Quenching of Excited-state Xanthone and Thioxanthone† by Inorganic Anions

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The quenching rates of both singlet and triplet states of thioxanthone by a group of inorganic anions have been determined, enabling a comparison of their reactivities. The quenching rates of triplet xanthone were also measured. All determinations were made in MeCN–H_2O (3:2 v/v). The various rates are correlated with the free-energy change for electron-transfer, ΔG_{23}°, according to the treatments of Rehm and Weller and of Polanyi; an unexpectedly good fit is given by the latter.

There are several indications that the quenching of the triplet states of carbonyl compounds involves a charge-transfer state or exciplex. Thus the rate constants for quenching by reductants such as amines,[1,2] amides,[3] sulphides,[4] indoles,[5] alkenes,[6] ethers,[7] and methoxybenzenes[8] can be correlated with the gas-phase ionisation potentials or the solution oxidation potentials of the donors as expected for a charge- or electron-transfer mechanism. The triplet exciplex,[1,2,4–6] by analogy with the well developed concept of a singlet exciplex due to Weller,[9] is believed to be formed in the primary step of electron-transfer (Scheme) and either dissociates into radical species or reverts to ground-state reactants (*via* intersystem crossing). Anion-induced quenching of excited carbonyl compounds has been accounted for in terms of partial or full electron transfer in the cases of singlet and triplet quenching of biacetyl,[10] a group of carbonyl triplets,[11] and the triplet states of duroquinone[12,13] and 5-nitrofuroic acid;[14] in the last mentioned case observation was made of the semioxidised species $X_2^{-\bullet}$ (X = I or CNS). In a related paper,[15] Martins and Kemp fit accumulated rate data for triplet quenching of duroquinone, 5-nitrofuroic acid, 2-nitrothiophene, and *N*-butyl-5-nitro-2-furamide by a variety of anions to a single plot of the type developed by Rehm and Weller[9] (see later). Recently Shizuka and Obuchi[16] obtained good agreement between their experimental data on the quenching of aromatic ketone triplets by various anions and the linear free energy relation due to Polanyi,[17] rather than that of Rehm and Weller, although they could not detect any species of the type $X_2^{-\bullet}$.

The results in this paper confirm that electron-transfer is responsible for the quenching of both singlet and triplet states of thioxanthone, and allow a direct comparison of the reactivities of these states towards a range of donor anions. Similar conclusions are reached for triplet xanthone.

Experimental

Thioxanthone (Aldrich) was recrystallised twice from light petroleum (b.p. 60—80 °C); m.p. 212—215 °C (lit.,[18] 212 °C). Xanthone (Hopkin and Williams) was recrystallised twice from ethanol; m.p. 173—175 °C (lit.,[18] 175 °C). Triply distilled water was prepared by a previously published method,[19] and acetonitrile (Fluka) was of spectroscopic grade. The solvent mixture used throughout was MeCN–H_2O (3:2 v/v). Other chemicals were of the highest purity commercially available and were used without further purification. The anions used were employed either as sodium or potassium salts. All test solutions were deoxygenated by flushing with high purity argon (B.O.C. 99.999%) for 15 min. Fluorescence spectra were recorded with a Perkin-Elmer MPF-3 spectrofluorimeter (Figure 1). The fluorescence lifetime of thioxanthone was measured at the Royal Institution (London) by time-correlated single-photon counting.

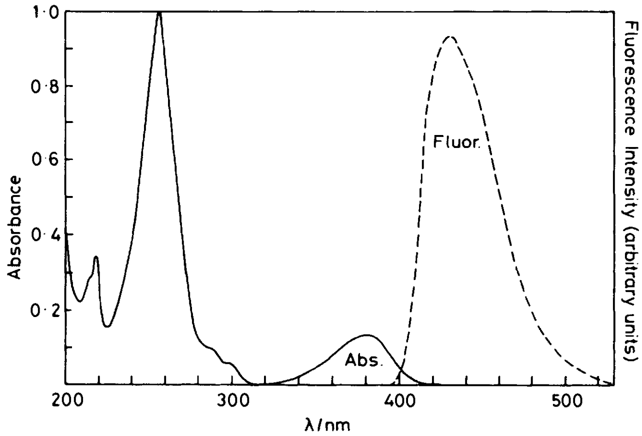

Figure 1. Absorption and fluorescence spectra of thioxanthone in MeCN–H_2O (3:2 v/v); [thioxanthone] = 2 × 10^{-5} mol dm^{-3}, λ_{exc} = 380 nm

Nanosecond laser flash photolysis was carried out with an Oxford Lasers KX2 excimer laser, using a Kr–F_2 mixture which generates a 249 nm pulse of energy of *ca.* 250 mJ and of 15 ns duration; the detection equipment has been described before.[20] The concentrations of thioxanthone and xanthone were adjusted to give an absorbance of about 2.0 at the laser excitation wavelength of 249 nm for the kinetic quenching experiments. Triplet–triplet absorption spectra were taken point-by-point by varying the monochromator setting (Figure 2). The decay traces were photographed from the oscilloscope and kinetic analysis was made by computer as described before.[20]

Results

The broad absorption spectra of the triplet states of xanthone and thioxanthone in MeCN–H_2O (3:2 v/v) are shown in Figure 2; their first-order decays were monitored at the $\lambda_{max.}$ values of 610 ± 5 and 605 ± 5 nm, respectively. The first-order triplet-state decay rate constants (k_1) of the two xanthones increased with increasing concentrations of added anions to give pseudo-first-order rate constants (k_2) (This quenching is not caused by the countercation as there was no differential effect of using sodium or potassium salts.[21c]) The second-order quenching rates of the two triplet xanthones (^3k_q) were obtained from the slope of the plot of equation (1), *i.e.*, by plotting k_2 *versus* anion

$$k_2 = k_1 + {}^3k_q[Q] \qquad (1)$$

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† Thioxanthen-9-one.

concentration (Q), as indicated in Figures 3 and 4 for xanthone and thioxanthone, respectively, where k_1^{-1} is the lifetime of the xanthones without added quencher. It is known that the triplet lifetime of the xanthones depends upon their concentration, indicating self-quenching,[22] and we took the precaution of retaining the same concentration of ketone throughout all the experiments. Rate constants (^1k_q) for the singlet quenching of fluorescence of thioxanthone by anions were obtained from conventional Stern–Volmer plots, typified by Figure 5, of I_0/I *versus* [Q], to give a slope K^{SV} (the Stern–Volmer constant) which was factorised using the relation $K^{SV} = {}^1k_q\tau_0$ (τ_0 = fluorescence lifetime of thioxanthone in absence of quencher). In no case was there evidence for any new emitting species such as an exciplex on addition of anions. In general we were unable to detect the presence of the semioxidised inorganic ion in absorption following the laser pulse; however, in the case of SCN^- ion, a weak absorption maximising at 500 ± 5 nm was found in MeCN–H_2O (3:2 v/v) following flash photolysis of either xanthone or thioxanthone. This is similar to that of $(SCN)_2^{-\bullet}$ previously reported in aqeuous solution,[13] acetone,[14] and MeCN.[15] (The yields of such semioxidised species are usually particularly small in water as compared with pure MeOH or MeCN.[23,24])

In Table 1 are presented spectral and physical constants for photosensitisers utilised in this study. Values of the quenching constants of the singlet and triplet ketones at room temperature are summarised in Tables 2 and 3.

Table 1. Spectral and physical data for ketones in MeCN–H_2O (3:2 v/v)

Molecule	τ_0/ns	$\Delta^1E_{0,0}$/eV	$\Delta^3E_{0,0}$[a]/eV	$E_{\frac{1}{2}}$[b](*vs.* n.H.e.)/V
Thioxanthone	4.9[c]	3.069[d]	2.84	−1.37[e]
Xanthone			3.21	−1.40[f]
Biacetyl			2.48	−0.78[g]

[a] S. L. Murov, 'Handbook of Photochemistry,' Dekker, New York, 1973. [b] After correction for change of reference electrode from s.c.e. to n.H.e. by addition of 0.25 V. [c] Monitored at λ_F = 432 nm (maximum emission). [d] Obtained from intersection of absorption and fluorescence spectrum (see Figure 1). [e] T. Aruga, O. Ito, and M. Matsudo, *J. Am. Chem. Soc.*, 1979, **101**, 7585 (measured in Me_2NCHO and $Bu^n{}_4NClO_4$ as supporting electrolyte). [f] C. K. Mann and K. K. Barnes, 'Electrochemical Reactions in Nonaqueous Systems,' Dekker, New York, 1970, ch. 6 (measured in Me_2NCHO and $Bu^n{}_4NI$ as supporting electrolyte). [g] From ref. 2 (measured in 50% aqueous ethanol at pH 12.65; a figure of −1.21 V *vs.* n.H.e. is given in ref. 1).

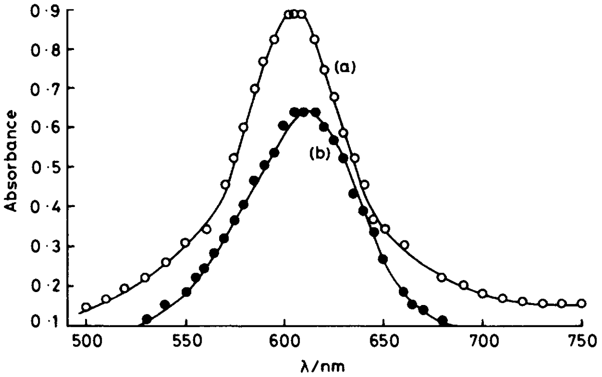


Figure 2. Spectrum of the transient absorption obtained by laser flash photolysis of deaerated solutions of (a) thioxanthone (2 × 10^{-4} mol dm^{-3}) and (b) xanthone (2 × 10^{-4} mol dm^{-3}) in MeCN–H_2O (3:2 v/v) taken 10 μs after the pulse

Table 2. Fluorescence-quenching rate constants of thioxanthone by inorganic anions in MeCN–H_2O (3:2 v/v)

Inorganic anion	(no.)	$E(D^{+\bullet}/D)$[a]/V *vs.* s.H.e.	$\Delta G_{23}°$/kJ mol^{-1}	$10^{-9}\,{}^1k_q$/$dm^3\,mol^{-1}\,s^{-1}$
$[Fe(CN)_6]^{4-}$	(1)	0.356[b]		See text
$[IrCl_6]^{3-}$	(2)	0.892 ± 0.009[c]		See text
NO_2^-	(3)	1.0 ± 0.1[d]	−73.25	9.27 ± 0.05
$SeCN^-$	(4)	1.27[e]	−47.20	9.23 ± 0.19
I^-	(5)	1.33 ± 0.03,[f] 1.4 ± 0.05[d]	−41.41	9.38 ± 0.23
$S_2O_3^{2-}$	(6)	1.34,[g] 1.35[h]	−40.44	2.78 ± 0.05
N_3^-	(7)	1.37 ± 0.02,[h] 1.87[k]	−37.55	4.60 ± 0.060
SCN^-	(8)	1.60 ± 0.03,[f] 1.601,[g] 1.50[k]	−15.26	8.58 ± 0.10
Br^-	(9)	1.904,[g] 2.0 ± 0.1[k,d]	+13.97	2.54 ± 0.07

[a] The first figure listed was utilised in calculating $\Delta G_{23}°$. [b] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, 1935, **39**, 945. [c] D. W. Margerum, K. L. Chellappa, F. P. Bossu, and G. L. Bruce, *J. Am. Chem. Soc.*, 1975, **97**, 6894. [d] V. M. Berdnikov and N. M. Bazhin, *Russ. J. Phys. Chem.*, 1970, **44**, 395. [e] Calculated using E(ctts) = 5.27 eV from M. J. Blandamer and M. Fox, *Chem. Rev.*, 1970, **70**, 59, and $E(\text{ctts}) = 1.35\,E(D^{+\bullet}/D) + 3.55$ (in eV) given in ref. 21. [f] D. M. Stanbury, W. K. Wilmarth, S. Khalaf, H. N. Po, and J. E. Byrd, *Inorg. Chem.*, 1980, **19**, 2715. [g] From ref. 12*b*. [h] W. K. Wilmarth, D. M. Stanbury, J. E. Byrd, H. N. Po, and C.-P. Chua, *Coord. Chem. Rev.*, 1983, **51**, 155. [k] From ref. 21.

Table 3. Triplet-quenching rate constants of ketones by inorganic anions in MeCN–H_2O (3:2 v/v)

Inorganic anion (no.)[a]	Thioxanthone		Xanthone		Biacetyl	
	$\Delta°G_{23}$/kJ mol^{-1}	^3k_q/$dm^3\,mol^{-1}\,s^{-1}$	$\Delta°G_{23}$/kJ mol^{-1}	^3k_q/$dm^3\,mol^{-1}\,s^{-1}$	$\Delta°G_{23}$/kJ mol^{-1}	^3k_q/$dm^3\,mol^{-1}\,s^{-1}$[a,b]
(1)	−113.31	(5.02 ± 0.13) × 10^9	−146.08	(5.14 ± 0.22) × 10^9		
(2)	−61.59	(4.10 ± 0.12) × 10^9	−94.36	(4.56 ± 0.11) × 10^9		
(3)	−51.17	(4.02 ± 0.17) × 10^9	−83.94	(5.37 ± 0.17) × 10^9		
(4)	−25.12	(7.76 ± 0.12) × 10^9	−57.89	(7.68 ± 0.12) × 10^9	−47.28	5.7 × 10^9
(5)	−19.23	(6.60 ± 0.18) × 10^9	−52.10	(7.13 ± 0.12) × 10^9	−41.49	5.5 × 10^9
(6)	−18.37	(1.60 ± 0.05) × 10^9	−51.14	(2.68 ± 0.05) × 10^9		
(7)	−15.47	(3.78 ± 0.03) × 10^9	−48.24	(4.88 ± 0.13) × 10^9		
(8)	+6.81	(2.98 ± 0.17) × 10^7	−25.95	(6.10 ± 0.11) × 10^9	−15.34	1.7 × 10^9
(9)	+36.05	(1.14 ± 0.10) × 10^6	+3.28	(1.42 ± 0.04) × 10^8	+13.89	5.6 × 10^7

[a] Numbering as in Table 2. [b] From ref. 10, measured by phosphorescence quenching in aqueous solution at room temperature.

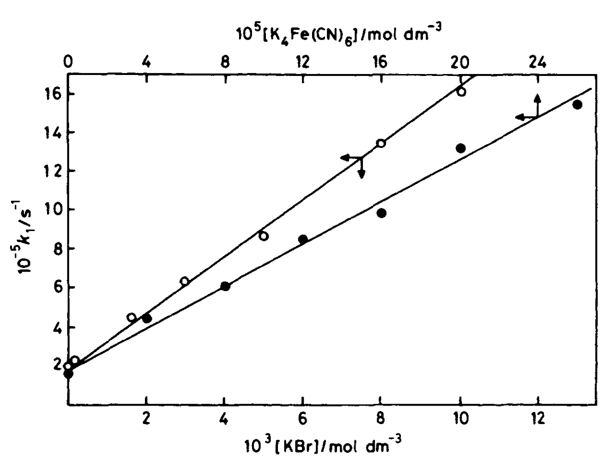


Figure 3. Triplet quenching of xanthone by electron donors

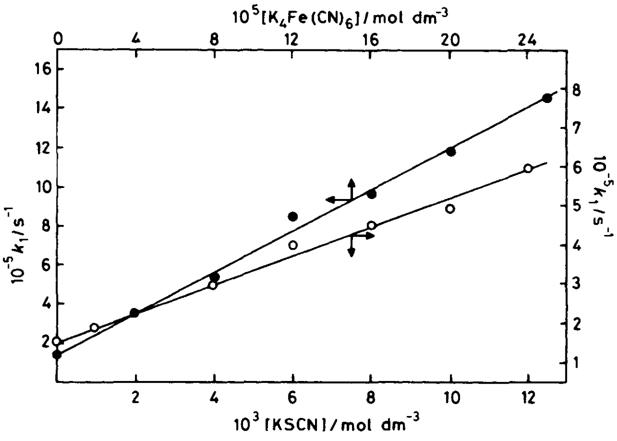


Figure 4. Triplet quenching of thioxanthone by electron donors

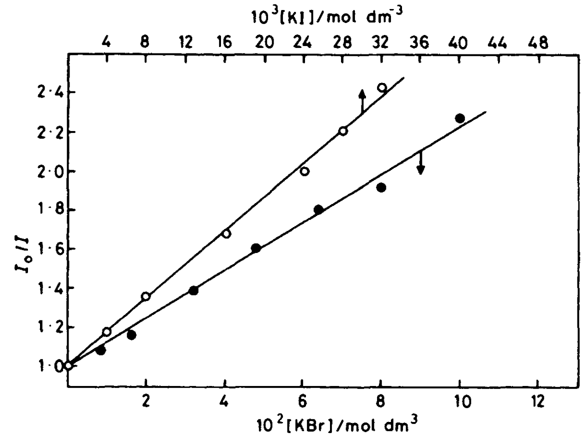


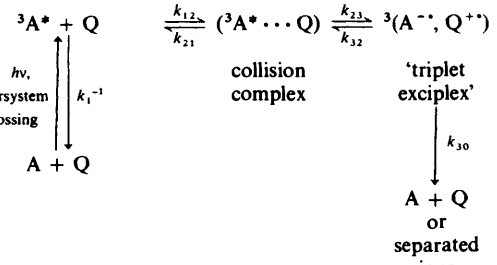
Figure 5. Stern–Volmer plots for the quenching of singlet thioxanthone by anions; λ_{exc} = 380 nm, λ_F = 432 nm

Discussion

Excited-state Spectra.—It is known that flash photolysis of aromatic carbonyl compounds in aqueous solution produces two distinct transients, namely the short-lived triplet-state absorption and the much longer-lived absorption due to ketyl radicals or radical anions (depending on pH). The transient produced upon laser photolysis of xanthone in MeCN–H_2O with $\lambda_{max.}$ 610 ± 5 (Figure 1) has been observed both in water and in 95% ethanol by other workers,[25,26] and it has been assigned[25b] to the triplet–triplet absorption on the basis of energy-transfer data, *etc.*, rather than to a ketyl radical. Kinetic quenching of the transient due to triplet thioxanthone in MeCN–H_2O was monitored at 605 ± 5 nm, a wavelength close to that for the transient observed at 625 ± 5 nm in pure acetonitrile by Yip *et al.*[22] (Our value for $\lambda_{max.}$ in pure acetonitrile is 630 ± 10 nm.)

The fluorescence of thioxanthone shows increases both in φ_F and λ_F with solvent polarity.[27,28] One explanation[27] of this behaviour invokes a decrease in the rate of intersystem crossing, $S_1(\pi\pi^*) \longrightarrow T_2(n\pi^*)$, with increasing solvent polarity as the energy-gap increases, but an alternative view[28] is that solvent influences the internal conversion $S_1(n\pi^*) \longrightarrow S_0$ because of the proximity of the $S_1(\pi\pi^*)$ and $S_2(n\pi^*)$ levels which are subject to vibronic coupling.[28,29] Our fluorescence spectrum for thioxanthone (Figure 1) is in good agreement with that of Lai and Lim.[28]

Quenching Data.—Singlet thioxanthone is quenched very effectively by anions covering a range of oxidation potentials of nearly 1.0 V (Table 2). The short lifetime of 4.9 ns prevented examination of quenching by sparingly soluble materials such as $K_4[Fe(CN)_6]$ and $K_3[IrCl_6]$. With the notable exception of $S_2O_3^{2-}$ ion, quenching is near the diffusion-controlled rate throughout the exoergonic region, which suggests that heavy-atom-induced spin–orbit effects in promoting intersystem crossing make an insignificant contribution to the quenching process. The deviance of $S_2O_3^{2-}$ may be associated with the problem of accuracy of associated thermodynamic data: electrochemical potentials for such inorganic radical systems are inherently more imprecise than for reversible systems. Triplet state quenching for both ketones (Table 3) can be accounted for by the electron-transfer mechanism developed by Rehm and Weller,[9] and modified by others for triplet-state quenching[5,6,21,30] (see Scheme). The standard free-energy change $\Delta G_{23}°$ for the electron-transfer process is calculated from equation (2) (in kJ mol^{-1}), where the coulombic term is



Scheme.

$$\Delta G_{23}° = 96.48[E(D/D^{+\bullet}) - E(A^{-\bullet}/A) - e^2/\varepsilon a - \Delta^3E_{0,0}] \quad (2)$$

taken as 0.06 eV and the other terms have their customary meaning.[9] Application of the steady-state approximation to the Scheme leads to equation (3).

$$^3k_q = k_{12}/[1 + (k_{21}/k_{23})(1 + k_{32}/k_{30})] \quad (3)$$

The rate-determining step, defined by k_{23}, can be expressed by equation (4), which leads to equation (5). Simplifying

$$k_{23} = K^{\circ}\exp(-\Delta G_{23}^{\ddagger}/RT) \qquad (4)$$

$$k_{32}/k_{23} = \exp(\Delta G_{23}^{\circ}/RT) \qquad (5)$$

assumptions lead to equation (6) where k_{21}/K° is often taken

$$^{3}k_{q} = k_{12}/\{1 + (k_{21}/K^{\circ})[\exp(\Delta G_{23}^{\ddagger}/RT) + \exp(\Delta G_{23}^{\circ}/RT)\} \qquad (6)$$

as 0.25. The activation barrier $\Delta G_{23}^{\ddagger}$ is related to ΔG_{23}° in various ways, *viz.*: (*a*) the Marcus equation (7);[31] (*b*) the

$$\Delta G_{23}^{\ddagger} = \Delta G_{23}^{\ddagger}(0)[1 + \Delta G_{23}^{\circ}/4\Delta G_{23}^{\ddagger}(0)]^{2} \qquad (7)$$

empirical relation of Rehm and Weller[9] (8); (*c*) the theoretically derived equation (9) of Scandola and Balzani[32] (which gives

$$\Delta G_{23}^{\ddagger} = \Delta G_{23}^{\circ}/2 + \left\{\left[\Delta G_{23}^{\circ}/2\right]^{2} + \left[\Delta G_{23}^{\ddagger}(0)\right]^{2}\right\}^{\frac{1}{2}} \qquad (8)$$

$$\Delta G_{23}^{\ddagger} = \Delta G_{23}^{\circ} + \frac{\Delta G_{23}^{\ddagger}(0)}{\ln 2}\ln\left\{1 + \exp\left[\frac{-\Delta G_{23}^{\circ}\ln 2}{\Delta G_{23}^{\ddagger}(0)}\right]\right\} \qquad (9)$$

results not unlike those of Rehm and Weller);[33] and (*d*) the linear equation (10) due to Polanyi.[17] $\Delta G_{23}^{\ddagger}(0)$ is the so-called

$$\Delta G_{23}^{\ddagger} = \alpha\Delta G_{23}^{\circ} + \beta \qquad (10)$$

'intrinsic barrier,' *i.e.*, the free energy of activation for a reaction with ΔG_{23}° equal to zero; it is often taken as 10.04 kJ mol^{-1} but other values have been found necessary to fit experimental data.[33] The parameter β fulfils a similar conceptual role to $\Delta G_{23}^{\ddagger}(0)$ (but is not identical with it),[34] and α is usually between 0 and 1. If electron-transfer is rate determining then $k_{21} > k_{23}$; assuming also that $k_{30} > k_{32}$ then equation (3) simplifies to equation (11); this taken with equation (4) yields equation (12),

$$^{3}k_{q} = k_{12}k_{23}/k_{21} \qquad (11)$$

$$^{3}k_{q} = (k_{12}K^{\circ}/k_{21})\exp(-\Delta G_{23}^{\ddagger}/RT) \qquad (12)$$

which can be rendered approximately by equation (13).

$$^{3}k_{q} = 1 \times 10^{10}\exp(-\Delta G_{23}^{\ddagger}/RT) \qquad (13)$$

From equations (10) and (13), a plot of log ($^{3}k_{q}$) *versus* ΔG_{23}° should be linear with slope α and intercept (at $\Delta G_{23}^{\circ} = 0$) β.

Figure 6 illustrates both this plot for all our data and the curve derived from equations (6) and (8), *i.e.*, the Rehm–Weller curve: a slightly better agreement is given by the Polanyi equation (10) than by the Rehm–Weller treatment, as is found to be the case with anion quenching both of triplet states of benzophenone and similar ketones[16] and of singlet excited aromatic hydrocarbons.[21] Quenching of excited uranyl ion by organosulphur, organometals (of Group IVB), and organohalogens also fits the Polanyi equation well over a wide range of ΔG_{23}°.[35] In all these cases, adherence to the Polanyi equation occurs beyond the expected limits of its validity, *i.e.*, that $\Delta G_{23}^{\ddagger} > \Delta G_{23}^{\circ}$ and $\Delta G_{23}^{\ddagger} > 0$ [indeed the Polanyi equation is sometimes viewed as a 'tangent' to the curves based on fuller treatments of the electron-transfer process, equations (7)—(9)].[34] Our values for α and β are: $\alpha = 0.367 \pm 0.027$, and $\beta = 9.83 \pm 0.57$ kJ mol^{-1}, which are compared with others obtained recently in Table 4. The value of β is similar to that found for other triplet ketones but that of α is much nearer the 'ideal' value of 0.5 in our case. Otherwise our Polanyi plot resembles that of Shizuka and Obuchi[16] and it includes literature data for quenching of triplet biacetyl by anions in the weakly exoergonic and endoergonic regions.[10] One explanation for adherence to the Polanyi equation outside its limits of validity may be found in the participation of a weak charge-transfer state, *i.e.*, *not* corresponding to complete electron-transfer.[16]

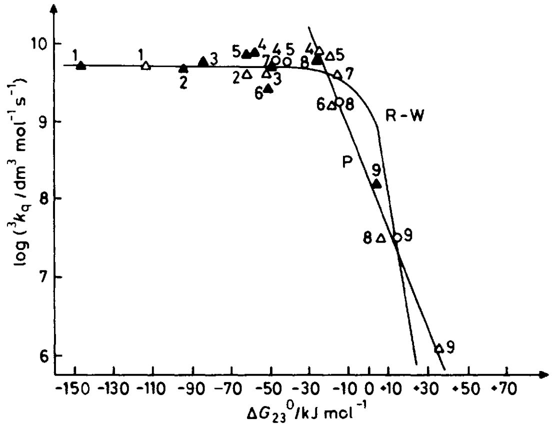


Figure 6. Plots of log $^{3}k_{q}$ *versus* ΔG_{23}° for the quenching by anions of triplet thioxanthone (Δ), triplet xanthone (▲), and triplet biacetyl (○). Lines drawn corresponding to theoretical treatments based on Polanyi equation (P) and Rehm–Weller treatment (R–W). For key to numbering of quenching ions see Table 2. Best-fit parameters for the Rehm–Weller plot: $k_{12} = 6.5 \times 10^{9}$ dm^{3} mol^{-1} s^{-1}, $\Delta G_{23}^{\ddagger}(0) = 6.70$ kJ mol^{-1}

Table 4. Values of the Polanyi coefficients α and β for excited-state electron-transfer quenching

System	α	β/kJ mol^{-1}	Ref.
[^{3}Ar$_{2}$CO]–inorganic anions	0.207	10.3	16
[^{1}ArH]*–inorganic anions	0.138	6.56	21*a*
[UO$_{2}^{2+}$]*–organosulphur compounds	0.046 ± 0.004	8.46 ± 0.4	35
[UO$_{2}^{2+}$]*–organometallic compounds	0.120 ± 0.003	26.01 ± 0.4	35
[UO$_{2}^{2+}$]*–halogenoalkanes	0.110 ± 0.004	9.69 ± 0.2	35
[^{1}DCA]*–inorganic anions[a]	0.487 ± 0.068	5.805 ± 0.843	*b*
[^{3}ArH]–quinones	1.0	4.824 ± 0.482	*c*

[a] DCA = 9,10-dicyanoanthracene. [b] Computed from the data of K. A. Abdullah and T. J. Kemp, *J. Photochem.*, 1985, **28**, 61. [c] F. Wilkinson and J. Schroeder, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 441.

Finally, comparison of Tables 2 and 3 reveals that singlet thioxanthone is quenched at rates exceeding 2.5×10^9 dm^3 mol^{-1} s^{-1} in all cases, whereas triplet thioxanthone is quenched 10^2-fold more slowly by SCN$^-$ and Br$^-$ ions; this accords with the general observation of relatively higher reactivity of singlet states in electron-transfer quenching,[30] which may be understood in terms of a higher value for $\Delta G_{23}°$ for the same acceptor in singlet and triplet states, and also the relatively higher polarisability of singlet states.[10]

Acknowledgements

K. A. A. thanks the University of Mosul for study leave and the Iraqi Government for financial support.

References

1 S. G. Cohen, A. Parola, and G. H. Parsons, *Chem. Rev.*, 1973, **73**, 141; J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 1972, 2163.
2 A. A. Gorman, C. T. Parekh, M. A. J. Rodgers, and P. G. Smith, *J. Photochem.*, 1978, **9**, 11.
3 R. V. Bensasson and J. C. Gramain, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1801.
4 J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.*, 1973, **38**, 2001.
5 F. Wilkinson and A. Garner, *J. Chem. Soc., Faraday Trans. 2*, 1977, **75**, 222.
6 R. O. Loutfy, S. K. Dogra, and R. W. Yip, *Can. J. Chem.*, 1979, **57**, 342.
7 J. C. Ronfard-Haret and R. V. Bensasson, *Chem. Phys. Lett.*, 1983, **96**, 31.
8 P. K. Das and K. Bobrowski, *J. Chem. Soc., Faraday Trans. 2*, 1981, **77**, 1009.
9 D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 834; D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.
10 P. Bortolus and S. Dellonte, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 1338.
11 A. Treinin and E. Hayon, *J. Am. Chem. Soc.*, 1976, **98**, 3884.
12 R. Scheerer and M. Gratzel, *J. Am. Chem. Soc.*, 1977, **99**, 865; J. C. Scaiano and P. Neta, *ibid.*, 1980, **102**, 1608.
13 L. J. A. Martins, *J. Chem. Soc., Faraday Trans. 1*, 1982, 533.
14 T. J. Kemp and L. J. A. Martins, *J. Chem. Soc., Faraday Trans. 1*, 1981, **78**, 1425.
15 L. J. A. Martins and T. J. Kemp, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2509.
16 H. Shizuka and H. Obuchi, *J. Phys. Chem.*, 1982, **86**, 1297.
17 M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11; J. Horiuchi and M. Polanyi, *Acta Physicochim. URSS*, 1935, **2**, 505.
18 'Handbook of Chemistry and Physics,' CRC Press, Cleveland, 58th edn., 1975—1976.
19 W. Armarego, D. R. Perrin, and D. D. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966.
20 K. R. Butter and T. J. Kemp, *J. Chem. Soc., Dalton Trans.*, 1984, 923.
21 (*a*) H. Shizuka, M. Nakamura, and T. Morita, *J. Phys. Chem.*, 1980, **84**, 989; (*b*) H. Shizuka, T. Saito, and T. Morita, *Chem. Phys. Lett.*, 1978, **56**, 519; (*c*) H. Shizuka, K. Takada, and T. Morita, *J. Phys. Chem.*, 1980, **84**, 994.
22 R. W. Yip, A. G. Szabo, and P. K. Tolg, *J. Am. Chem. Soc.*, 1973, **95**, 4471.
23 G. Winter, H. Shioyama, and U. Steiner, *Chem. Phys. Lett.*, 1981, **81**, 547.
24 G. Winter and U. Steiner, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 1203.
25 (*a*) J. F. Ireland and P. A. H. Wyatt, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1053; (*b*) A. Garner and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1010.
26 J. C. Scaiano and N. Kim-Thuan, *Can. J. Chem.*, 1982, **60**, 2286.
27 J. C. Dalton and F. C. Montgomery, *J. Am. Chem. Soc.*, 1974, **96**, 6230.
28 T. Lai and E. C. Lim, *Chem. Phys. Lett.*, 1980, **73**, 244.
29 K. Suga and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1651.
30 E. Vogelmann, S. Schreiner, W. Rauscher, and H. E. A. Kramer, *Z. Phys. Chem. Neue Folge*, 1976, **101**, 321; E. Vogelmann, W. Rauscher, R. Traber, and H. E. A. Kramer, *ibid.*, 1981, **124**, 13.
31 R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155.
32 F. Scandola and V. Balzani, *J. Am. Chem. Soc.*, 1979, **101**, 6140.
33 L. Eberson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
34 F. Scandola, V. Balzani, and G. B. Schuster, *J. Am. Chem. Soc.*, 1981, **103**, 2519.
35 H. B. Ambroz, K. R. Butter, and T. J. Kemp, *Faraday Discuss. Chem. Soc.*, 1984, **78**, 107.

Received 16*th November* 1984; *Paper* 4/1944