CHAPTER-III
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ALASER FLASH STUDY WITH POTENTIAL REDUCTIVE QUENCHERS.
EFFECTS OF LIGAND SUBSTITUENTS ON EXCITED-STATE
REACTIVITY AND PHOTO REDOX BEHAVIOUR FOR RuL' COMPLEXES

Introduction :-

A large number of investigations with polypyridyl complexes of ruthenium (II), osmium(II), iridium(III), and chromium(III) have shown that excited states of these complexes can be both oxidised and reduced by a variety of reagents [1-19]. The well-characterised spectroscopic properties [20-29] of these complexes and their one electron redox products have facilitated study of processes where simple electron transfer quenching occurs. Since electron transfer-quenching often occurs with high efficiency and can result in efficient conversion of excitation energy through high energy product formation, there has been considerable interest in coupling ensuing reactions with these processes to achieve net chemical change. Various approaches have included the use of scavengers, [25-31] quenchers whose redox products undergo rapid reactions with solvent or other reagents [16-32] organised assemblies, [33-36] and/or highly reactive colloidal or heterogeneous catalysts, [27-31, 37-42] in addition, a number of studies have focused on tuning of the photo redox behaviour of these complexes by modifying the net charge on the complex [41-43] or by adjusting ligand substituents [16, 32, 44].

In several cases of quenching, photoreactions and net photoredox conversion for these complexes, both the primary photo process and ensuing reactions involve only simple one electron transfer processes. However, in a number of cases there is evidence that primary or competitive reactions involving other types of
interactions may be of importance. For example, in the well-studied system involving interaction of excited Ru(bpy)$_3^{2+}$ with Co(III) complexes, [2,37,45,50] it is clear that rapid unimolecular decomposition of the labile Co(II) complex permits not photoconversion to occur. In recently reported comes, such as the quenching of Ru(bpy)$_3^{2+}$ by inorganic ions [Hg$^{2+}$ (49), Ti$^{3+}$ (50) and Ag$^+$ (51-52)], it is clear that the reduced metal ion can undergo a variety of rapid reactions not involving electron transfer in competition with the normally observed back-electron-transfer process. In several cases the net chemical change observed is potentially useful. In the case of Hg$^{2+}$ result in a survival time for [Ru(bpy)$_3$I$^+$ on the scale of minutes without the use of other sacrificial agents [49]. In contrast, for Ti$^{3+}$ reduction rapid reaction of Ti$^{2+}$ with water has been suggested to prevent back electron transfer [50]. The question of solvent particularly water interaction with excited states of these complexes or primary products of their photoreaction remains an area of active investigation. Interest in these reactions and interactions is due in part to questions/Concerning the mechanism of catalyst involvement in transition metal complexes mediated water redox processes and also to the observation of strong solvent effects on the lifetime constants and properties of metal complex charge transfer and ligand field excited states. Several studies have focused on pronounced changes in acid-base properties which occur ligand sites upon excitation of these transition-metal complexes in aqueous solutions, [43-54], other studies have indicated that reaction with water or solute anions can occur at the metal center following excitation and in some cases, partial labilisation of bipyridine type ligand [55-59]. While in a few cases stable monodentate complexes have been isolated or clearly indicated to be formed [57], their lability [56-58] renders their intermediacy or precise structure difficult to establish in many photoreactions. The question of reaction of water or other ions with excited metal complexes or their primary
photoproducts remains an extremely important one since, for several systems it is likely that protonated or reprotonated species or other adducts are key intermediates in sequence leading to water spoiling or other useful chemical conversions [60-62].

The present study deals with excited state quenching processes and ensuing reactions occurring with RuL₃⁺ ruthenium (II) complexes in which (2, 2' bpy) ligands have been replaced with (diphenyl-bpy) and (diphenyl-phen) ligands. We have used laser flash and conventional spectroscopic techniques to examine the reactions of these excited. Complexes with potential reductants ranging from tertiary amines to water. Results of our study indicate that quenching can occur by net electron transfer reduction as well as by interactions not involving electron transfer at all. Not surprisingly, our experiments indicate that readily observable reactions subsquent to the primary quenching process play a dominant role in determining the overall chemical change occurring. A key result of the studies is the finding that ligand substituents not only play a major role in controlling reactivity but also provide a specific site for solvent interactions.

Experimental Section

Ruthenium complexes 1 and 2 were prepared as described previously [63]. Spectrograde acetonitrile was disitilled from anhydruous P₂O₅, Triethyl amine was purified by distillation. P-hydroquenone was purified by vacuum sublimation. All other chemicals used were of reagent grade (Fluka).

Time-correlated experiments were performed by using laser flash photolysis techniques. The double frequency pulse (630 nm) the Ok neodymium yag laser (pulse with 15nms, energy output 400mj.) was used as an exciting source. The details of the optical and detection systems have been described elseware [64-65]. The temporal behaviour of the transients formed was recorded with two tektronix transient digitizers
(R-7912) tandem, both coupled to a PDP II/04 computer.

Absorption spectra were recorded on a Cary 14 spectrometer or a Perkin-Elmer 576 ST spectrometer. Luminescence excitation and emission spectra were recorded on a Perkin-Elmer MPF-4 spectrometer. Conventional flash photolysis experiments were performed as previously described [2, 3].

**Result and Discussion :**

**Photoreduction of [Ru(diphenyl-bpy)₂Cl₂ and [Ru(diphenyl-phen)₂Cl₂ by Amines :**

Irradiation of complexes (I) in the presence of amines such as triethyl amine in dry deacrated aprotic solvent leads to luminescence quenching (K₉ = 1.2 x 10⁸ M⁻¹ S⁻¹) and to formation of a permanent photo product whose spectrum is shown in Figure-1. This behavior is similar to that observed upon irradiation of 2 under similar conditions and from ESR and electrochemical evidence it can be concluded that the spectrum is that of the one-electron-reduction product of (I), RuL₃⁺(32). For (2) the highest quantum yield.

\[
\begin{align*}
    \text{RuL}_3^{2+} \rightarrow hν \rightarrow \text{RuL}_3^{2+} \\
    \text{RuL}_3^{2+} + \text{NET}_3 & \rightarrow \text{RuL}_3^{2+} + \text{NEt}_3 \\
    \text{NET}_3 + \text{NEt}_3 & \rightarrow \text{CH}_3\text{CHNEt}_2 + \text{HN}^+\text{Et}_3 \\
    \text{CH}_3\text{CHNEt}_2 + \text{RuL}_3^{2+} & \rightarrow \text{CH}_3\text{CH} = \text{N}^+\text{Et}_2 + \text{RuL}_3
\end{align*}
\]

For metal complex reduction obtained is 0.35 in dry acetonitrile; in current studies with (I) we obtain \(\Phi_{\text{red}} = 0.44\) with triethylamine and \(\Phi_{\text{red}} = 0.52\) for di-isopropyl amine in dry degassed acetonitrile. Since the mechanism given by eq. 1-4 predicts limiting quantum yield of (2) for photoreduction, a question of fundamental importance
is the source of the observed inefficiency in the overall process, previous studies [68, 69] have suggested that net electron transfer quenching efficiencies (eq. 2) are often much lower than unity such some quenching can simply produce a net result of non-radiative decay (eq. 5).

\[ \text{RuL}_3^{2+} + :\text{NEt}_3^{2+} \rightarrow \text{RuL}_3^{2+} + :\text{NEt}_3 \quad \cdots \quad \cdots \quad \cdots \quad (5) \]

A second source of inefficiency could be the failure of radical such as \( \text{CH}_3\text{CHNEt}_2 \) (4) to participate in the dark reduction of the metal complex (eq. 4). Previous studies [70,71] have suggested that 4 is a strong reductant having a potential \( E'/0 \) in the range -1.0V vs SCE; however, this value represents an approximation since the 'true' potential would be very difficult to obtain, considering the instability of both 4 and its oxidation products.

In the present study we have examined the time dependence of the production of \( \text{RuL}_3^{2+} \) following laser flash excitation of (1) and (2) in the presence of triethylamine in dry degassed acetonitrile. Figure-2 shows the buildup of reduced (1) at 600 nm as a function of time. For both 1 and 2 it was found that there is no decay of the long wavelength-absorbing product following the laser flash. This indicates that there is no back-reaction of the "Free-lons" formed in equation 2 for either of the complexes. The temporal characteristics of reduced species following the initial rapid formation are different for reactions of (1) and (2) with triethyl amine. For (2) the product is stable but there appears to be no further detectable reaction up to milliseconds after the laser pulse. In contrast there are clearly two comments in the buildup of reduced species for 1 as shown in Figure2. The second component, which occurs on the microsecond time scale under the conditions employed, is evidently the dark reduction described by eq 4. Using only data from the initial flash, in each case, we found that over several replication with (1) roughly equal amounts of productare
generated in the fast and slow steps. The second step gives order process following approximate equal - concentration kinetics.

The secondary product generation indicated in Figure 2, is attributed to reaction 4. Consisting the quantum yield of ~ 0.5 to be due to equal contributions from reaction 2 and 4, the concentrations of RuI$_2^+$ and mine radical 4 after the photoreaction (eq. 2) and proton transfer steps (eq. 3) from an initial concentration of [H] = 8 x 10$^{-5}$M should be 6 x 10$^{-5}$ and 2 x 10$^{-5}$M, respectively. Using these concentrations and assuming $K_q = 10^{10}$ M$^{-1}$S$^{-1}$ (diffusion controlled) we calculate that the observed lifetime for the reaction should be several microseconds in good agreement with the observed grow-in time for the second component of product formation. Thus it appears reasonable that radical 4 is more powerful reductant than reduced (1) but perhaps a less powerful reductant than reduced (2), putting the potential for the couple in the range 0.92 \text{ V} \leq E'/0 < -0.65 \text{ V}.

These results suggest that the overall in efficiency in photoreductions of (1) by amine lies primarily in the initial quenching step. Thus under the present condition, the quantum yields indicate the yield of 'free' ions via eq-2, appears to be only in the range 0.2-0.3 and the remaining fraction of the excited states decays via a net reaction (eq. 5) of non radiative decay. The still lower field of reduction products from 2 can be attributed to inefficiency of reaction 4; although reaction 4 may account for some reduction of (2). It must occur at much slower rate since we were unable to observe it on the time scale accessible in these experiments. As pointed out previously low efficiencies in the generation of free ions (eq. 2) remain a serious barrier to practical employment of light induced electron transfer reactions. The Excersive sensitivity of these reactions to solvent effects and to structural features in both substrate and quencher remain to a large extent identified.
As indicated previously the product formed from irradiation of (I) in the presence of triethyl amine is stable in dry degassed acetonitrile solution. The absorption spectrum of this solution as well as the ESR spectrum [32], suggest this is best described as Ru(II) complex in which one of the ligands has been reduced to a radical anion. The electronic spectrum produced methyl viologen in both similar to that of reduced methyl viologen in both the visible and ultraviolet regions. Not surprisingly we find that the reduced product from (I) is quite reactive toward oxygen and water. For example admission of air to dry solutions does not suppress formation of the transient absorbing at 600 nm; however the product stable under the same conditions in the absence of air, is observed to decay with a lifetime of Ca 3 ms, regenerating the starting complex (I) [70].

Addition of water also results in rapid reaction of the initial product formed in eq 1-4. Once again (Figure-3), there is a rapid buildup of product absorbing at 600 nm and a subsequent decay. From a measured lifetime of 2.85 x 10^-5 S (600 nm) at (H2O) = 1.4M we obtain a rate constant K = 2.5 x 10^4 M^-1 S^-1 for reaction of the reduce complex with water.

The reaction of reduced (I) with water is evidently quite different from the corresponding reaction previously studied with reduced (2). In the latter case the reaction was found to result in regeneration of the starting complex together with some decomposition. As Figure (I) indicates a product having a slightly red shifted but generally similar spectrum to that produced in anhydrous acetonitrile is obtained when steady-state photolysis of (I) with triethyl amine is carried out in the presence of moderate amounts of water. The same and product is observed in laser flash experiment. This suggests that the net reaction with water is simply a protonation (or hydration) of the reduced species (eq. 6) rather then a redox process.
\[
\text{RuL}_3^2+ + \text{H}^+ \rightarrow \text{RuL}_3\text{H}^2+ \quad \text{(H2O)} \quad \text{(6)}
\]

Given the probable mechanism for hydrogen production it is reasonable that at high pH (~12) involved the reduced complexes from 1, RuL\text{H}^2+ or RuL\text{H}^2+ are not sufficiently powerful to reduced protons. Although it is not possible to measure the reducing potential for RuL\text{H}^2+, it appears reasonable that it should be only slightly lower than that of RuL\text{H}^2+. Thus it would be expected that reduction of (1) at lower pH in the presence of water and a reactive catalyst should result in hydrogen production by reaction 7. To test this possibility we use the disodium salt of ethylenediamine tetraacetic acid (EDTA) as a reductant

\[
\text{Catalyst} \quad 2\text{RuL}_3\text{H}^2+ \rightarrow 2\text{RuL}_3^{2+} + \text{H}_2 \quad \text{(7)}
\]

for (1) in a 4:1 mixture of water acetonitrile buffered to pH 4.7 with a carbow-supported platinum catalyst which has been shown highly reactive for hydrogen generation in other studies [38]. Although quenching of the excited state (1) by EDTA is incomplete at the concentration used (K_{sv} = 20), moderate evolution (1 ml of H\text{H}_2/(L of sample /h)) of hydrogen was obtained when these solutions were irradiated. Although a quantum yield was not measured for this process, the amount of hydrogen produced was clearly lower by at least 1 order of magnitude from the most reactive systems studied with this catalyst [71,72]. Thus while these studies clearly indicate reaction 7 occurs, the results indicate that the system at least with EDTA as a reductant is not an optimal one for hydrogen generation.

*Photoreaction of Complex (1) with other Reagents* :-
The cathodically shifted potentials of (I) suggest that it should be possible to obtain photoreductions with a variety of reductants not measurably reactive toward excited state of (2). Not surprisingly we have found that number of aromatic ethers and hydroquinone quench the luminescence of (I) in reactions which evidently involve net electron-transfer. We have investigated the transient behavior with these oxygen containing quenchers and have found that while quenching occurs in each case the type of transient and transient lifetime are quite department on the quencher.

A number of di-and tri methoxy ybenzenes having oxidation potential in the range 1.12 -1.5 V (vs SCE in acetonitrile) have been found to quench the luminescence of (I) with rate constants 1-3 orders of magnitude below diffusion controlled [73]. Clearly, considering the potentials involved, it is reasonable that quenching should involve net electron transfer from the other to excited (I). For the case of 1, 2, 3 trimethoxy benzene it was found that laser flash excitation of (I) at 530 nm in the presence of 0.8 M quencher resulted in essentially complete luminescence quenching with concurrent spectral changes consistent with reduction of (I) as in diatid by eq. 8. The transient spectrum produced, although very similar to that of RuL₃⁺ shown in Figure-I.

\[
\text{RuL}_{3}^{2+} + \text{OCH₃} \rightarrow \text{ReL}_{3}^{+} + \text{OCH₃} \quad \text{(8)}
\]

was quit short-lived and showed a clean - first-order decay with K= (1.4 + 0.2 x 10⁷ sec⁻¹ (correlation coefficients> 0.99 for each trace). The obseraion of first rather than second - order decay of the transient indicates that in this case 'free' ionic products are not formed. This could be atributed to the occurrence of back-reaction while the
product ions in eq 8 are within an effective cage [74, 75] or to decay of an exciplex, RuL₃[......]Q⁺ [76]. The lifetime of the transient in this case (100 ns) is clearly too short to make this substrate quencher.

Combination an attractive one for obtaining net useful chemistry although high concentrations of reactive scavengers might enable the net production of one of the products.

In similar experiments P-hydroquinone was found to react with excited (1) to give similar transient spectra but with a much longer transient lifetime. Figure-4 and 5 show transient spectra obtained following laser flash excitation of (1) with hydroquinone in the absence and the presence of water respectively. As with the ethers the transient spectra generated are clearly indicative of an excited state electron-transfer.

Process to generate reduced complex and oxidised quencher (eq 9) Initially it was thought that this,

$$\text{RuL}_3^{2+} + \text{QH}_2 \rightarrow \text{RuL}_3^- + \text{QH} + H^+$$

reaction might offer the possibility of forming one-half of a useful two-component system for accomplishing water splitting since we and others have found several cases where similar metal complexes are oxidised photochemically by quenones to produce oxidised substrate and reduced quenones as permanent products by the sequence given by eq.-10-12 [78]. Since a similar sequence can be written,

$$S^+ + Q \rightarrow S^+ + Q^- \quad (10)$$
$$\overline{Q} + H^+ \rightarrow \text{QH} \quad (11)$$
$$2\text{QH} \rightarrow \text{QH}_2 + Q \quad (12)$$

following eq 9, it is obviously possible to conceive system in which $S^+$ and RuL₃ (or RuL₃H₂ in the presence of water) are used to effect separately the oxidation and
reduction of water, respectively while the $Q, QH_2$ system acts as a shuttle similar to its role in photosynthesis.

In the present case the initial findings are some what disappointing since even with highly purified $QH_2$ as quencher, we observe a rapid decay of the product $\text{RuL}_2^+$, although the initial eficiency of product formation (eq. 9) appears to approach unity in both dry and aqueous acetonitrile solutions. The decay of $\text{RuL}_2^+$ in this case is first order and we have established that it is due to minute amounts of quenchrine impurity in the starting hydroquinone. Thus in separate experiments we have measured the rate constants for oxidation of $\text{RuL}_2^+$ by quinone to be $3.5 \times 10^9 \text{ M}^{-1}\text{S}^{-1}$. This indicates that even an impurity of 0.01% quinane (virtually impossible to exclude, even with highly purified hydroquinone)

The"natural" back-reaction, even if diffusion controlled will be overwhelmd by destruction of $\text{RuL}_2^+$ by quinone impurity. This emphaziser the difficulty in finding a suitable relay to function on both sides of a two - absorber system not employing sacrificial regents. Thus while for many quinone - derivatives the hydroquinone formed in the 'anodic' half reaction does not hinder the build up 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.

*Photo reaction of (I) with water* :-

The observation that excited states of (I) are reactive toward a number of oxygen-containing substrates prompted us to examine its potential reactivity with water. Through laser investigation we find that water both quenches the luminescence of (I) and results in transient product formation even through no permanent chemical change occurs [79]. The excited state quenching constant for water in acetonitrile is $K = 1 \times 10^7 \text{ M}^{-1}\text{S}^{-1}$: a transient is product following the quenching which has the spectrum

56
given in Figure-6. The short-Lived transient [80] decay via first - order kinetics and shows general absorption in the visible range while the spectrum produced is not sufficiently resolved to give any definitive structural information the lack of congruence between it and that of the RuL₄⁺ 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 irradiation of a pure water - acetonitrile solution of (I), it appears that the photoreaction does not likely involve gross reorganization or decomposition of the complex such as might be expected by water attack at a metal ligand center [55, 59]. It appears much more reasonable that a reversible water attack on the ligand is the origin of the quenching here again a reasonable possibility appears that the enhanced ligand basicity in the CT excited state can result in a protonation either at a ligand carbon or more likely at the oxygen of a carboxy 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 anion, although interaction with the solvent can furnish a path for nonradiative decay via transient product formation the interaction does not result in any permanent chemical conversion.
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74. That the short lifetime was not due to reactions of reduced I am impurity present in the quencher was checked by conducting flash experiments with varying quencher
concentration (no change in $\Psi$ was observed) and by generating reduced $I$ by $\text{Et}_3\text{N}$ (1M) reduction of $I$ in presence of 0.05 M trimethoxybenzene, the buildup of reduced $I$ was not suppressed under these conditions.

75. The first-order lifetime of the I-I, 2,3- trimethoxy benzene transient is solvent dependent (acetonitrile 87 N, N-dimethylformamide 33 ns; dimethyl sulfoxide, 21 ns) as would be predicted for a cage process. This reaction is currently under investigation.

76. Several fairly analogous excited donor-acceptor systems giving emission have been found to give transients having spectra similar to that of the radical ions with rapid first-order decay.

77. Peters, K., Private communication.

78. Schmehl, R. H. Unpublished results.

79. In neutral aqueous solutions Hydrolysis of $I$ is extremely slow.

80. The transient lifetime is 250 ns.
Figure 1. Absorption spectra of starting complex I (A) and its reduction products in acetonitrile (B) and acetonitril water (C).

Figure 2. Temporal behavior observed at 600 nm following laser flash excitation of I in triethylamine - acetonitrile. Shown are traces on two time scale for the first flash on replicate samples.
Figure 3. Temporal behavior observed at 600 nm following laser flash excitation of 1 in triethylamine - water - acetonitrile.

Figure 4. Transient absorption spectra obtained following laser flash excitation of 1-hydroquinone in acetonitrile.
Figure 5. Transient absorption spectra obtained following laser flash excitation of 1-hydroquinone in acetonitrile - water.

Figure 6. Transient absorption spectra obtained following flash excitation or 1 in water-acetonitrile.