

Excited state electron transfer reactions of *tris*(2, 2'-bipyridine) chromium(III) ion with organic sulphides

G ALLEN GNANARAJ¹, S RAJAGOPAL^{1*} and C SRINIVASAN²

¹School of Chemistry, Madurai Kamaraj University, Madurai 625021, India

²Department of Materials Science, Madurai Kamaraj University, Madurai 625021, India

MS received 13 May 1991; revised 14 October 1991

Abstract. The quenching rate constants, k_q , for the excited state electron transfer reactions of *tris*(2, 2'-bipyridine)chromium(III) ion with several aryl methyl sulphides (ArSMe) obtained by the luminescence quenching technique, are accelerated by electron releasing groups and retarded by electron withdrawing groups present in the aryl moiety of ArSMe. The plot of $RT \ln k_q$ vs. $E_{1/2}$ values of different sulphides is linear, indicating the electron transfer nature of the reaction. Studies with alkyl phenyl sulphides demonstrate the importance of the steric effect in these photoredox reactions.

Keywords. Excited state electron transfer reactions; chromium(III) complex; organic sulphides.

1. Introduction

Organic sulphides are good electron donors and undergo electron transfer reactions with singlet oxygen and excited states of organic sensitizers like 9, 10-dicyanoanthracene (Beecroft *et al* 1984; Clennan and Chen 1989). Though the excited states of polypyridine complexes of ruthenium(II), RuL_3^{2+} , are reductively quenched by organic donors like aromatic amines and phenols, they do not undergo photoredox reactions with organic sulphides (Kalyanasundaram 1982; Juris *et al* 1988). The 2E excited states of *tris*(2, 2'-bipyridine) chromium(III) ion, $^* \text{Cr}(\text{bpy})_3^{3+}$ and their substituted analogues are more powerful one-electron oxidising agents than $^* \text{Ru}(\text{bpy})_3^{2+}$ and have lifetimes long enough to permit bimolecular quenching events (Jamieson *et al* 1981). The redox potential of $^* \text{Cr}(\text{bpy})_3^{3+}$ ($E_{1/2} = 1.44 \text{ V}$) is also higher compared to that of $^* \text{Ru}(\text{bpy})_3^{2+}$ ($E_{1/2} = 0.75 \text{ V}$) (Jamieson *et al* 1981; Juris *et al* 1988). The results of excited state electron transfer reactions of $\text{Cr}(\text{bpy})_3^{3+}$ with several alkyl phenyl and aryl methyl sulphides in acetonitrile studied by the luminescence quenching technique are presented here.

2. Experimental

Tris(2, 2'-bipyridine) chromium(III) perchlorate was prepared and purified according to the procedure of Kane-Maguire and Hallock (1979). All alkyl phenyl and aryl

* For correspondence

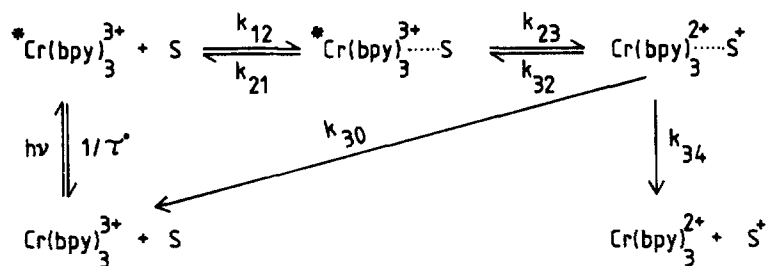
methyl sulphides were obtained by reported procedures and their purities checked by standard methods (Srinivasan *et al* 1985, 1990). The solvent acetonitrile was purified before use (Perrin *et al* 1980). The emission intensity was measured with a JASCO FP-770 spectrofluorometer. The sample solutions were deaerated for 30 min by purging with pure nitrogen gas. The quenching rate constant, k_q , was obtained from the Stern–Volmer plots,

$$I^0/I = 1 + k_q\tau[Q], \quad (1)$$

where I^0 and I are the emission intensities of $^*Cr(bpy)_3^{3+}$ in the absence and presence of quencher, respectively, and τ is the emission lifetime of $^*Cr(bpy)_3^{3+}$ in the absence of quencher. The τ value of 70 μs of $^*Cr(bpy)_3^{3+}$ (Jamieson *et al* 1981) has been used in the calculation of k_q . The solutions were excited at 400 nm and the emission intensity was monitored at the wavelength of 728 nm. In the quenching of $^*Cr(bpy)_3^{3+}$ with metal complexes and oxalate ions the same excitation and emission wavelengths were employed (Brunschwig and Sutin 1978; Steffan *et al* 1989).

3. Results and discussion

The k_q values for the various sulphides along with the values of oxidation potential (wherever available) are given in table 1. The $\log k_q$ values of sulphides are plotted against ΔG_{23} (see footnote) in figure 1 and the linear plot indicates that all sulphides have similar behaviour and thus the quenching process can be discussed by a mechanism depicted in scheme 1.



Scheme 1. Mechanism for the quenching of $^*Cr(bpy)_3^{3+}$ with organic sulphides.

Applying steady state approximation and Marcus theory (Marcus and Sutin 1985; Kavarnos and Turro 1986) (2) for the electron transfer step,

$$\Delta G_{23}^\ddagger = \lambda/4(1 + \Delta G_{23}/\lambda)^2, \quad (2)$$

k_q is related to ΔG_{23} by

$$k_q = K_{12}v_{23}F \exp[-\lambda/4(1 + \Delta G_{23}/\lambda)/RT], \quad (3)$$

ΔG_{23} values can be calculated from the redox potentials of $^*Cr(bpy)_3^{3+}$ and sulphides (S) by equation

$$\Delta G_{23} = E_{1/2}(S^+/S) - E_{1/2}(^*Cr^{3+}/Cr^{2+}) + W_p - W_r,$$

where W_p and W_r are the coulombic terms (Marcus and Sutin 1985).

Table 1. Quenching rate constants, k_q , for ${}^*Cr(bpy)_3^{3+}$ with organic sulphides in acetonitrile at 298 K and corresponding σ and E_s values.

Quencher [#]	No.	$k_q(M^{-1}s^{-1})$	σ/E_s
			σ
Methyl phenyl sulphide (1.53)	1	7.1×10^7	0
Methyl <i>p</i> -tolyl sulphide (1.41)	2	3.9×10^8	-0.17
Methyl <i>m</i> -tolyl sulphide	3	1.1×10^8	-0.07
<i>p</i> -Chlorophenyl methyl sulphide (1.55)	4	1.3×10^7	0.23
<i>m</i> -Chlorophenyl methyl sulphide	5	3.2×10^7	0.37
<i>p</i> -Fluorophenyl methyl sulphide	6	3.0×10^7	0.07
<i>p</i> -Methoxyphenyl methyl sulphide (1.26)	7	2.5×10^9	-0.27
<i>p</i> -Nitrophenyl methyl sulphide (1.85)	8	9.2×10^4	0.78
			E_s
Ethyl phenyl sulphide	9	2.6×10^7	-0.07
Isopropyl phenyl sulphide	10	1.3×10^7	-0.47
<i>t</i> -Butyl phenyl sulphide	11	4.8×10^6	-1.54

[#] Values in parentheses are the redox potentials of the quenchers in V vs. SCE (Watanabe *et al* 1980)

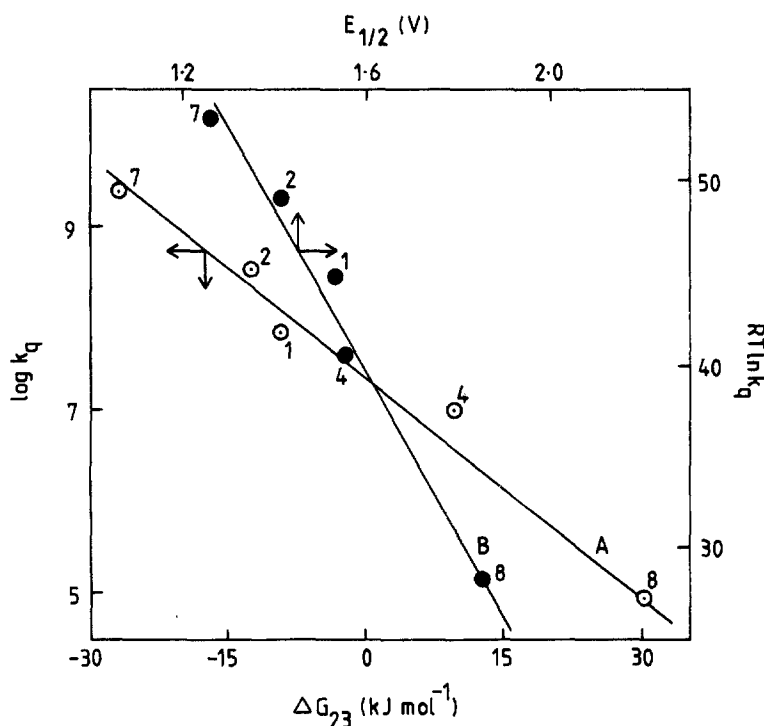


Figure 1. A. Plot of $\log k_q$ vs. ΔG_{23} . B. Plot of $RT \ln k_q$ vs. $E_{1/2}$ values of sulphides. The points in the figure are referred to by the same numbers as represented in table 1.

where ΔG_{23} and ΔG_{23}^\ddagger are the free energy change and the free energy of activation of the electron transfer step respectively, λ is the reorganisation energy which includes changes both in the inner coordination spheres (λ_i) and in the outer solvation shells (λ_o) accompanying electron transfer. ν_{23} is the frequency factor, F , the fraction of

electron transfer quenching event, is represented by

$$F = (k_{30} + k_{34}) / (k_{30} + k_{32} + k_{34}). \quad (4)$$

If $k_{30} + k_{34} \gg k_{32}$, according to Bock *et al* (1979), (3) is reduced to (5),

$$RT \ln k_q = RT \ln k_q(0) - \Delta G_{23}/2, \quad (5)$$

where $k_q(0)$ is a constant for a series of structurally and electronically analogous quenchers. The linear plot of $RT \ln k_q$ vs. ΔG_{23} values of sulphides gives a slope of 0.5 (figure 1) indicating the absence of back electron transfer to form ${}^*Cr(bpy)_3^{3+}$ (Bock *et al* 1979).

The k_q values collected in table 1 show that the rate of quenching is accelerated by electron-releasing groups and retarded by electron-withdrawing groups present in the aryl moiety of ArSMe. To understand the influence of substituents on the rate of electron transfer, the Hammett plot of $\log k_q$ vs. σ has been made (figure 2) and the correlation is satisfactory ($r = 0.953$), the ρ value being -3.64 . However the correlation is substantially improved ($r = 0.990$) if *m*-Cl is excluded and the ρ value is -3.97 . There is no improvement in the correlation if σ^+/σ^- are used instead of σ . The behaviour of substituents is 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 ${}^*Cr(bpy)_3^{3+}$ whereas the electron-withdrawing groups have the reverse trend.

The k_q values given for different alkyl phenyl sulphides indicate the importance of the steric effect in the electron transfer reaction of sulphides with ${}^*Cr(bpy)_3^{3+}$. The

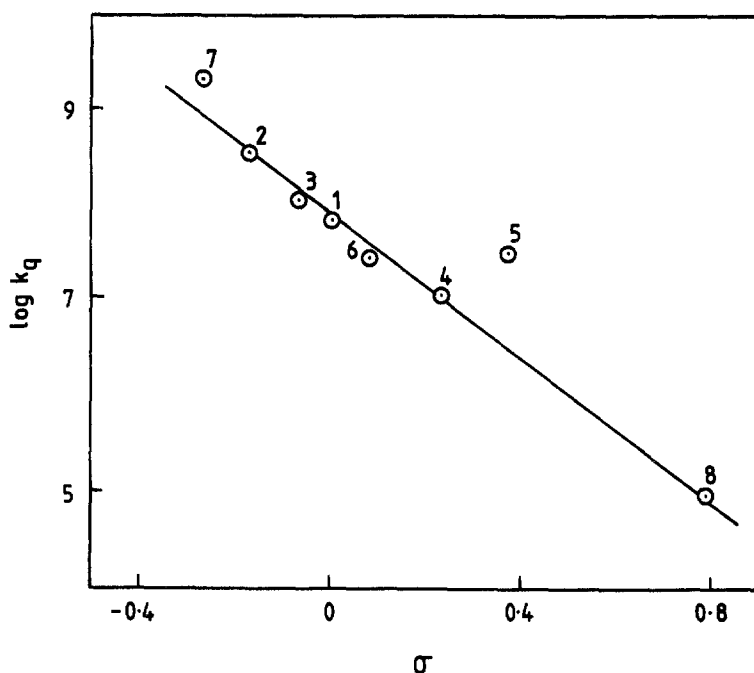


Figure 2. Hammett plot of $\log k_q$ vs. σ . The points in the figure are referred to by the same numbers as given in table 1.

steric effect in a reaction can be evaluated by Taft's steric parameter, E_s (Taft 1956):

$$\log k_q = \delta E_s + h, \quad (6)$$

where E_s and δ are the steric substituent and steric susceptibility constants respectively. The plot of $\log k_q$ vs. E_s is poor with a correlation coefficient of $r = 0.908$ and a slope = -0.634 (δ). Though the correlation is poor, the lower k_q values obtained with sulphides containing bulky groups indicate the significant role of the steric effect in the luminescence quenching of $^*Cr(bpy)_3^{3+}$ with organic sulphides. The importance of steric effect in the excited state electron transfer reactions of RuL_3^{2+} with aromatic amines has been realised in our previous study (Rajagopal and Vijayalakshmi 1991).

Acknowledgement

GA thanks Madurai Kamaraj University for a fellowship.

References

- Becroft R A, Davidson R S, Goodwin D and Pratt J E 1984 *Tetrahedron* **40** 4487
Bock C R, Conner J A, Guitierrez A R, Meyer T J, Whitten D G, Sullivan B P and Nagle J K 1979 *J. Am. Chem. Soc.* **101** 4815
Brunschwig B and Sutin N 1978 *J. Am. Chem. Soc.* **100** 7568
Clennan E L and Chen X 1989 *J. Am. Chem. Soc.* **111** 8212
Jamieson M A, Serpone N and Hoffmann M Z 1981 *Coord. Chem. Rev.* **39** 121
Juris A, Balzani V, Barigelletti F, Campagna S, Belzer P and von Zelewsky A 1988 *Coord. Chem. Rev.* **84** 85
Kalyanasundaram K 1982 *Coord. Chem. Rev.* **46** 159
Kane-Maguire N A P and Hallock J S 1979 *Inorg. Chim. Acta* **35L**309
Kavarnos G J and Turro N J 1986 *Chem. Rev.* **86** 401
Marcus R A and Sutin N 1985 *Biochim. Biophys. Acta* **811** 265
Perrin D D, Armargo A L F and Perrin D R 1980 *Purification of laboratory chemicals* (New York; Pergamon)
Rajagopal S and Vijayalakshmi N 1991 *Indian J. Chem.* **A30** 604
Srinivasan C, Chellamani A and Rajagopal S 1985 *J. Org. Chem.* **50** 1201
Srinivasan C, Rajagopal S and Chellamani A 1990 *J. Chem. Soc. Perkin Trans.* **2** 1839
Steffan C R, Bakac A and Espenson J H 1989 *Inorg. Chem.* **28** 2992
Taft R W 1956 *Steric effects in organic chemistry* (ed.) M S Newman (New York; John Wiley and Sons) Chap. 13
Watanabe Y, Iyanagi T and Oae S 1980 *Tetrahedron Lett.* **21** 3685