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Reductive Quenching Of Excited States Of Chromium(III)-Polypyridyl Complexes With Alkyl Aryl Sulphides

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Abstract: The variation in the quenching rate constants, k_q, of $^*Cr(NN)_3^{3+}$ with the change in the structure of organic sulphides in deaerated acetonitrile solutions is explained with Marcus model. The retardation in k_q values for sulphides with bulky alkyl groups in RSPh is accounted for in terms of change of electron transfer distance. The formation of oxidised products in aerated solutions is explained by the formation of singlet oxygen in the system.

Introduction

The lowest energy doublet excited states (^2E) of Cr(III) complexes are a unique class of electronic excited states in that their orbital populations and molecular geometries are similar with those of the ground state.[1-3] The photophysics of Cr(III) complexes in general and tris(polypyridyl) complexes, $Cr(NN)_3^{3+}$, in particular have been very well studied.[2,3] $Cr(NN)_3^{3+}$ complexes luminesce in fluid solution at room temperature, showing two bands at ~695 and ~725nm corresponding to emission from the thermally equilibrated lowest doublet states designated, $^2T_1$ and ^2E, respectively.[1] The excited states of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ (bpy=2,2'-bipyridyl;phen=1,10-phenanthroline) are among the most long-lived in ambient aqueous and acetonitrile solutions. The relatively long lifetimes of these complexes have been ascribed to their relatively large quartet-doublet excited state energy differences. Thus, the photochemistry of (^2E) $Cr(NN)_3^{3+}$ complexes is almost universally ascribed to doublet excited state behaviour.[2] The long lifetimes of ^2E, the high ionic charges of the complexes and the hydrophobic nature of the environment around the ligands make the photochemistry of these complexes very interesting and attractive.

For the past several years we have been interested in the redox reactions of organic sulphur compounds with metal ions.[4-6] Recently we have initiated work on the photoredox reactions of Ru(II) complexes with organic electron donors and acceptors with special emphasis on the structural and solvent effects.[7,8] When we attempted to study the redox quenching reactions of $^*Ru(NN)_3^{2+}$ with organic sulphides we realised that these reactions were highly endoergic (> 0.7V). When we looked for other metal complexes, polypyridyl Cr(III) complexes appeared to be the suitable photosensitizers as they are very powerful oxidants ($E_{1/2}$ of $^*Cr(bpy)_3^{3+}/Cr(bpy)_3^{2+}$ is 1.44V) compared to Ru(II) complexes ($E_{1/2}$ of $^*Ru(bpy)_3^{2+}/Ru(bpy)_3^{+}$ is 0.80V).[1,9] A survey of literature reveals that though organic sensitizers and singlet oxygen have been extensively used for the photooxidation of organic sulphides,[10-13] no systematic approach has been attempted so far to study the photoredox reactions of organic sulphides with metal complexes. Thus to our knowledge this report seems to be a first detailed study for the reductive quenching of polypyridyl metal complexes with organic sulphides. A preliminary report of this work has already appeared.[14]

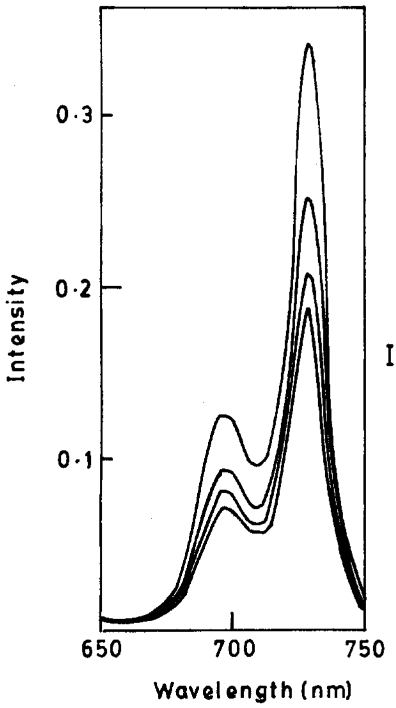
Experimental details

The tris-chelated chromium(III) complexes of 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine and 1,10-phenanthroline had been synthesised and purified by reported procedures.[15-17] All the organic sulphides (quenchers) used in this study were obtained by known methods.[4-6] Acetonitrile was purified before use[18] and double distilled water was used to prepare aqueous solutions. All the solutions were deoxygenated (unless otherwise stated) by purging purified dry N_2 gas for about 30 min. before recording emission spectra. Room temperature luminescence spectra of Cr(III) complexes were recorded with a JASCO FP-770 spectrofluorometer using Xenon lamp as the source. Absorption spectra were recorded using a JASCO-7800 spectrophotometer. Luminescence quenching experiments were carried out at room temperature (~25°C) in deaerated acetonitrile solutions. The concentrations of Cr(III) complexes and quenchers were in the range of 5×10^{-5}M and 1×10^{-4}-0.01M respectively.

The change of emission intensity of $^{*}Cr(NN)_3^{3+}$ with the change of [quencher] is shown in Figure 1. The Cr(III) complexes were excited at ~400 nm and the emission intensity was monitored at the wavelength range of ~695-725 nm. Excitation at 365 nm also leads to similar results. The quenching rate constant, k_q, was obtained from Stern-Volmer plots (eq.1)

$$I^{o}/I = 1 + k_q \tau^{o} [Q] \qquad (1)$$

where I^{o} and I are the emission intensities of $^{*}Cr(NN)_3^{3+}$ in the absence and presence of quencher, respectively and τ^{o} is the emission lifetime of $^{*}Cr(NN)_3^{3+}$ in the absence of quencher. The sample Stern-Volmer plots for the luminescence quenching of each complex with the quencher are shown in Figure 2.



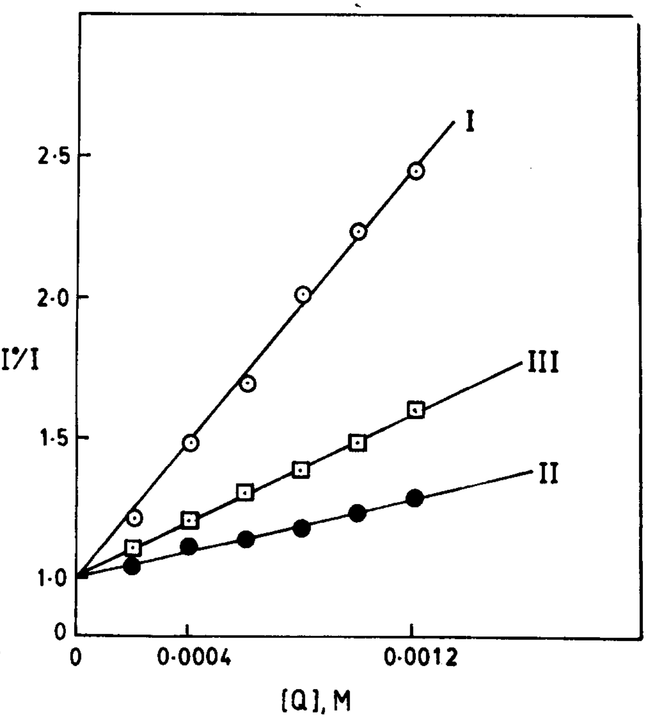


Figure 1 **Figure 2**

Left, Figure 1. The emission intensities for the luminescence quenching of $Cr(bpy)_3^{3+}$ by organic sulphide at different concentration. Right, Figure 2. Stern-Volmer plot for methyl phenyl sulphide.

Results and Discussion

The structure of the ligands (NN) and the abbreviations of the $Cr(NN)_3^{3+}$ complexes used in the present study are shown in Figure 3.

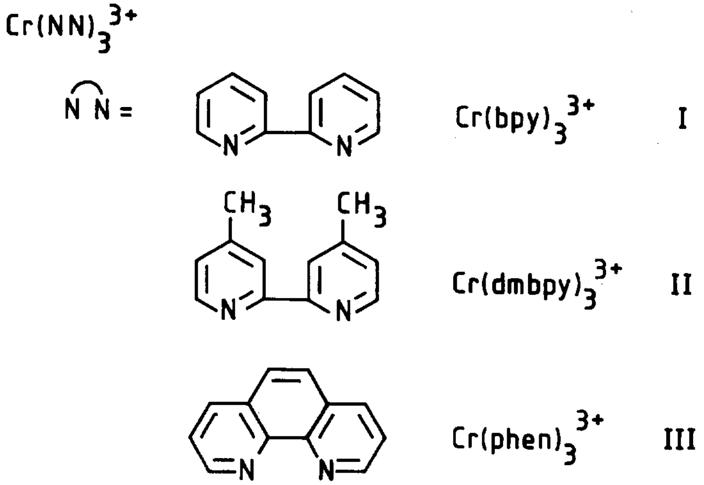


Figure 3. Structure of the ligands and abbreviations of chromium(III) complexes

The excited state lifetime and the redox potential values for the three Cr(III) complexes have been collected from previous studies and are given in Table 1.[1]

Tabel 1. Emission lifetime(τ) and excited state redox potentials ($E_{1/2}$) of $Cr(NN)_3^{3+}$ in acetonitrile at 298 K.

$Cr(NN)_3^{3+}$	$\tau/(\mu s)$	$E_{1/2}(^*Cr^{3+}/Cr^{2+})$ (V)
$^*Cr(bpy)_3^{3+}$	73	+1.44
$^*Cr(dmbpy)_3^{3+}$	200	+1.25
$^*Cr(phen)_3^{3+}$	330	+1.42

The quenching rate constant, k_q, values estimated from the luminescence quenching technique for the three $Cr(NN)_3^{3+}$ complexes with the various substituted phenyl methyl sulphides are given in Table 2 and for alkyl aryl sulphides in Table 3. The oxidation potentials of organic sulphides are also given in Tables 2 and 3.[19,20]

Table 2. Experimental and Calculated Quenching Rate Constants, k_q, for $^*Cr(NN)_3{}^{3+}$ in Acetonitrile at 298 K

No	Quencher	$Cr(bpy)_3{}^{3+}$		$Cr(dmbpy)_3{}^{3+}$		$Cr(phen)_3{}^{3+}$	
		Cal	Exp	Cal	Exp	Cal	Exp
1	Methyl phenyl sulphide(1.53V)#	$1.2x10^{8}$	$7.1x10^{7}$	$2.2x10^{6}$	$2.9x10^{6}$	$8.0x10^{7}$	$7.4x10^{6}$
2	*p*-Tolyl methyl sulphide(1.41V)	$1.0x10^{9}$	$3.9x10^{8}$	$3.2x10^{7}$	$1.4x10^{7}$	$7.2x10^{8}$	$8.1x10^{7}$
3	*m*-Tolyl methyl sulphide(1.50V)	$2.1x10^{8}$	$1.1x10^{8}$	$1.7x10^{6}$	$9.3x10^{6}$	$1.4x10^{8}$	$1.9x10^{6}$
4	*p*-Chlorophenyl methyl sulphide(1.55V)	$8.0x10^{7}$	$1.3x10^{7}$	$1.4x10^{6}$	$1.7x10^{6}$	$2.8x10^{5}$	$1.9x10^{6}$
5	*m*-Chlorophenyl methyl sulphide(1.65V)	$9.9x10^{6}$	$3.2x10^{7}$	$1.1x10^{5}$	$4.6x10^{5}$	$6.4x10^{6}$	$7.2x10^{5}$
6	*p*-Fluorophenyl methyl sulphide(1.54V)	$9.2x10^{7}$	$3.0x10^{7}$	$1.7x10^{6}$	$2.4x10^{6}$	$6.6x10^{7}$	$3.7x10^{6}$
7	*p*-Methoxyphenyl methyl sulphide(1.26V)	$9.3x10^{10}$	$2.5x10^{9}$	$5.5x10^{8}$	$5.3x10^{7}$	$7.0x10^{9}$	$3.2x10^{8}$
8	*m*-Methoxyphenyl methyl sulphide(1.45V)	$1.5x10^{7}$	$3.5x10^{7}$	$1.3x10^{7}$	$2.2x10^{6}$	$3.6x10^{8}$	$5.0x10^{6}$
9	*p*-Acetylphenyl methyl sulphide(1.73V)	$2.0x10^{6}$	$1.0x10^{6}$	$1.6x10^{4}$	$1.9x10^{5}$	$6.3x10^{6}$	$7.2x10^{4}$
10	*p*-Nitrophenyl methyl sulphide(1.85V)	$7.6x10^{4}$	$9.2x10^{4}$	$3.3x10^{2}$	$5.0x10^{4}$	$1.6x10^{5}$	$1.2x10^{4}$
11	β-Naphthylphenyl methyl sulphide	-	$1.1x10^{9}$	-	$8.9x10^{7}$	-	$5.4x10^{8}$

#Data in the parenthesis are the oxidation potentials in acetonitrile measured by electrochemical methods and collected from the literature.[19,20]

k_q values are in $M^{-1}s^{-1}$.

Table 3. Quenching Rate Constants, k_q, for $^*Cr(NN)_3^{3+}$ with Alkyl Phenyl Sulphides in Acetonitrile at 298 K

No	Quencher	$Cr(bpy)_3^{3+}$		$Cr(dmbpy)_3^{3+}$		$Cr(phen)_3^{3+}$	
		Cal	Exp	Cal	Exp	Cal	Exp
1	Methyl phenyl sulphide(1.53V)#	$1.2x10^8$	$7.1x10^7$	$2.2x10^6$	$2.9x10^6$	$8.0x10^7$	$7.4x10^6$
2	Ethyl phenyl sulphide(1.65V)	$1.0x10^7$	$2.6x10^7$	$1.1x10^5$	$7.3x10^5$	$6.4x10^6$	$2.3x10^6$
3	<u>i</u>-Propyl phenyl sulphide(1.63V)	$1.5x10^7$	$1.3x10^7$	$1.8x10^5$	$2.8x10^5$	$9.9x10^6$	$1.9x10^6$
4	<u>t</u>-Butyl phenyl sulphide(1.65V)	$1.0x10^7$	$4.8x10^6$	$1.1x10^5$	$8.3x10^4$	$6.4x10^6$	$6.7x10^5$
5	Diphenyl sulphide(1.65V)	$1.0x10^7$	$6.0x10^6$	$1.1x10^5$	$6.6x10^5$	$6.4x10^6$	$1.4x10^6$

#Data in parantheses are the oxidation potentials in acetonitrile measured by electrochemical methods and collected from the literature.[20]

k_q values are in $M^{-1}s^{-1}$.

In fluid solution, the deactivation of an excited state in the presence of a quencher may take place by several distinct mechanisms.[21,22] For excited states of transition metal complexes, when the bimolecular quenching constants are as large as those reported in Tables 2 and 3, only energy and electron transfer quenching processes have to be considered. The energy of the triplet state of the sulphides used in the present study is not known. However triplet energy of these sulphides will not be less than 60 kcal mol^{-1}. Thus the electronic energy transfer is energetically an unfavourable process for all systems examined here because the energy of the (^2E) chromium(III) species (39.3 kcals mol^{-1})is lower than that for the sulphides.[23] Then, the role of energy transfer in the quenching process may be considered negligible. From the luminescence quenching study, Beecroft et al[11] have concluded that sulphides exhibit behaviour analogous to amines in their ability to quench the excited states of aromatic hydrocarbons. It has already been established that the quenching of the emitting excited state of $Cr(bpy)_3^{3+}$ by amines proceeds by electron transfer mechanism.[23] In addition to these reports, the linear plots of RT lnkq vs. $E_{1/2}$ of quenchers observed for the quenching of all complexes (Figure 4) indicate that all sulphides quench the excited states of Cr(III) complexes by electron transfer mechanism.

Thus the luminescence quenching process can be discussed by a mechanism depicted in Scheme 1, which has been applied to electron transfer quenching of Cr(III) and other metal complexes in acetonitrile.[1,21]

$$\begin{tikzcd}
Cr(NN)_3^{3+} + S \arrow[r, shift left, "k_{12}"] \arrow[d, shift left, "1/\tau^\circ"] & {\underset{\text{I}}{[{}^*Cr(NN)_3^{3+}...S]}} \arrow[l, shift left, "k_{21}"] \arrow[r, shift left, "k_{23}"] & {\underset{\text{II}}{[Cr(NN)_3^{2+}...S^+]}} \arrow[l, shift left, "k_{32}"] \arrow[dl, "k_{30}"'] \arrow[d, "k_{34}"', "\text{dissociation}"] \\
Cr(NN)_3^{3+} + S \arrow[u, shift left, "h\nu"] & {[Cr(NN)_3^{3+}...S]} \arrow[l, dashed] & Cr(NN)_3^{2+} + S^+
\end{tikzcd}$$

Scheme 1

The reactants form a precursor complex (I) with the diffusion rate constant k_{12}. Electron transfer takes place within this precursor complex (k_{23}) to give the successor complex i.e., the radical-ion pair,

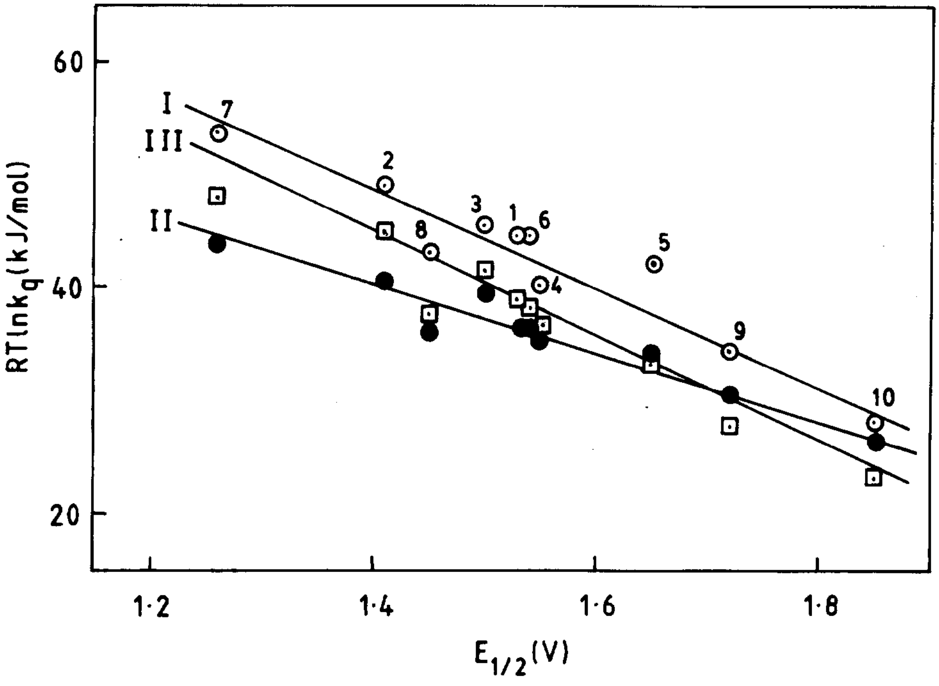


Figure 4. Plot of RT ln k_q vs.$E_{1/2}$ values of sulphides. The points in the figure are referred to by the same numbers as represented in Table 2.

$Cr(NN)_3^{2+}....S^+$(II). During this step there is reorganisation of the inner spheres of the complex (λ_i) as well as the reorganisation of the outer spheres of the solvent molecules (λ_o). These are responsible for the reorganisation energy,λ ($\lambda = \lambda_o + \lambda_i$). The successor complex may decompose to give the electron transfer products ($Cr(NN)_3^{2+}$ and S^+) with rate constant, k_{34}. It may as well give back the reactants either in the excited state (k_{32}) or in the ground state (k_{30}).

Applying the steady-state approximation for [$^*Cr(NN)_3^{3+}....S$] the expression for quenching rate constant is given by eq.(2)[14,21]

$$k_q = \frac{k_{12}}{1+k_{21}/k_{23}(1+k_{32}/k_{30}+k_{34})} \qquad (2)$$

If the rate of reverse electron transfer to give the excited state, k_{32}, is negligible relative to the rate of dissociation (k_{34}) or recombination, (k_{30}), i.e., $k_{32} << (k_{30} + k_{34})$, then eq.(2) becomes eq. (3)

$$k_q = k_{12}/(1+k_{21}/k_{23}) = k_{12}/(1+k_{12}/k_{23}K_{eq}) \qquad (3)$$

$K_{eq}=(k_{12}/k_{21})$ is the equilibrium constant for the formation of the precursor complex (I). The electron transfer rate constant, k_{23}, can be expressed as eq. (4)

$$k_{23} = \upsilon_n \exp(-\Delta G^{\ddagger}/kT) \qquad (4)$$

where υ_n is the nuclear frequency factor and $\Delta G^{\ddagger}$ is the free energy of activation of the electron transfer step. $\Delta G^{\ddagger}$ is related to the free energy change, ΔG, by Marcus equation (5)[25]

$$\Delta G^{\ddagger} = \lambda/4(1+ \Delta G/\lambda)^2 \qquad (5)$$

Substitution of eqs.(4) and (5) in eq.(3) leads to eq. (6)

$$k_q = \frac{k_{12}}{1+(k_{12}/\upsilon_n Keq) \quad \exp[- \lambda/4kT(1+\Delta G/\lambda)2]} \qquad (6)$$

According to Bock et al[26] the logarithmic form of eq.(6) is simplified to eq.(7) under the condition $k_{32}<<(k_{30}+k_{34})$

$$RT\ln k_q = RT\ln k_q(o) - \Delta G/2 \qquad (7)$$

where $k_q(o)$ is a constant for a series of structurally and electronically analogous quenchers. The linear plots of $RT\ln k_q$ vs. $E_{1/2}$ values of sulphides for all the three complexes give a slope of ~0.5 in all cases (Figure 4) indicating the absence of back electron transfer to form $^*Cr(NN)_3^{3+}$.

The k_q values collected in Table 2 show that the rate of luminescence quenching is accelerated by electron-releasing groups and retarded by electron-withdrawing groups present in the phenyl ring of ArSMe with all Cr(III) complexes. The application of the Hammett equation (eq.8) of physical organic chemistry[27]

$$\log k_q = \log k_o + \rho\sigma \qquad (8)$$

to the quenching data in Table 2 leads to linear $\log k_q$ vs. σ plots (Figure 5) in all cases. The ρ values (correlation coefficient, r, is given in the parentheses and n=10 in all three cases) for the quenching of $^*Cr(bpy)_3^{3+}$, $^*Cr(dmbpy)_3^{3+}$ and $^*Cr(phen)_3^{3+}$ are -3.64(r=0.959), -2.72(r=0.986) and -3.96 (r=0.988) respectively. The correlation is not substantially improved if $\log k_q$ values are plotted against σ^+ values. The corresponding ρ^+ values are -2.05(r=0.945), -1.97(r=0.990) and -2.82(r=0.973). The influence of substituents in the aryl moiety of ArSMe on k_q and the

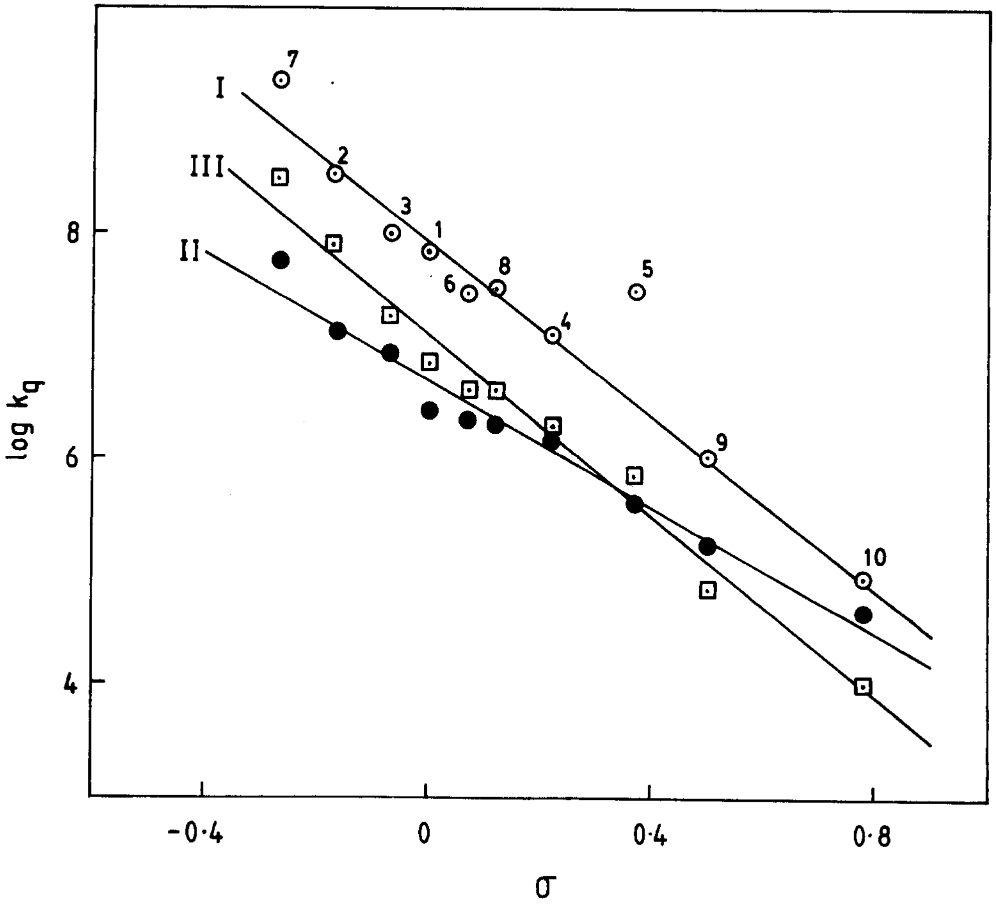


Figure 5.Hammett plot of $\log k_q$ vs.σ. The points in the figure are referred to by the same numbers in Table 2.

negative ρ values observed are understandable as the electron-releasing groups increase the electron density on the sulphur atom of the sulphide thereby enhancing the electron donating ability of the sulphide to $^*Cr(NN)_3^{3+}$, whereas the electron withdrawing groups have the reverse trend. The higher k_q values obtained with methyl β- naphthyl sulphide compared to methyl phenyl sulphide (cf. Table 2) is understood from negative σ (-0.04) and σ^+(-0.132) values of β-naphthyl group. Similar structure-reactivity relationships have been observed in the quenching of $^*Ru(NN)_3^{2+}$ complexes with phenolate ions and aromatic amines by us[7,8] and others.[28]

The k_q values obtained for different alkyl phenyl sulphides and diphenyl sulphide collected in Table 3 indicate the importance of change of alkyl group in RSPh on the electron transfer reaction of sulphides with $^*Cr(NN)_3^{3+}$. The change of ålkyl group in RSPh alters the polar as well as steric effects. The effect of change of alkyl group in RSPh on the reactivity of sulphides with the excited states of Cr(III) complexes may be understood from the analysis of the k_q data in terms of Taft's equations (9) and (10).[29]

$$\log k_q = \log k_o + \rho^* \sigma^* \qquad (9)$$

$$\log k_q = \log k_o + \delta E_s \qquad (10)$$

where σ^* and E_s are the Taft's polar and steric substituent constants and ρ^* and δ are the corresponding susceptibility constants. If the polar effect of alkyl group is the predominant factor in this reaction, then the change of methyl group by ethyl, isopropyl and t-butyl should increase the k_q value. But the k_q data given in Table 3 are in the opposite order. Thus the polar effect does not play the major role in the reactions of alkyl phenyl sulphides. An increase in the size of the alkyl group may bring in the importance of steric effect and thereby a decrease in k_q value. As the observed k_q value decreases with the increase in the bulkiness of the alkyl group in RSPh, k_q values have been correleted with the Taft's steric substituent constant, E_s, and the correlations are poor and δ values are small. To confirm the insignificant role of steric effect in this reaction, the k_q values have also been correlated with Hancock's, Dubois's and Charton's steric substituent parameters.[29] Though the correlation with Hancock's steric parameter is satisfactory (r=0.956) with the limited number of data, the value of the coefficient is very small compared to ρ values obtained in aryl methyl sulphides. But the correlations with other steric parameters are not satisfactory giving small δ values confirming the minor role of steric effect in these reactions. This analysis laeds us to conclude that the steric effect is not significant in these reactions. It is pertinent to point out that Davidson and co-workers[11] realised the less significant role of steric effect in the luminescence quenching of cyanoaromatics with dialkyl sulphides in acetonitrile medium compared to that in nonpolar cyclohexane though the quenching reaction is more efficient in acetonitrile.

Another approach for the steric influence on the rate of electron transfer reactions is in terms of change of electron transfer distance. The exponential decrease of electron transfer rate constant with an increase in the electron transfer distance has been well established theoretically[25] as well as experimentally.[30] The differences in the quenching constants, k_q, with bulky quenchers are best related to the preexponential factor K (transmission coefficient which is mainly determined by the degree of electronic coupling) for the electron transfer step, as noted by Jones and Chatterjee[31] in the quenching of Eosin Y dye by hindered phenols (eq.11). Incorporating a term for transmission coefficient, K, the expression for the rate constant of electron transfer reaction, eq. (4), becomes eq. (11)

$$k_{el} = K\upsilon_n(-\Delta G^{\ddagger}/RT) \qquad (11)$$

For the analysis of the distance dependence of electron transfer in a reaction series, ΔG should almost remain constant in the series.

In the present instance, the thermodynamic driving force, ΔG, is not significantly varied for the series of alkyl phenyl sulphides (cf. Table 4), so that lower k_q values for sulphides containing bulky alkyl groups is not associated with the free energy barrier ($\Delta G^{\ddagger}$) for electron transfer. As the differences in ΔG are small, variation in k_q will then depend on the transmission coefficient, K, the size of which reflects the degree of electronic coupling between the electron transfer reactant and product states. Under circumstances in which there is relatively poor overlap of donar and acceptor wavefunctions, K << 1, the electron transfer step is nonadiabatic and the value of preexponential term in eq.(11) is related to the electron transfer distance by eq. (12)

$$K(r)\upsilon_n = 10^{13}\exp[-\beta(r-r_o)] \qquad (12)$$

where K(r) is the transmission coefficient at distance r(r is the sum of the radii of the reactants) and r_o is defined so that the reaction is adiabatic (i.e., K=1) at $r=r_o$.[25,32] Thus one may expect that the principal source of steric retardation involves the exponential fall off in transmission coefficient with distance and that $r=r_o$ for electron transfer with PhSMe. If the bulky t-butyl group contributes to the distance of separation (r) an increment of 2.0Å compared to ethyl (ΔG remains almost constant for ethyl, isopropyl,t-butyl and phenyl cf Table 4) the result is a reduction in k_q for t-BuSPh of Ca.7, which is of the proper order of magnitude observed with PhSEt and PhSt-Bu quenching. A value of $\beta = 1Å^{-1}$ is assumed for this reaction[30].

The ΔG values for the redox reactions of $^{*}Cr(NN)_3^{3+}$ with organic sulphides are given in Table 4. All these photoredox reactions fall in endoergic and slight exoergic regions. Within this ΔG region (normal region) both Marcus and Rehm-Weller models of electron transfer predict similar results i.e., the k_q value should increase with the decrease in ΔG values.[21,25] All the k_q values are less than the diffusion controlled rate constant i.e., all reactions are activation controlled. To check the validity of theories of electron transfer to these quenching data, the log k_q values are plotted against ΔG. The linear plots (Figure 6) observed for the quenching of all complexes indicate that the behaviour of all $^{*}Cr(NN)_3^{3+}$-sulphides photoredox systems is in accordance with the Marcus and Rehm-Weller theories of electron transfer (Scheme 1).

The quenching rate data given in Tables 2 and 3 reveal that the k_q values are higher for $^{*}Cr(bpy)_3^{3+}$ with all sulphides compared to the complexes $^{*}Cr(dmbpy)_3^{3+}$ and $^{*}Cr(phen)_3^{3+}$. The lower k_q values observed for $^{*}Cr(dmbpy)_3^{3+}$ is probably due to the higher ΔG values compared to $^{*}Cr(bpy)_3^{3+}$ (Table 4). Though the $E_{1/2}$ values are almost equal and the difference in the reactant radius between $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ is negligible,[33] the lower k_q values obtained with $^{*}Cr(phen)_3^{3+}$ may be explained by applying the Marcus theory of electron transfer processes to these reactions.

Table 4. ΔG_{23}(k J/mol), for the Quenching of $^{*}Cr(NN)_3^{3+}$ with Alkyl Aryl Sulphides in Acetonitrile at 298 K

No	Quencher	$Cr(bpy)_3^{3+}$	$Cr(dmbpy)_3^{3+}$	$Cr(phen)_3^{3+}$
1	Methyl phenyl sulphide	-0.96	17.36	0.96
2	*p*-Tolyl methyl sulphide	-12.55	5.77	-10.58
3	*m*-Tolyl methyl sulphide	-3.85	18.32	-1.92
4	*p*-Chlorophenyl methyl sulphide	0.96	19.28	2.89
5	*m*-Chlorophenyl methyl sulphide	10.62	28.91	12.51
6	*p*-Fluorophenyl methyl sulphide	0	18.32	1.92
7	*p*-Methoxyphenyl methyl sulphide	-26.98	-8.66	-25.06
8	*m*-Methoxyphenyl methyl sulphide	-8.66	9.64	-6.73
9	*p*-Acetylphenyl methyl sulphide	17.36	35.69	19.28
10	*p*-Nitrophenyl methyl sulphide	29.90	48.24	31.70
11	Ethyl phenyl sulphide	10.58	28.91	12.54
12	*i*-Propyl phenyl sulphide	8.70	27.01	10.61
13	*t*-Butyl phenyl sulphide	10.58	28.91	12.54
14	Diphenyl sulphide	10.58	28.91	12.54

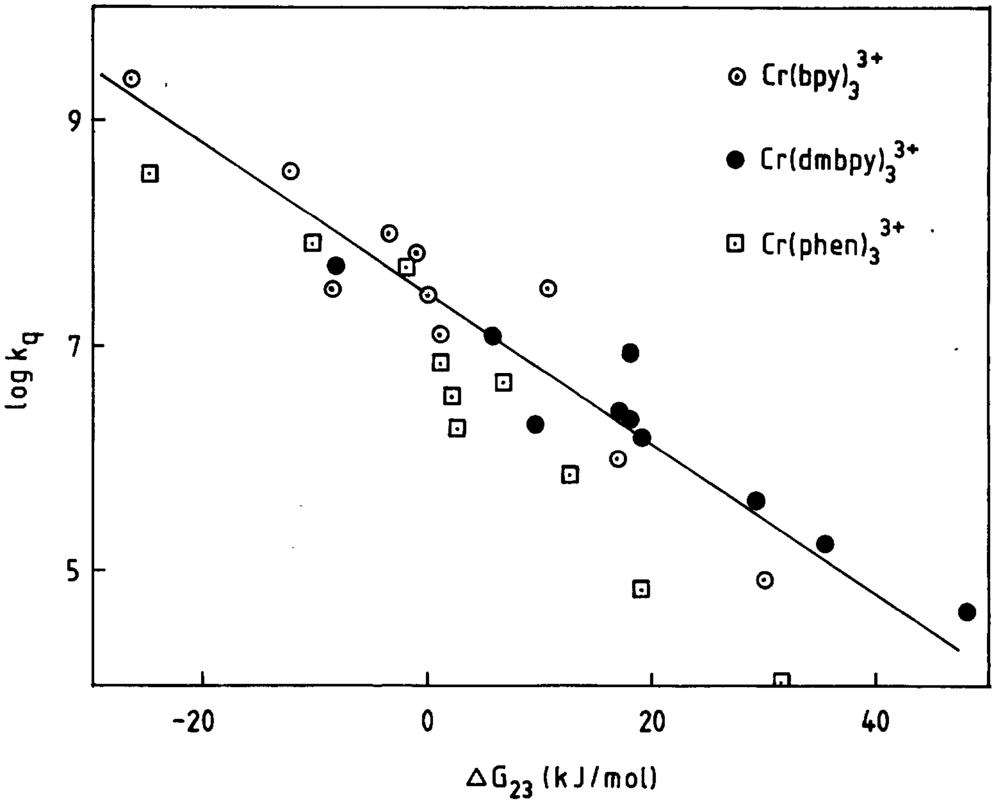


Figure 6. A plot of log k_q vs. ΔG_{23}

From eq.(6), it can be deduced that in situations of slow electron transfer, such as in the normal region, k_q is the product of "activated" rate of electron transfer and K_{eq} i.e.,[24]

$$k_q = K_{eq}\, k_{23} \tag{13}$$

$$= K_{eq}\nu_n \exp[-(\Delta G+\lambda\ )^2/4\lambda kT] \tag{14}$$

Taking logarithm, eq.(14) becomes

$$\log k_q = [\log(K_{eq}\nu_n) - \frac{\lambda}{4(2.303kT)}] - \frac{\Delta G(1+\Delta G/2\lambda)}{2(2.303kT)} \tag{15}$$

when $-\lambda \ll \Delta G \sim 0$, eq.(15) indicates that log k_q should vary linearly with ΔG with a slope of -0.366 and with an intercept of $\log(K_{eq}\upsilon_n)-\lambda/4(2.303kT)$. However, as ΔG becomes more negative the dependence of log k_q on ΔG will become quadratic. In the present study, the limiting slope of the plot of logk_q versus ΔG near zero free energy change region is -0.324 for $Cr(bpy)_3^{3+}$ and -0.339 for $Cr(phen)_3^{3+}$. In the acetonitrile solvent system, the values of K_q and υ_n are taken as 3.36[≠] and $1\times10^{11}s^{-1}$ respectively.[34] Using eq.(15), the experimental value, λ^{exp} can be estimated from the intercept of log k_q versus ΔG plot and λ^{exp} values for the three $Cr(NN)_3^{3+}$ complexes are collected in Table 5.

Table 5. Theoretical and experimental values of solvent reorganization energy (λ)[‡]

Complex	λ_o(Theoretical)	λ^{exp}(Experimental)
$Cr(bpy)_3^{3+}$	78.2	95.0
$Cr(dmbpy)_3^{3+}$	77.4	98.3
$Cr(phen)_3^{3+}$	78.2	112.1

[‡] in k J/mole

From the consideration of the nonequilibrium polarization of the medium, employing a dielectric continuum model for the solvent, the Marcus formula for the solvent reorganization energy[25], λ_o, is

$$\lambda_o = (e)^2(1/2r_a+1/2r_b-1/d)(1/D_{op}-1/D_s) \qquad (16)$$

where e is the electronic charge, r_a and r_b are the radii of the reactants $Cr(NN)_3^{3+}$ and ArSMe respectively, $d=r_a+r_b$, is the sum of radii of the reactants, D_{op} and D_s are the optical and static dielectric constant respectively. Taking r_a = 7.1 Å for $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$, 7.9Å for $Cr(dmbpy)_3^{3+}$[ǂ] and r_b = 4.0Å, according to

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[≠] $K_{eq} = 4\pi N\sigma^3/3000$ when one of the reactants is neutral.[34] σ is taken as 11.0 Å. Similar value has been taken in the quenching of $^*Cr(bpy)_3^{3+}$ with phenols.[35]

[ǂ] 7.1 and 7.9 Å are the radii of $Ru(bpy)_3^{2+}$ and $Ru(dmbpy)_3^{2+}$ estimated from space filling model in our previous work.[7] Weaver and co-workers[36] have assumed similar radii for Ru(II) and Cr(III) polypyridyl complexes.

eq.(16), λ_o values have been calculated and given in Table 5. From this comparison, we understand that the λ^{exp} is slightly larger than λ_o in all cases but the reorganization energy is mainly contributed by solvent dipole reorientation. The λ values in Table 5 lead us to conclude that higher λ_i $(=\lambda^{exp}-\lambda_o)$value with $Cr(phen)_3^{3}$ is mainly reponsible for the lower k_q values. Similar higher λ^{exp} values have also been estimated by Kitamura et al[37] in the reductive quenching of $^{*}Ru(bpy)_3^{2+}$ by aromatic amines. However they explained this difference between λ^{exp} and theoretical λ_o values with the assumption that the solvent reorganization around an amino group is more relevant than that around an aromatic ring or a whole molecule.

The electron transfer quenching constants calculated by Marcus theory (eq.6) are also given in Tables 2 and 3. Considering the assumptions involved in this theoretical treatment, the agreement between the calculated and experimental k_q values is good and supports the arguments presented above for $^{*}Cr(NN)_3^{3+}$-sulphides systems.

$^{*}Cr(NN)_3^{3+}$ can form transient ions, $Cr(NN)_3^{2+}$, efficiently following quenching by a variety of inorganic and organic substrates.[1] Transient cations of the organic quenchers have also been observed by flash photolysis.[23] In a study employing laser photolysis Brunchwig and Sutin[15] have verified the formation of $Cr(bpy)_3^{2+}$ when $Fe(aq)^{2+}$ ions were employed as quenchers. To check the nature of electron transfer, reversible or irreversible, we recorded the absorption spectrum of the solution after quenching reaction but we could not succeed to identify a peak corresponding to $Cr(NN)_3^{2+}$ in deaerated acetonitrile or aqueous acetonitrile. However if the quenching study is performed with $Cr(phen)_3^{3+}$ in aerated solution of acetonitrile, a broad absorption in the range 500-660 nm corresponding to $Cr(phen)_3^{2+}$ was observed (Figure 7) which confirms the irreversible electron transfer reaction in aerated acetonitrile solutions. A similar absorption spectrum for $Cr(phen)_3^{2+}$ has been observed by Bakac et al[38] in the reductive quenching of $^{*}Cr(phen)_3^{3+}$ by oxalate ions. In aerated acetonitrile solutions, the other product, highly reactive sulphide cation radical ($ArS^{\bullet +}R$) may react with oxygen to form finally the corresponding sulphoxide, ArS(O)R. The analysis of the products after quenching reaction confirms the formation of the oxidised product of the substrate, ArS(O)R. An alternative explanation for the formation

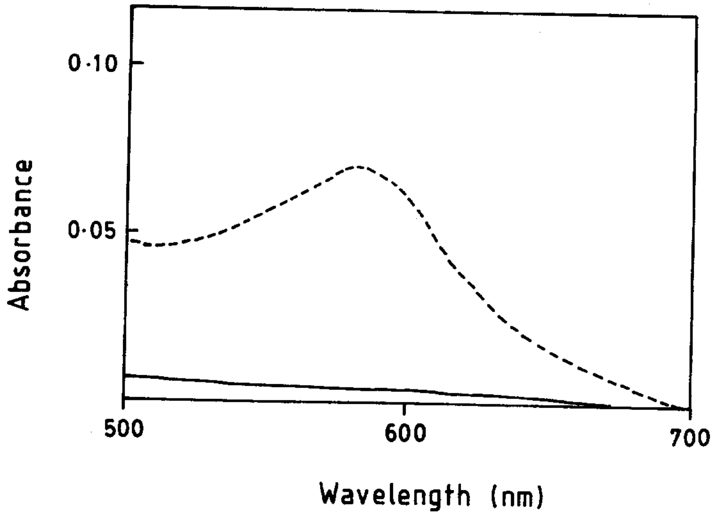

Figure 7. Absorption spectra of reaction mixture before(—) and after(--) quenching reaction.

of sulphoxide can be given from the recent results of Hoffmann and co-workers[39] on the photooxidation of phenols with $Cr(bpy)_3^{3+}$. The formation of singlet oxygen has been postulated (eq.18) when $Cr(bpy)_3^{3+}$ is irradiated in aerated solutions.

$$Cr(bpy)_3^{3+} \xrightarrow{h\upsilon} {}^*Cr(bpy)_3^{3+} \qquad (17)$$

$$ {}^*Cr(bpy)_3^{3+} + O_2 \xrightarrow{k_q'} Cr(bpy)_3^{3+} + {}^1O_2 \qquad (18)$$

The oxidation of organic sulphides with singlet oxygen to form the corresponding sulphoxides is a well investigated reaction.[12,13] In a recent study on the photooxidation of thioethers by polyoxotungstates, Chambers and Hill[40] have established that different products are obtained when the reactions are carried out in aerobic and anaerobic conditions. Davidson and Pratt[41] have also postulated cleavage products in the TiO_2 sensitized photooxidation of sulphides in addition to the oxidation products. The extensive study of estimation of product quantum yields in the photoreduction of $Cr(NN)_3^{3+}$ with different organic sulphides in different reaction conditions will be taken up in the near future.

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References

1. Jamieson,M.A.; Serpone, N.;Hoffmann,M.Z. *Coord.Chem.Rev.* 1981,39, 121; Neshvad,G.; Hoffmann,M.Z.; Bolte, M.;Sriram,R.; Serpone,N. *Inorg.Chem.* 1987,26,2984.
2. Endicott,J.F.; Ramasami,T.; Tamilarasan,R.; Lessard,R.B.; Ryu,C.K.; Brubaker,G.R. *Coord.Chem.Rev.* 1987,77,1; Ryu,C.K.; Endicott,J.F. *Inorg.Chem.* 1988,27,2203.
3. Forster,L.S. *Chem.Rev.* 1990, 90, 331.
4. Srinivasan,C.; Kuthalingam,P.; Chellamani,A.; Rajagopal,S.; Arumugam,N. *Proc. Indian Acad. Sci. (Chem. Sci).* 1984, 93, 157; Srinivasan, C.; Chellamani,A.; Rajagopal,S. *J.Org.Chem.*1985, 50, 1201.
5 Srinivasan,C.; Jegatheesan,P.P.; Rajagopal,S.; Arumugam,N. *Can.J.Chem,* 1987,65,2421; Srinivasan,C.; Rajagopal,S.; Chellmani,A. *J.Chem.Soc., Perkin Trans.2* 1990,1839; Pitchumani,K.; Subramanian,V.; Jegatheesan, P.P.;Srinivasan,C. *Proc.Indian Acad.Sci.(Chem.Sci.)* 1992,104, 67.
6. Rajagopal,S.; Sivasubramanian,G.; Suthakaran,R.; Srinivasan,C. *Proc. Indian Acad.Sci.(Chem.Sci.)*1991,103,637; Rajagopal,S.; Manohar,T.C.; Srinivasan,C. Submitted to *J.Mol.Cat.*
7. Kitamura,N.; Rajagopal,S.; Tazuke,S. *J.Phys.Chem.* 1987, 91, 3767; Rajagopal, S.; Vijayalakshmi, N. *Indian J.Chem.* 1991, 30A, 604; Rajagopal,S.; Rajendran,S.; Suthakaran,R.; Srinivasan,C. *Indian J .Chem.* 1991, 30A, 765.
8. Rajagopal,S.; Allen Gnanaraj,G.; Mathew,A.; Srinivasan,C. *J.Photochem. Photobiol.A.Chem.* 1992, 69, 83.
9 Kalyanasundaram,K. *Coord. Chem.Rev.*1982,46,159; Juris,A; Balzani,V; Barigelletti,F; Campagna,S;Belzer,P; von Zelewsky,A. *Coord.Chem.Rev.* 1988,84,85.
10. Clennan,E.L.; Oolman,K.A.; Yang,K.; Wang,D.X. *J.Org.Chem.* 1991, 56, 4286 and references cited therein.
11. Beecroft,R.A.;Davidson,R.S.; Goodwin,D.; Pratt,J.E. *Tetrahedron* 1984, 40, 4487.
12. Jensen,F.; Foote,C.S. *J.Am.Chem.Soc.*1988,110, 2368 and references cited therein.
13. Akasaka,T.;Haranaka,M.; Ando,W. *J.Am.Chem.Soc.* 1991,113,9898 and references cited therein.

14. Allen Gnanaraj,G.; Rajagopal,S.;Srinivasan,C. *Proc.Indian Acad.Sci. (Chem.Sci.)* 1992, 104, 9.
15. Brunchwig,W.; Sutin,N. *J.Am.Chem.Soc.* 1978, 100, 7568.
16. Kane-Maguire,N.A.P.; Hallock,J.S. *Inorg.Chim.Acta.* 1979, 35L,309.
17. Bakac,A.; Zahir,K.; Espenson,J.H. *J.Am.Chem.Soc.*1988,110,5059.
18. Perrin,D.D.; Armargo,A.L.F.; Perrin,D.R. *Purification of laboratory chemicals*,Pergamon Press, New York, 1980.
19. Watanabe,Y.; Iyanagi,T.; Oae,S. *Tetrahedron Lett.* 1980, 21, 3685.
20. Ando,W. *Sulphur Reports* 1981, 1, 147.
21. Kavarnos,G.J.; Turro,N.J. *Chem.Rev.* 1986, 86, 401.
22. Fox,M.A.; Chanon,M.Eds. *Photoinduced Electron Transfer* Elsevier: Amsterdam, 1988.
23. Ballardini,R.; Varani,G.; Indelli,M.T.; Scandola,F.; Balzani,V. *J.Am.Chem.Soc.*, 1978, 100, 7219; Ohno T.; Kato,S. *Bull.Chem.Soc. Jpn.* 1984, 57,1528; Ohno,T.; Yoshimura,A.; Shioyama,H.; Mataga,N. *J. Phys. Chem.* 1987,91,4365.
24. Chen,J.M.; Ho,T.I.; Mou,C.Y. *J.Phys.Chem.* 1990, 94, 2889.
25. Marcus,R.A.; Sutin,N. *Biochim.Biophys.Acta.*1985,811, 265.
26. Bock,C.R.; Connor,J.A.; Guitierrez,A.R.; Meyer,T.J.; Whitten,D.G.; Sullivan,B.P.; Nagle,J.K. *J.Am.Chem.Soc.* 1979, 101, 4815.
27. Hansch,C.; Leo,A.; Taft,R.W. *Chem.Rev.* 1991, 91, 165.
28. Miedlar,K.; Das.P.K. *J.Am.Chem.Soc.* 1982, 104, 7462.
29. Shorter,J. *Correlation Analysis of Organic Reactivity,* John Wiley & Sons, New York, 1982.
30. McLendon,G. *Acc.Chem.Res.* 1988, 21, 160.
31. Jones,II G.; Chatterjee,S. *J.Phys.Chem.*1988,92, 6862.
32. Isied,S.S.; Vassilian,A.; Wishart,J.; Creutz,C.; Schwarz,H.A.; Sutin,N. *J.Am.Chem.Soc.* 1988, 110, 635.
33. Ohno,T.; Yoshimura,A.; Mataga,N. *J.Phys.Chem.* 1990, 94, 4871.
34. Sutin,N, *Prog.Inorg.Chem.* 1983, 30, 441.
35. Gsponer,H.;Arguello,G.A.;Arguello,G.A.;Staricco,E.H. *Inorg. Chim.Acta.* 1991, 189, 207.
36 Gennett,T; Milner,D.F; Weaver,M.J.*J.Phys.Chem.*1985, 89, 2787.
37 Kitamura,N.; Kim,H.B.; Okano,S.;Tazuke,S. *J.Phys.Chem.*1989, 93,5750.
38. Steffan,C.R.;Bakac,A.;Espenson,J.H. *Inorg.Chem.* 1989,28, 2992.
39. Pizzocaro,C.; Bolte,M.; Hoffmann,M.Z. *J. Photochem. Photobiol.A. Chem.* 1992, 68, 115.
40. Chambers,R.C.; Hill,C.L. *J. Am. Chem. Soc.* 1990, 112, 8427.
41. Davidson,R.S.;Pratt,J.E. *Tetrahedron Lett.*1983,24,5903.