Electron transfer quenching studies of luminescent complex's of Ru (iii) with mixed ligands

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Abstract

In the present paper the reaction of Ru (III) perchlorates with some polytertiary phosphines and arsines has been investigated. The study of quenching of excited states of Ru $(LL'-)_3^{3+}$ complexes and subsequent reaction occuring with potential reductant - amines, aromatic ether, nitro compounds, p-hydroquinone and water have been observed. Both laser flash and convensional spectroscopic techniques have been used to monitor the quencher products. The photo reduction of complex (I) with triethylamine can be shown to consists of two component, a primary photoprocess and a subsequent dark reaction while for complex (II) only the first process is observed. The reduced complex Ru $(LL')^{+2}_3$ produced in the reaction are relatively stable and dry deacrated solution but can be observed rapidly with both oxygen and water. The reaction of reduced (I) with water is a relatively produce Ru (LL') $^{+}_3H^{+2}$ which yields hydrogen and to starting. Complex (I) with colloidal platinum excited states of (I) are also quenched by aromatic ether and hydroquionones in process giving transients having spectra similar to that the reduced (I). The reaction between excited (I) with water

(K = 1x $10^7M^{-1}S^{-1}$) gives a short lifed transient (ϑ= 245ns) more lightly an adduct or ligand protonated species more lightly and adduct or ligand protonated species.

Keywords: LL = LL' - Ligand, phen = Phenanthrene, bpy = Bipyridyl, Q = Quencher, ph = Phosphine dpa = 2- diphenyl phosphinoethylamine, daa = 2- diphenylarsinoethylamine

INTRODUCTION

The poly pyridyl complexes of Ru (II) having excited states can be oxidised and reduced by a number of reagents [3-12] and well characterised due to their single electron redox product by simple electron transfer quenching. The difficient conversion excitation energy through high product formation is coupling insuing reaction was of keen interest. Various studies have been done regarding the use of the scavengers [13-18] quenchers whose redox products undergo rapid reaction with reagents [9-20] and highly reactive colloidal and heterogenous catalysts [15-19, 21-24].A number of studies were carried out regarding the photo redox behaviour of these complexes by modifying the net char on the complexes [25-27] (or by adjusting ligands substituents [9,20,28].

The primary photo process and ensuing reaction with these complexes involves only one single electron transfer process. It is evident that competitive reactions involving interaction of excited Ru(bpy)$_3^{2+}$with cobalt (III) complexes [1,21,29,30] that rapid unimolecular decomposition of the cobalt (II) complexes permits net photo conversion to occur.

The quenching of Ru (bpy) $_3^{2+}$ by inorganic ions [31,32,33-35] can undergo with the normally observed back electron process to yield the initial product Ru(bpy)$^{2+}_3$ without the use of other sacrificial reagent [31]. The mechanism of catalytic redox process in transition metal complexes provide the observation of strong solvent effect on the life times and properties of metal complexes, charge transfer and ligand field excited, states. The pronounced change in acid-base properties and the other properties have shown that reaction with water or solutions occur following excitation and in sum cases labilisation of bipyridine type of ligands [36,38].

In some of the stable monodentate complexes, renders precise structure difficult to establish in many photoreactions. The cationic complexes of Ru(II) and Ru (III) containing phosphines and arsines were studied due to their importance as catalytic species in various homogeneous reactions [40-43]. Recently the excited state quenching process and ensuing reaction with Ru(L)$^{+}_3$ (L= 4,4' - dipheny1, 2, 2'-bipyridine) and (4,4'-dipheny1, 1, 10-phenanthroline) have been studied along with laser flash and convensional spectroscopic techniques [44]

The present study deals with excited state quenching process and ensuing reactions of cationic complexes with Ru(III) containing phosphines and arsines. The use laser flash and spectroscopic techniques to obeserve the reactions of the cationic complexes having several potential reductants indicates that quenching can occur by net electron transfer reduction as well as by interactions not involving electron transfer at all.

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EXPERIMENTAL SECTION

Ru(III) chloride, ligands triphenylarsine, 1, 2 bis- (diphenylphosphino) ethane, and 1,2-bis (diphenylarsino) ethane and 1-diphenylarsino- 2- diphenylphosphino ethane were purchased from Aldrich U.S.A. bis (2-diphenylphosphino ethyl) amine (dpa) [45] bis

(2-diphenylarsino ethyl) amine (daa) [46] and the complex [RuCl$_3$ (AsPh$_3$)$_2$Me OH] [47] were prepared by standard methods.

Preparations
Ruthenium (III) Perchlorate

Ru(III) chloride (0.261 gm 1 mmol) was stirred with a stoichiometry amount of silver perchlorate (0.62 gm 3 mmol) in absolute methanol for about 3hrs. A red brown solution of Ru (III) perchlorate was obtianed. A fresh sample was prepared for each preparations and used immediately.

I. Bis (perchlorato) triphenylarsine tris (triphenylphosphine) Ruthenium (III) perchlorate methanol.

A methanolic suspension contianing [Ru Cl$_3$ (AsPh$_3$) (MeOH)] (0.425 gm. 0.5 mmol) and sodium perchlorate (0.70gm, 5 mmol) was refluxed under a nitrogen atmosphere for 1-2 hrs when the solid dissolved to give a light brown homogeneous solution. At this stage triphenylphosphine (0.524gm, 2 mmol) dissolved in methanol was added dropwise to the refluxing solution over a period of an hour. After the addition of PPh$_3$ was complete the solution turned dark brown. It was refluxed for another 6 hrs. The solution was concentrated to one fourth of its volume and water was added when floating solid was obtained. The solid was dissolved in dichloromethane and precipitated with light petroleum ether boiling point 60-80 ^{0}C as dark grey product. After several washing with diethylether, the complex was dried over P$_2$O$_5$ under vacuum,

II- Bis (2-diphenylphosphineethyl) amine perchlorato bis(triphenylarsine (III) perchlorate-methanol and (III) bis (2-diphenyl-arsinoethyl) amine perchlorato bis (triphenyl arsine) Ru (III) perchlorate-methanol.

A suspension of the green complex [Ru Cl$_3$(AsPh$_3$) (MeOH] (0.425 m, 0.5 mmol) in methanol was refluxed with 5 mmol of sodium perchlorate (0.70gm) for about 2 hrs. to give clear light brown solution. Complex II. and III. were obtained by the addition of dpa and daa (1mol) respectively to the above refluxing solution. The colour of the solution changed from light to dark brown in the case of dpa and to light orange in the case of daa. The reaction mextures were heated for 4 hrs evaporated to dryness under vacuum and the compounds extracted with dichloromethane. The brown dpa and orange daa solutions thus obtained were reduced to small volumes and the respective complexes precipitated as grey and pink products respectively.

RESULTS AND DISCUSSIONS

Photo reduction of (I.) [Ru(LL')2 (ClO4)] ClO4 and (II) /[Ru()III(AsPh3)2- L(ClO4)] -ClO4; [LL' = Ph3 As CH2 CH2 PPh2 and L=NH (CH2 CH2 PPh2)2 or NH(CH2CH2 AsPh2)2]
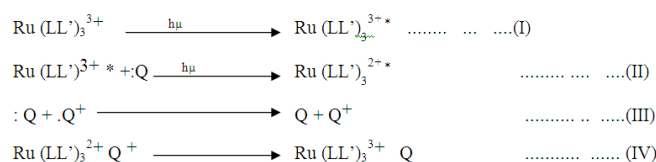
With Nitro Compounds

Several nitrobenzene derivatives as quenchers were choosen in our investigation because in some cases they have relatively high triplet energies [47]. And a series they undergo reversible one electron reductions at potentials in the range -1.5 to -0.5 V vs. SCE in acetonitrile. Rate constant for intensity quenching of the Ru (LL)$_3$$^{3+}$emission are given in Table -I together with the quenchers reduction potentials for some neutral organic compounds. All the nitro aromatics quenched the emission and the rates were found monotonically with the quencher reduction potential.

Neither the spectral evidence for ground state complexes were deducted for any of the nitro aromatics nor new emission and stable chemical products were observed in steady state and flash photolysis observations as no transients of life time more than 50 microseconds could be deducted [48]. The lack of free ion formation with nitro aromatics and amines as quenchers in an electron transfer process is not surprising since the immediate product is most probably an ion pair as shown in the quenching scheme (scheme-1).

Scheme 1.

$$Ru (LL')_3{}^{3+} \xrightarrow{h\mu} Ru (LL')_3{}^{3+\,*} \quad \dots\dots\; \dots\; \dots(I)$$

$$Ru (LL')_3{}^{3+\,*} +:Q \xrightarrow{h\mu} Ru (LL')_3{}^{2+\,*} \quad \dots\dots\;\dots\;\dots(II)$$

$$:Q + .Q^+ \longrightarrow Q + Q^+ \quad \dots\dots\;..\;\dots(III)$$

$$Ru (LL')_3{}^{2+}\, Q^+ \longrightarrow Ru (LL')_3{}^{3+}\; Q \quad \dots\dots\;\dots(IV)$$

The plot in the figure I indicates that the slope of the linear portion is (16.9 ± 1.0 V^{-1}) which is in good agreement with the anticipated value of 16.7 V^{-1}. For the points in the linear portion of figure - I extrapolation of lines with limiting slopes to this region gives K^{½} [(Ru (L-L')$^{3+}$ 3/Ru (L-L')$_3$$^{3+}$] = -0.80 ± 0.02 V. From the potential in the ground state [Ru(L-L') $^{3+}$ 3/Ru(L-L' $^{3+}$3*] couple in the same medium (+1.28v) [49] It may be observed that excitation increases the reducing power of Ru(L-L')$_3$$^{3+}$ by 1.90V. This indicate so that the entropy difference between the excited and ground state is small.

Table I. Ru (LL')$_3$$^{3+}$*Ouenching rate constat and reduction potential data for some neutral organic compounds.

	Quencher	-E$_{½}$ ^{a}	K$_q$ $^{obsd.}$ (M-1sec.$^{-1}$)$^{b-d}$
1.	p-Nitro nitrosobenzene	0.520	(8.95 ± 0.ll)x 10^9
2.	p-Dinitrobenzene	0.61	(6.15 ± 0.05)x 10^9
3.	ortho-dinitrobenzene	0.75	(2.90 ± 0.02)x 10^9
4.	p- Nitrobenzaldehyde	0.81	(1.75 ± 0.0l)x 10^9
5.	m-dinitrobenzene	0.84	(1.35 ± 0.02)x 10^9
6.	methyll-4-nitrobenzoate	0.90	(6.15 ± 0.06)x 10^8
7.	4,4-Dinitrobiphenyl	1.00	(1.1 0 ± 0.0 l)x 10^8
8.	3-Nitrobenzaldehyde	1.014	(4.60 ± 0.12)x 10^7
9.	Methyl- 3-nitrobenzoate	1.04	(1.35 ± 0.04)x 10^7
10.	4' -Chloronitrobenzene	1.06	(7.81 ± 0.12)x 10^6

^{a}Acetonitrile containing 0.lm tetra-n-propyl ammoniumperchlorate,
^{b} Acetonitrile containing 0.lM tetraethyl ammoniumperchlorate, (TEAP).
^{C}[Ru(LL')$_3$$^{3+}$] 10^{-5}M
^{d}K$_q$was calculated using ϑ_o = (0.850 ± 0.010) μsec. measured in 0.1M TEAP single proton counting technique.
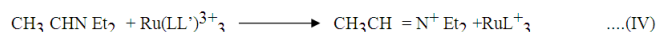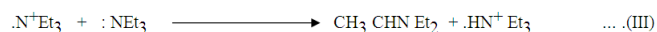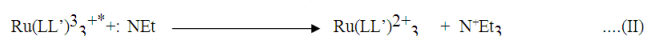
With Amines

These complexes have reduction potential for both the +4/+3 (1.62V vs. SCE) and 3$^+$/2$^+$ (0.64 V vs.SCE) in acetonitrile cathodically shifted compared to those for Ru(L-L')$^{3+}$ 3 [20,52]. The shift is more pronounced to make its excited state potentially subject
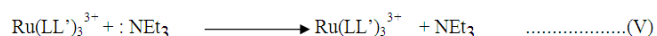
to reactive quenching by a number of reagents. Red shifts in the absorption and emission spectra of the complexes indicate a slightly lower excited state energy for first* trannsient (E4+/3+* = - 0.26 V and E 3+*/2+ = 1.24V) [3,11,12].

Irridation of I. in the presence of amines such as triethylamine in dry deacrated a protic solvents leads to luminescence quenching (Kq=1.2 x 10^8 M^{-1} S^{-1}) and the formation of permanent photo product whose spectrum is shown in figure-2. This behaviour is similar to that observed / irriadiation of II. under similar conditions [52] and from ESR and electro chemical evidence it can be concluded that the spectrum is that of the one electron reduction product of I., Ru(LL')$^{2+}$3 [20].

Photo reduction of I.and II. by amines such as triethylamine to the mechanism given by equation [1-4][20] for II. the highest quantam yield for metal complex reduction obtained, is 0.32 in dry acetonitrile with I. We obtained ØRed = 0.45 with triethylamine and ØRed = 0.49 for di-iso-propyl amine.

$$Ru(LL')_3^{3+} \xrightarrow{\quad h\mu \quad} Ru(LL')_3^{3+} \qquad \text{.... (I)}$$

$$Ru(LL')_3^{+*} + : NEt \xrightarrow{\quad\quad} Ru(LL')^{2+}_3 + N^-Et_3 \qquad \text{....(II)}$$

$$.N^+Et_3 + : NEt_3 \xrightarrow{\quad\quad} CH_3 CHN Et_2 + .HN^+Et_3 \qquad \text{... .(III)}$$

$$CH_3 CHN Et_2 + Ru(LL')^{3+}_3 \xrightarrow{\quad\quad} CH_3CH = N^+Et_2 + RuL^+_3 \qquad \text{....(IV)}$$

This mechanism predicts a limiting quantum yield of II. For photo reductants. However, carlier [53,54] it has been suggested that net electron transfer quenching efficiencies are after lower than unity such that some quenching can simply produced a non readitive decay.

$$Ru(LL')_3^{3+} + : NEt_3 \xrightarrow{\quad\quad} Ru(LL')_3^{3+} + NEt_3 \qquad \text{.............(V)}$$

Hence, we have studied the time dependance of the production of Ru(LL')$^{3+}$3 following laser flash excited of I. and II. in the presence of triethylamine in dry degassed acetonitrile. Figure-3 shows the build up of reduced I. at 595 nm as for both I. and II. It was observed that there is no decay of the long wave length.

Irridation (I) in the presence of amines such as triethylamine in dry deacrated aprotic solvents leads to luminescence quenching absorbing product following the laser flash. This indicates that there is no back reaction of the "free ions" formed in equation (II) for either of the complexes. Though product being stable there appears to be no further detectable reactants upto milliseconds after the laser puls, In contrast, there are clearly two components in the buildup of reduced species for (I) as shown in figure-3.
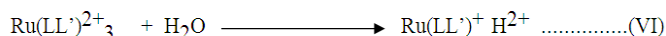
The second step gives a reasonable linear plot of $1/A^{595}$ vs. time. showing a second order processes with approximate equal concentration kinetics. Considering the quantum yield of (0.48) with these initial concentration of I.=8x10^{-5}M should be 6x10^{-5} and 2x10^{-5}M and assuming K=10^{10} M^{-1} S^{-1} (diffusion controlled) we calculate the observed life time for the reaction should be several micro second which is in good agreement with the observed grow intime for the second component of product formation. Which shows that radical IV is a more powerful reductant than reduced (II).

The above results indicates that the overall efficiency in photo reduction of I.by amines lies primarily in the initial quenching step.Thus, under the present conditions, the quantum yield indicate the yield of "free ions" via equation (II) appears to be only in the range 2.03 and the remaining fraction of the excited state decays in

a net reaction equation (V) of non radiative decay. The still lower yield of reduction product from II. We can be attributed to inefficency reaciton 4, it must occur at a much slower rate.

The product formed from irridation of I.in presence of triethylamine is stable in dry degassed acetonitrile solution. The absorption spectrum of this solution in Ru(III) complex that one of the ligands has been reduced to a radical anion. We observed that the reduced product from I. is quite reactive towards oxygen and water. The addition of water results in rapid reaction of the initial product formed in equation (I to IV). Figure -4 there is a rapid build up product absorbing at 595nm and a subsequent decay. From a measured transient life time of 2.80 x10^{-5} s (595nm. at H_2O ± 3.5 M we obtain a rate constant K = 2.4 x 10^4 M^{-1} S^{-1} for reaction of reduced complex with water.

The raction of reduced I. with water evidently quite different from the corresponding studied reaction with reduced to.2, figure-2, indicates the product having slightly red shifted but generally similar spectrum the end product is observed in laser flash experiments which results that the net reaction of Ru(LL')$_3^{2+}$ with water is simply a protonation rather than a redox redox process.

$$Ru(LL')^{2+}_3 + H_2O \xrightarrow{\quad\quad} Ru(LL')^+ H^{2+} \text{...............(VI)}$$
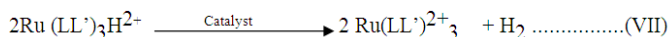
Since (I) and (II) are much more reactive towards water reduced (III) even though, reduced (III) is obviously a more powerful reductant and potentially more reactive. The reaction product of reduced I with water suggest protonation of an oxygen of the ligand carboxy easter group is the initial step.

The carboxy ester complexes are liable to ester hydrolysis in triethylamine - water solution in the dark. Net hydrolysis is quite slow compared with photo reduction and the reaction of reduced I. with water. In the present result the facet that prolonged irradiation does not at all enchance hydrolysis over the dark process suggests that reaction (VI) does not promote hydrolysis.

In fact reduced I. is more stable in triethylamine - water-acetonitrile solution than I. towards hydrolysis. However, in our complex I. no Hydrogen could be detected. It is reasonable to assume that mechanism that at the high pH (~12) involved the reduced complex from I. Ru(LL')$_3^{2+}$
(or Ru(LL')$^{3+}$ H^{2+}) are not sufficiently powerful to reduced protons.

Thus, it would be expected that the reduction of I at lowers pH in the presence of water and a reactive catalyst should result in hydrogen production by reaction (VII).
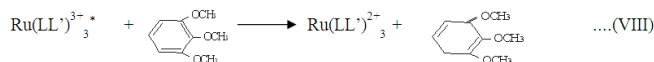
$$2Ru(LL')_3H^{2+} \xrightarrow{\quad Catalyst \quad} 2 Ru(LL')^{2+}_3 + H_2 \text{................(VII)}$$

The reaction (VII) occurs the results indicate that the system atleast with EDTA as a reductant is not an optimal one for hydrogen generation.
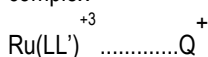
With Aromatic Ether

We observed the transients behaviour a number of aromatics ethers quench the luminescence of I. In reaction which evidently involve net electron transfer. A number of di and trimetoxybenzenes having oxidation potentials in the range 1.10 -1.50 V(vs.SCE in acetonitrile) have been found to quench the luminescence of I. with rate constant 2-3 orders of magnitude below diffusion controlled [55]. It is reasonable that quenching involved net electron transfer from

the ether to excited I.

For the case of 1,2,3- trimethoxybenzene   it was found that laser flash excitation of I. at 525 nm in the presence of 0.8M quencher resulted in essentially complete luminescence quenching with concurrent spectral changes consistant with reduction I as indicated by equation (VIII).

$$Ru(LL')_3^{3-}{}^* \ + \ \underset{OCH_3}{\underset{|}{\bigcirc}}\text{—OCH}_3 \longrightarrow Ru(LL')_3^{2-} + \underset{OCH_3}{\underset{|}{\bigcirc}}\text{—OCH}_3 \qquad ....(VIII)$$

The transit spectrum produced was quite short lived and showed a clean I order decay with K=(1.2 ± 0.2)   x 10^7 Sec^{-1}. This observation of I. rather than second   order of the transient indicates that in this case "free" ionic product are not formed. This could be attributed to the occurence of back reaction while the product ions in equation (VIII) are within an effective case or to decay of one complex
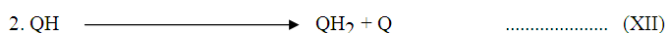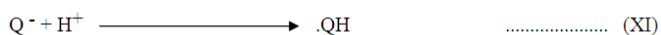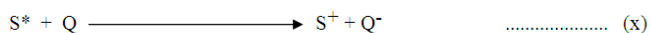
$$Ru(LL')^{+3} \ \text{............} Q^+$$

With p-hydroxyquionone

Further p-hydroquinone was found to react with excited I to give similar transient life time. Figure 4 and 5 shows transient spectra obtained following laser flash excitation of I with hydroquionone in the absence and presence of water respectively. The transient spectra generated are clearly indicative of an excited state electron transfer process to generate reduced complex and oxidised quencher equation (IX). Initially it was suspected that the possibility of forming a useful two component system for accomplishing water splitting as observed earlier.

$$Ru(LL')_3^{3}{}^{+*} \ + QH_2 \longrightarrow Ru(LL')_3^{2+} + QH + H^+ \qquad ....(IX)$$

Since a similar sequence can be written following equation (IX) it is obviously possible to conceive a system in which S$^+$ and Ru(LL')$^{2+}$3 (or Ru(LL')$^{+3}$ H^{2+}) in presence of water) are used to effect separately the oxidation and reduction of water respectively. While Q, QH^2 system acts as a shuttle similar to its role in photosynthesis.

In the present case we observed a rapid decay of the product Ru(LL')$^{2+}$3, although the initial efficiency of product formating eq.(IX) appears to approach unity in both dry and aqeous acetonitrile solutions. The decay of Ru(LL')$^{2+}$3 in this case is first order and all have establish that it is due to minute amounts of quionone in purity. We have measured the rate constant for oxidation of Ru(LL')$^{2+}$3 by quinone to be 3.4 x 10^9 M^{-1} S^{-1}. This indicates that even an impurity of 0.01% quinone "The natural back reaction" even if diffusion controlled will be over whelmed by destruction of Ru(LL')$^{2+}$3 by quinone impurity. Thus, while for many quinone derivatives the hydroquinone formed in the anodic half reaction does not hinder to buildup of oxidised substrate, it is clear that it will be difficult to find a system in which a reduced substrate is not oxidised by the quinone produced in the cathodic half reaction.

$$S^* + Q \longrightarrow S^+ + Q^- \qquad \text{.....................} (x)$$

$$Q^- + H^+ \longrightarrow .QH \qquad \text{.....................} (XI)$$

$$2.QH \longrightarrow QH_2 + Q \qquad \text{.....................} (XII)$$

With Water

The observation that excited states of I. and II. are reactive towards a number of oxygen containing substrats prompted us to examine its potential reactivity with water. Through laser flash investigation we find that water bath quenchers the luminescence of I and results in transient product formation   though no permanent chemical change occurs.The excited state quenching constant for water in acetonitrile is K=1x10^7 M^{-1} S^{-1}. A transient is produced following the quenching which has the spectrum gives in figure - 7.The short-lived transient decays via first order kinetics and shows general absorption in the visible range. While the spectrum produced is not sufficiently resolved to give any definite structural information.The lack of congurance between it and that of the Ru(LL')$^{2+}$3 produced by the other quenchers makes it clear that the quenching is not a redox process since there appears to be little or no net decomposition upon irradition of a pure water acetonitrile solution of I. It appears that the photo reaction does not likely involve gross reorganisation or decomposition of the complex such as might be expected by water attack at a metal ligand centre. It appears much more reasonalbe that a reversible water attack on the ligand is the origin of the quenching here again a reasonable possibility appears that the enchance ligand basicity in the C.T. excited state can result in a protonation either at a ligand carbon or, more likely, at the oxygen of a carbon ester group. In parallel with the reduced species, the analogy can be drawn between the charge transfer excited state and a metal oxidised ligand radical an ion, although interaction with the solvent can furnish a path for non-radioactive decay via transient product formation, the interaction does not result in any permanent chemical conversion.
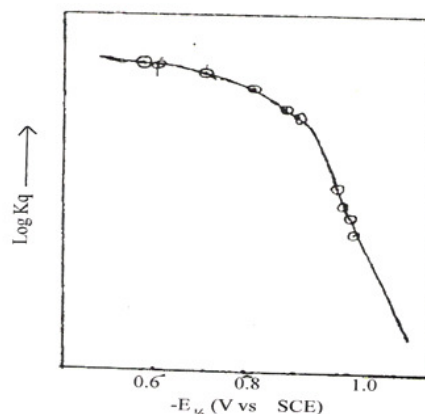

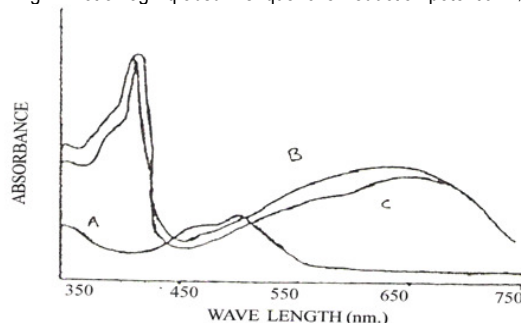Fig 1. Plot of log Kq obsd. Vs. quencher reduction potential E½

Fig 2. Absorption spectra of starting complex 1.(A) and its reduction products in acetonitrile (B) and acetonitrile-water (C).
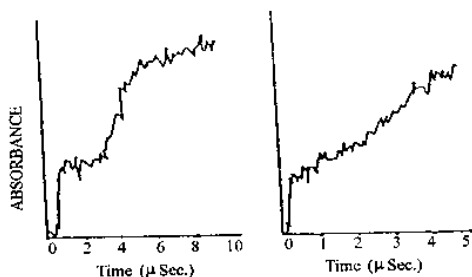
Fig 3. Temporal behaviour observed at 595nm, following laser flash excitaion of I. in triethylamineacetonitrile shown are trace on two times scales for the I, flash on replicate samples
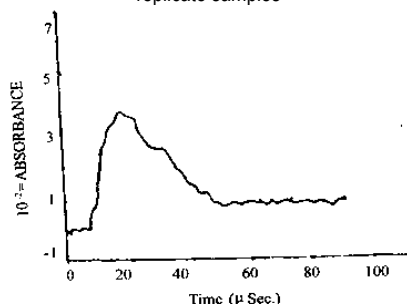

Fig 4. Temporal behaviour observed at 595 nm. Following laser flash excitation of I. in triethylaminewater-acetonitrile
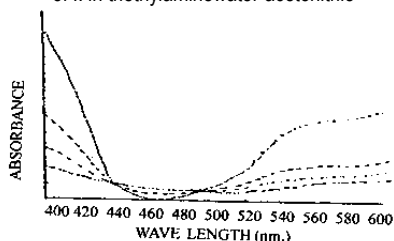

Fig 5. Transient absorption spectra obtained following laser flash excitation of first hydroquinone in acetonitrile.
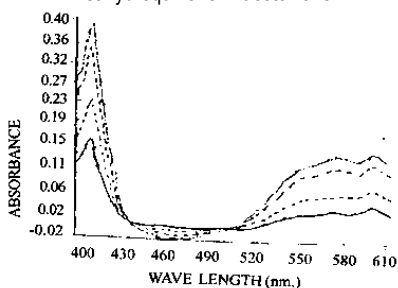

Fig 6. Transient absorption spectra obtained following laser flash excitation of first hydroquinone in acetonitrile-water
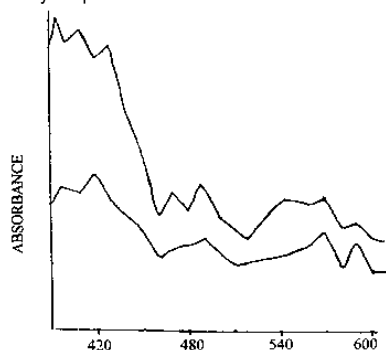

Fig 7. Transient absorption spectra obtained following laser flash excitation of first in water acetonitrile.

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