3}$ mole l^{-1},

$$R_{ex} = 1.8 \times 10^{-3}\ [Pt(II)] \text{ mole } l^{-1} \text{ min}^{-1}.$$

As the observed rate of exchange in this study = 1.8×10^{-4} mole l^{-1} min^{-1}, then $[Pt(II)]$ would have to be 10^{-1} mole l^{-1} for reaction to occur by this mechanism. This is obviously impossible in a total platinum concentration of 3×10^{-3} mole l^{-1}.

2. Dreyer suggested that in the hexachloride reaction, photocatalysis occurred through absorption by the platinum(II) - platinum(IV) complex postulated as an intermediate in the thermal exchange reaction. However, it is difficult to see how this mechanism can give quantum yields greater than one, as one quantum only catalyses one reaction.

C. Mechanism of Net Photolysis

The photolysis reaction was followed by the increase in the ratio of free chloride to complexed chloride, so the Pt product of the reaction must contain less bound chloride than the Pt(IV) reactant. (Possibly the separation procedure will remove chloride from a more labile complex.) The quantum yield for the release of two chloride ions is .022 ±.02. It is independent of light intensity and chloride concentration at 254 mμ. These observations suggest a simple unimolecular reaction of an excited state. Three reactions would account for the release of complexed chloride.

(1) Hydrolysis of an excited state. For example,

$$\overset{\neq}{\mathrm{Pt}}(\mathrm{en})_2\mathrm{Cl}_2{}^{2+} + \mathrm{H_2O} \rightarrow \mathrm{Pt}(\mathrm{en})_2\mathrm{ClH_2O}^{3+} + \mathrm{Cl}^-$$

where $\neq$ represents an excited species (probably d-d excited). If the reaction were an equilibrium, increasing the concentration of chloride ion would decrease the quantum yield.

(2) Hydrolysis of a Pt(III) intermediate might also lead to the release of chloride.

(3) Reduction of Pt(IV) to Pt(II). For example,

$$\overset{\neq}{\mathrm{Pt}}(\mathrm{en})_2\mathrm{Cl}_2{}^{2+} \rightarrow \mathrm{Pt}(\mathrm{en})_2{}^{2+} + \mathrm{Cl}_2$$

The observation that oxidizable products are formed is consistent with a mechanism of this type, but apparently inconsistent with mechanism (1). The variable results on the amounts of oxidizable product suggest that the products are perhaps volatile. The observation that a volatile aldehyde is a product of the reaction confirms this, and suggests that ethylenediammine is oxidized in the reaction. (However, some non-volatile reductant was also observed, suggesting Pt(II).)

Also, the unusual products of base hydrolysis of trans $Pt(en)_2Cl_2^{2+}$ lends support to the mechanism involving ethylenediamine oxidation. Basolo et al reported that the base hydrolysis of this complex is accompanied by reduction to Pt(II), with simultaneous oxidation of the ethylenediamine ligand. (Another alternative, of simultaneous reduction of the complex and oxidation of water, is not consistent with the observation that photochemical decomposition occurs in the dry solid perchlorate.)

Thus, a mechanism involving hydrolysis of the complex, leading to unstable hydrolysed products which reduce to Pt(II) with oxidation of ethylenediamine is considered most likely. In contrast to the $Pt(en)_2Cl_2^{2+}$ complex, both the photochemical and thermal hydrolysis reactions of $PtBr_6^{2-}$ occur without reduction. (This further suggests a connection between the photochemical and thermal reactions.) Mechanism (2), involving hydrolysis of Pt(III) cannot be ruled out, and it has the added advantage of possibly explaining the linear termination implied in the dependence of quantum yield on $I_{abs}^{-.37}$.

D. Mechanism of the Exchange Reaction: Quantitative Aspects

It is proposed to compare some possible mechanisms, with the quantitative results on the dependence of the quantum yield for exchange, on the experimental variables. The most obvious mechanism to try, is the mechanism analogous to that initially proposed by Adamson for the $PtBr_6^{2-}$ - Br^- exchange.

$$\mathrm{Pt(en)_2Cl_2}^{2+} + h\nu \xrightarrow{\phi_1} \mathrm{Pt(en)_2Cl}^{2+} + \mathrm{Cl}$$

$$\mathrm{Pt(en)_2Cl}^{2+} + \overset{*}{\mathrm{Cl}}{}^{-} \overset{K_1}{\rightleftarrows} \mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}^{2+} + \mathrm{Cl}^{-} \qquad (1)$$

$$\mathrm{Pt(en)_2Cl_2}^{2+} + \mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}^{2+} \overset{K_2}{\rightleftarrows} \mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}_2^{2+} + \mathrm{Pt(en)_2Cl}^{2+} \qquad (2)$$

$$\mathrm{Pt(en)_2Cl}^{2+} + \mathrm{Cl} \xrightarrow{K_t} \mathrm{Pt(en)_2Cl}^{2+} \qquad (3)$$

Treatment analogous to the method in the appendix of Section II, yields the expression: (for $\phi_{ex} \gg \phi_1$)

$$\phi_{ex} = \frac{K_2[\mathrm{Pt(en)_2Cl_2}^{2+}]K_1[\mathrm{Cl}^-]}{K_2[\mathrm{Pt(en)_2Cl_2}^{2+}] + K_1[\mathrm{Cl}^-]} \left\{\frac{I_{abs}\phi_1}{K_t}\right\}^{\frac{1}{2}}$$

If $K_1[\mathrm{Cl}^-] \gg K_2[\mathrm{Pt(en)_2Cl_2}^{2+}]$, this approximates to

$$\phi_{ex} = K_2[\mathrm{Pt(en)_2Cl_2}^{2+}] \left\{\frac{I_{abs}\phi_1}{K_t}\right\}^{\frac{1}{2}}$$

The observed linear dependence of ϕ_{ex} on $[\mathrm{Pt(en)_2Cl_2}^{2+}]$ is in accord with the expression, but it does not fit the chloride ion concentration dependence or the I_{abs} dependence.

Possible modifications that may show better agreement with the experimental data are now considered.

(i) The initiation reaction must involve the absorption of light by the reactant complex $\mathrm{Pt(en)_2Cl_2}^{2+}$, to produce a Pt(III) chain carrier. Quadratic termination also necessitates the simultaneous production of a geminate species which may back react with the Pt(III) ion. Considering these points, alternatives to the initiation reaction above might be

$$\mathrm{Pt(en)_2Cl_2}^{2+} + h\nu \rightarrow \mathrm{Pt(en)_2Cl_2}^{+} + (\mathrm{H_2O})^{+}$$

$$\mathrm{Pt(en)_2Cl_2}^{2+} + h\nu \rightarrow \mathrm{Pt(en)\ Cl_2}^{+} + (\mathrm{en}^{+})$$

No significant change in the expression for $\emptyset_{ex}$ would be found with these initiation reactions, if the termination reaction is the reverse of initiation.

(ii) A probable alternative to the propagation reaction (1) above is

$$\mathrm{Pt(en)_2Cl}^{2+} + \overset{*}{\mathrm{Cl}}{}^{-} \underset{K_1'}{\overset{K_1}{\rightleftharpoons}} \mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}_2^{+} \qquad (1a)$$

The Pt(III) intermediate might be hexa-coordinated, so that upon the loss of a chloro-ligand, an aquo species is formed. This may exchange chloride through a hydrolysis reaction (e.g. (1a)). With this reaction and the second propagation reaction

$$\mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}_2^{+} + \mathrm{Pt(en)_2Cl_2}^{2+} \overset{K_2}{\rightleftharpoons} \mathrm{Pt(en)_2Cl_2}^{+} + \mathrm{Pt(en)_2}\overset{*}{\mathrm{Cl}}{}_2^{2+} \qquad (2a)$$

and the termination reaction (3), $\emptyset_{ex}$ can be shown to be

$$\emptyset_{ex} = K_2[\mathrm{Pt(en)_2Cl_2}^{2+}] \left\{\frac{I_{abs}\emptyset_1}{K_t}\right\}^{\frac{1}{2}} \left\{\frac{K_1[\mathrm{Cl}^-].K_1[\mathrm{Cl}^-]}{K_1'(K_1[\mathrm{Cl}^-] + K_1')}\right\}^{\frac{1}{2}}$$

In agreement with the experimental results, this expression shows a decrease in $\emptyset_{ex}$ with increase in $[\mathrm{Cl}^-]$, but the quantitative correlation is still not satisfactory. Other variations were tried, but did not yield satisfactory expressions. This may be due to complications arising from point (iii) below.

(iii) A further termination reaction is necessary as the intensity exponent of −.37 in the equation

$$\phi_{ex} \propto I_{abs}^{-.37}$$

implies competing linear and quadratic termination. This situation is difficult to analyse as the solution of a cubic equation is involved. Thus, complete analysis of the results has not been possible, which is perhaps not surprising for a complicated system of this type; possibly involving more than one chain carrier and several termination reactions.

E. Wavelength Dependence

The independence of the quantum yields of both exchange and photolysis on the wavelength of irradiation warrants further discussion at this stage.

At 254 mμ the charge-transfer band (max 207 mμ) and the d-d band ($^1T_{2g} \leftarrow {}^1A_{1g}$) (max 267 mμ) overlap strongly and approximately equal absorption by both bands occurs.

At 366 mμ however, more than 99% of the absorption may be attributed to d-d absorption. (Mainly absorption in the $^1T_{1g} \leftarrow {}^1A_{1g}$ (max 331 mμ).)

The similarity of the quantum yields for both exchange and photolysis at these two wavelengths prompts two postulates about the intermediates involved.

(1) The exchange and photolysis reactions have a common precursor.

(2) The precursor is formed with the same quantum yield independently of the band of irradiation.

In view of these observations, the following mechanism is proposed.

(a) Irrespective of the band of irradiation a d-d excited state is formed. This requires, for light of wavelength 254 mμ, efficient conversion from a charge-transfer state to a d-d excited state, which would be unique to Pt(IV). However, Pt(IV) is the only reported example in which hydrolysis products are formed on irradiation in a charge-transfer band. Balzani et al(19) made this suggestion for the hexabromide hydrolysis reaction. Perhaps the ease of this conversion is due to large intermixing of d-d and charge-transfer states in these complexes.

(b) Charge-transfer in this state leading to formation of the Pt(III) chain carrier. (In photochemical terminology - conversion to a charge-transfer state from the d-d state.)

This mechanism is preferred to the alternative possibility of formation of a charge-transfer excited state at all wavelengths, by analogy to the hexabromide case where hydrolysis occurs with high quantum yield.

F. Further Study

Several lines of study suggest themselves as helpful in confirming the ideas gleaned from the present study.

1. Irradiation of frozen solutions in an attempt to trap excited

states. Pt(III) might be detected by electron spin resonance spectroscopy. Excited Pt(IV) species might be detected by the observation of fluorescence or phosphorescence. In fact, a study of these phenomena could indicate the ease of crossing from one excited state to another.

2. A study of analogous systems such as $Pt(en)_2Br_2^{2+}$, and $Pt(NH_3)_4Cl_2^{2+}$ might help to resolve the reaction paths involved. For the bromide complex the rate of substitution of the complex by chloride ion, would distinguish between a Pt(III) mechanism and a Br atom mechanism, as the propagation reaction

$$Br + Cl^- \rightarrow Cl + Br^-$$

necessary in the Br atom mechanism does not occur.

3. A study of $Pt(NH_3)_5Cl^{3+}$ might show that this compound does not undergo a chain photoexchange reaction. This could be interpreted as due to the absence of a Pt(III) chain carrier containing chloride ion, either due to the loss of chloride in the formation step or by later hydrolysis. This would help to establish that Pt(III) is the chain carrier. The mechanism may also be simpler as the intermediate can only have one exchangeable chloride ion.

4. A complete wavelength study might also yield useful results. Irradiation in the region of the weak band at 380 mμ might produce a triplet state, yielding different products or different quantum yields. The difficulty lies in separating the influence of the overlapping bands.

5. It would be interesting to attempt to induce water exchange in an aquo complex such as $Pt(en)_2(H_2O)_2^{4+}$.

6. A more extensive study of the quantum yield as a function of wavelength, would be useful to prove that the similarity of quantum yields at 254 mμ and 366 mμ is not just coincidence. In particular, a study of the quantum yield at a wavelength where charge-transfer absorption predominates would be most instructive.

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