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ELECTRON DONOR AND ACCEPTOR QUENCHING OF THE FLUORESCENCE OF 9,10-DICYANOANTHRACENE IN POLAR AND NON-POLAR SOLVENTS

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Summary

Fluorescence quenching of 9,10-dicyanoanthracene is effected by both donors, *i.e.* inorganic anions in MeOH–H$_2$O and trialkyl and tetra-alkyl metals in cyclohexane, and acceptors, *i.e.* organic acceptors in MeOH. Sufficiently wide ranges of redox potentials for the three series of quenchers were utilized to enable rigorous tests to be undertaken of current theories of electron transfer quenching, relating to both polar and non-polar solvents.

1. Introduction

Since the pioneering work of Rehm and Weller [1] on electron transfer quenching of the fluorescence of aromatic molecules in MeCN solution, which related the quenching rate constant k_q with the standard free-energy change ΔG°_{23} of the electron transfer step, there have been developments covering electron transfer quenching of the luminescence of inorganic complexes [2], of triplet states of carbonyl and nitroheterocyclic compounds [3 - 5], of exciplexes [6] and of excited radical ions [7]. There have also been efforts to improve the relation between $\Delta G^{\ddagger}_{23}$ and ΔG°_{23}; as originally given by Rehm and Weller [1] in

$$\Delta G^{\ddagger}_{23} = \frac{\Delta G^{\circ}_{23}}{2} + \left[\left(\frac{\Delta G^{\circ}_{23}}{2}\right)^2 + \{\Delta G^{\ddagger}_{23}(0)\}^2\right]^{1/2} \tag{1}$$

and using their symbolism (see eqn. (8) below) the relation was empirical but it was amended to

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

by Scandola and Balzani [8] using a bond energy–bond order approach. Reductive quenching of excited singlet 9,10-dicyanoanthracene (^{1}(DCA)*)

by organic donors in heptane solution was treated by Kuz'min and co-workers [9] using a simplification of the Rehm–Weller kinetics model (by setting $k_{32} = 0$) yielding

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

Writing $k_{23} = Z_{23} \exp(-\Delta G^{\ddagger}_{23}/RT)$ and invoking the Polanyi [10] equation

$$\Delta G^{\ddagger}_{23} = \alpha\, \Delta G^{\circ}_{23} + \Delta G^{\ddagger}_{23}(0) \qquad (4)$$

yields

$$k_q = \frac{k_{12}}{1 + \exp\{\alpha(I - A - C_0)/RT\}} \qquad (5)$$

where

$$C_0 = C + \Delta G^{\ddagger}_{23}(0) + \frac{RT}{\alpha} \ln\!\left(\frac{Z_{23}}{k_{12}}\right) \qquad (6)$$

and

$$\Delta G^{\circ}_{23} = I - A - C \qquad (7)$$

where I refers to the ionization energy of the donor, A refers to the electron affinity of the acceptor and C is the coulombic term. Equation (4) has also been used successfully by Shizuka et al. [11] in the fluorescence quenching of aromatic molecules by inorganic anions in aqueous EtOH. A comprehensive review of theories of electron transfer has been provided recently by Eberson [12].

Other previous investigations of the quenching of ^{1}(DCA)* are due to Eriksen and Foote [13] who used electron-rich aromatic molecules in MeCN, obtaining excellent agreement with the Rehm–Weller treatment, and Weiss and coworkers [14], who quenched various anthracenes including ^{1}(DCA)* with Ph_3P in MeCN and benzene solutions.

Rather few examples have been reported of alkyl metals acting as quenchers of excited states although Ph_3P has attracted some interest [14, 15] as have mercury, tin and lead alkyls in respect of heavy-atom effects [16].

2. Experimental details

DCA (Eastman) was recrystallized from toluene (melting point, 335 °C (335 °C reported in ref. 17)). Triphenylphosphine, tri(p-tolyl)phosphine and triphenylantimony were from Lancaster Syntheses Ltd. and tetra-n-butylstannane and tetraethylgermane were from Ventron Ltd. Organolead compounds were gifts from the Associated Octel Co. Ltd. (Ellesmere Port), while other organotin compounds were synthesized and purified by standard procedures [18]. Methanol and cyclohexane (Fisons Ltd.) were of spectro-

scopic grade and water was quadruply distilled. Other chemicals were of the highest purity commercially available.

Fluorescence spectra were recorded using a Perkin–Elmer model MPF-3 spectrofluorometer, exciting solutions of DCA (10^{-5} mol dm^{-3}) at 400 nm. Absorption spectra were taken on a Shimadzu model 365 UV–visible–IR spectrophotometer. Fluorescence lifetimes were determined by time-correlated single-photon counting at the Royal Institution. Deoxygenation was by bubbling with purified nitrogen for 15 min.

Stern–Volmer constants were evaluated by a least-squares analysis using at least five concentrations (and usually about eight) of the quencher molecule, and the correlation coefficients were always better than 0.97. Neither the absorption nor the fluorescence spectra of DCA were affected by the presence of any quencher, indicating the absence of charge transfer complex formation in the ground state and of emissive exciplexes.

3. Results

In Table 1 are presented fluorescence spectral and lifetime data for DCA in the solvents utilized in this study, together with values of the electronic excitation energy $\Delta^1 E_{0,0}$ estimated from the crossing point of the absorption and the emission spectra of DCA in each solvent.

Fluorescence from ^{1}(DCA)* in oxygen-free solutions at room temperature (293 ± 1 K) was quenched by a wide variety of donors in both MeOH–H$_2$O (1:1 by volume) (inorganic anions and Ag$^+$ (Table 2)) and cyclohexane (organophosphorus, organoantimony, organotin, organolead and organogermanium compounds (Table 3)). ^{1}(DCA)* is also an electron donor, and it is quenched in MeOH solution by acceptors with half-wave potentials more positive than —1.7 V (measured with respect to a saturated calomel electrode (SCE)), reaching the diffusion-controlled value when $E_{1/2} > -1.0$ V (SCE) (Table 4). In all cases there was no evidence for any new emitting species such as an exciplex on addition of the quencher, and Stern–Volmer plots of I_0/I versus [quencher] were linear to give a slope equal to the Stern–Volmer constant K_{SV} which was factorized using the relation $K_{SV} = K_q \tau_0$ (where τ_0 is the lifetime of ^{1}(DCA)* in the absence of quencher).

TABLE 1

Spectral and lifetime data for ^{1}(DCA)*

Solvent	τ_0 (ns)	λ_{fl} (nm)	$\Delta^1 E_{0,0}$ [a] (eV)
MeOH	15.1[b]	436, 457	2.897
MeOH–H$_2$O (1:1 by volume)	14.8	442, 465	2.870
Cyclohexane	11.7[c]	423, 448, 475	2.945

[a]Obtained from the intersection of the absorption and the fluorescence spectra.
[b]Reference 13 gives 15.3 ns in MeCN.
[c]Reference 19 gives 11.2 ns in heptane.

TABLE 2

Fluorescence quenching of ^{1}(DCA)* by anions in MeOH–H$_2$O (1:1 by volume) solution

Number	Donor	$E°(D^+|D)$ [a] (V (SHE))	$\Delta G°_{23}$ (kJ mol^{-1})	k_q (dm^3 mol^{-1} s^{-1})
1	NO$_2^-$	1.0 ± 0.1[b]	-115.8	$(6.17 \pm 0.42) \times 10^9$
2	I$^-$	1.33 ± 0.03[c], 1.40 ± 0.05[b,d]	-84.0	$(8.28 \pm 0.20) \times 10^9$
3	S$_2$O$_3^{2-}$	1.34 ± 0.03[e], 1.35[f]	-83.0	$(5.62 \pm 0.19) \times 10^9$
4	N$_3^-$	1.37 ± 0.02[f], 1.87[d]	-80.1	$(6.38 \pm 0.20) \times 10^9$
5	SCN$^-$	1.60 ± 0.03[e], 1.66[c], 1.50[d]	-57.8	$(8.94 \pm 0.23) \times 10^9$
6	CN$^-$	1.90 ± 0.3[b]	-29.0	$(3.46 \pm 0.47) \times 10^9$
7	Br$^-$	1.90 ± 0.03[e], 2.0 ± 0.1[b,d]	-29.0	$(6.96 \pm 0.16) \times 10^9$
8	OH$^-$	2.11 ± 0.09[e], 1.9 ± 0.1[b], 2.29[d]	-8.7	$(4.22 \pm 0.07) \times 10^9$
9	CO$_3^{2-}$	2.15[e]	-4.8	$(2.98 \pm 0.23) \times 10^9$
10	Cl$^-$	2.20[e], 2.55 ± 0.1[b,d]	0.0	$(7.86 \pm 0.21) \times 10^8$
11	Ag$^+$	2.25[e], 1.987[g]	$+4.8$	$(6.61 \pm 0.33) \times 10^8$
12	OAc$^-$	2.32[h], 2.41[i]	$+11.6$	$(7.07 \pm 0.16) \times 10^7$
13	F$^-$	3.6 ± 0.1[b]	$+135.0$	$(2.78 \pm 0.09) \times 10^7$

[a]The first values listed were utilized in calculating $\Delta G°_{23}$; $E°(D^+|D)$ was measured with respect to a standard hydrogen electrode (SHE).
[b]From ref. 20.
[c]From ref. 21.
[d]From ref. 11.
[e]From ref. 5 (confidence limits for S$_2$O$_3^{2-}$, SCN$^-$ and Br$^-$ were imposed using data for I$^-$).
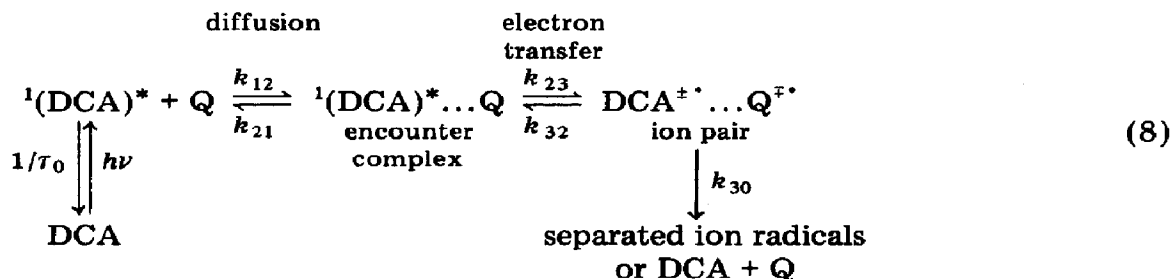[f]From ref. 22.
[g]From ref. 23 for 4 mol dm^{-3} HClO$_4$ solution.
[h]Calculated from data given in ref. 5.
[i]From ref. 24.

4. Discussion

The customary starting point for discussion of quenching in polar solvents is the scheme developed by Rehm and Weller [1], *i.e.*

$$^1(DCA)^* + Q \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} {}^1(DCA)^*...Q \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} DCA^{\pm\cdot}...Q^{\mp\cdot} \qquad (8)$$

diffusion — electron transfer — encounter complex — ion pair

$1/\tau_0$, $h\nu$; DCA ; k_{30} ; separated ion radicals or DCA + Q

where Q represents either a donor or an acceptor quencher. Use of the steady state approximation leads to the empirical equation

TABLE 3

Quenching of ^{1}(DCA)* by organometallic compounds in cyclohexane solution

Number	Donor	I (eV)	k_q (dm^3 mol^{-1} s^{-1})
1	$(p\text{-}MeC_6H_4)_3P$	7.60[a]	$(8.03 \pm 0.26) \times 10^9$
2	Ph_3P	7.92[a]	$(11.67 \pm 0.21) \times 10^9$
3	Et_4Pb	8.13[b]	$(10.10 \pm 0.23) \times 10^9$
4	Ph_3Sb	8.18[c]	$(8.62 \pm 0.19) \times 10^9$
5	Et_3MePb	8.26[d]	$(10.39 \pm 0.19) \times 10^9$
6	$(s\text{-}Bu)_4Sn$	8.45[b]	$(8.97 \pm 0.13) \times 10^9$
7	$(i\text{-}Pr)_4Sn$	8.46[b]	$(8.54 \pm 0.21) \times 10^9$
8	$EtMe_3Pb$	8.65[d]	$(7.78 \pm 0.14) \times 10^9$
9	$(n\text{-}Bu)_4Sn$	8.76[b]	$(2.47 \pm 0.04) \times 10^9$
10	$(n\text{-}Pr)_4Sn$	8.82[e]	$(1.53 \pm 0.03) \times 10^9$
11	Me_4Pb	8.90[b]	$(1.55 \pm 0.03) \times 10^9$
12	Et_4Sn	8.93[b]	$(1.55 \pm 0.05) \times 10^9$
13	$(n\text{-}Bu)Me_3Sn$	9.00[e]	$(5.12 \pm 0.26) \times 10^7$
14	$EtMe_3Sn$	9.10[b]	$(3.55 \pm 0.14) \times 10^7$
15	Et_4Ge	9.41[b]	$(1.02 \pm 0.05) \times 10^7$
16	Me_4Sn	9.69[b]	$(1.97 \pm 0.07) \times 10^7$
17	Et_4Si	9.78[b]	$(7.21 \pm 0.07) \times 10^6$

[a]From ref. 25.
[b]From ref. 26 and the compilation given therein.
[c]From ref. 27.
[d]From ref. 28.
[e]From ref. 18.

$$k_q = \frac{k_{12}}{1 + (k_{21}/K^\circ)\{\exp(\Delta G^{\ddagger}_{23}/RT) + \exp(\Delta G^\circ_{23}/RT)\}} \tag{9}$$

k_{12} is normally taken as 2×10^{10} dm^3 mol^{-1} s^{-1} and k_{21}/K° as 0.25, while ΔG°_{23} (kJ mol^{-1}) is calculated from

$$\Delta G^\circ_{23} = 96.48\left\{E^\circ(D|D^{\dagger}) - E^\circ(A^{\dagger}|A) - \frac{e^2}{\epsilon r} - \Delta^1 E_{0,0}\right\} \tag{10}$$

Finally, $\Delta G^{\ddagger}_{23}$ is calculated from eqn. (1) and $\Delta G^{\ddagger}_{23}(0)$, the so-called intrinsic barrier, is often taken as 10.04 kJ mol^{-1}, although several researchers have favoured higher values in a number of recent studies [7, 12, 34].

In Fig. 1 are shown the data from Table 2 in the form of a plot of log k_q versus ΔG°_{23}, the latter being obtained from eqn. (10) with $e^2/\epsilon r$ taken as 0.06 eV, with k_{12} as 8.0×10^9 dm^3 mol^{-1} s^{-1} (a value more appropriate for this solvent) and with $\Delta G^{\ddagger}_{23}(0)$ as 6.5 kJ mol^{-1}. The agreement with the curve calculated from the Rehm–Weller theory is good except in the case of the F$^-$ ion, which has shown exceptional behaviour before [4, 5], possibly originating in the value for its oxidation potential.

Rather few studies have been undertaken concerning electron donor–acceptor quenching in alkane [9, 35] or aromatic [9, 36] solvents, which

TABLE 4

Fluorescence quenching of $^1(DCA)^*$ by organic acceptors in MeOH solution

Number	Acceptor	$E_{1/2}$ [a,b] (V (SCE))	$\Delta G°_{23}$ [c] (kJ mol^{-1})	k_q (dm^3 mol^{-1} s^{-1})
1	Misonidazole	-0.395[d]	-80.3	$(5.34 \pm 0.20) \times 10^9$
2	1,3,5-Trinitrobenzene	-0.60	-60.5	$(10.50 \pm 0.28) \times 10^9$
3	Methyl viologen	-0.69[e]	-51.8	$(9.53 \pm 0.23) \times 10^9$
4	1,4-Dinitrobenzene	-0.70	-50.9	$(15.64 \pm 0.56) \times 10^9$
5	1,2-Dinitrobenzene	-0.83	-38.3	$(10.25 \pm 0.35) \times 10^9$
6	1,3-Dinitrobenzene	-0.91	-30.6	$(16.41 \pm 0.20) \times 10^9$
7	3-Methylnitrobenzene	-1.045	-17.6	$(8.54 \pm 0.28) \times 10^9$
8	Nitrobenzene	-1.147	-7.7	$(6.37 \pm 0.23) \times 10^9$
9	2-Methylnitrobenzene	-1.26	$+3.2$	$(3.82 \pm 0.10) \times 10^9$
10	2,3-Dimethylnitrobenzene	-1.318	$+8.8$	$(3.40 \pm 0.09) \times 10^9$
11	2,6-Dimethylnitrobenzene	-1.402	$+16.9$	$(6.70 \pm 0.27) \times 10^8$
12	4-Cyanopyridine	-1.440[f]	$+20.7$	$(4.12 \pm 0.10) \times 10^8$
13	1-Nitropropane	-1.458	$+22.3$	$(4.44 \pm 0.20) \times 10^6$
14	1-Nitropentane	-1.51	$+27.3$	$(5.80 \pm 0.01) \times 10^6$
15	2-Methyl-2-nitropropane	-1.70	$+45.7$	$(1.61 \pm 0.05) \times 10^6$

[a]Measured in MeCN with respect to an SCE using 0.1 mol dm^{-3} NR$_4^+$ClO$_4^-$ (R = Et or n-Pr) as the supporting electrolyte.
[b]Except where indicated otherwise, values are taken from ref. 29.
[c]Calculated using a value of $E(D|D^+)$ for DCA of 1.73 V (SCE) from ref. 33 (after correction for a change in reference electrode from Ag|Ag$^+$ (nitrate) to an SCE).
[d]From ref. 30.
[e]From ref. 31 (after correction for a change in reference electrode from a standard hydrogen electrode to an SCE).
[f]Calculated from data of ref. 32.

introduces several complicating factors, namely (i) the possible formation of exciplexes (both emissive and non-emissive), (ii) a much more significant coulombic term in eqn. (10) and (iii) an absence of electrochemical data relating to the solvent medium. It becomes more appropriate therefore to use eqn. (7) to derive $\Delta G°_{23}$ and to plot log k_q versus $I - A$, as shown in Fig. 2. For $I - A < 4.0$ eV, k_q is about 10^{10} dm^3 mol^{-1} s^{-1} but, in the narrow range $4.0 < I - A < 4.6$ eV, k_q falls very sharply. In this range a plot of $\Delta G^{\ddagger}_{23}$ versus $I - A$ is linear, with slope α (eqn. (4)) of 0.24 ± 0.04 and $\beta = -1.02 \pm 0.19$ eV, and the theoretical values based on these parameters are given as the broken (sloping) line in Fig. 2. (The value of β is not strictly $\Delta G^{\ddagger}_{23}(0)$ because the ordinate is not $\Delta G°_{23}$.) A plot of $\ln\{(2 \times 10^{10}/k_q) - 1\}$ versus $I - A$, i.e. the linear form of eqn. (5), yields a straight line with $\alpha = 0.22 \pm 0.03$ and $C_0 = 4.03 \pm 0.60$ eV. The latter values compare with those of Kuz'min and coworkers [9] of $\alpha = 0.14 \pm 0.02$ and $C_0 = 3.42 \pm 0.5$ eV in heptane for quenching of both exciplexes and excited molecules.

In Fig. 3 are shown the results of Table 4 for quenching of $^1(DCA)^*$ by acceptor molecules in MeOH solution. Optimum fitting to the Rehm–Weller equation was achieved with $k_{12} = 1.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $\Delta G^{\ddagger}_{23}(0) =$
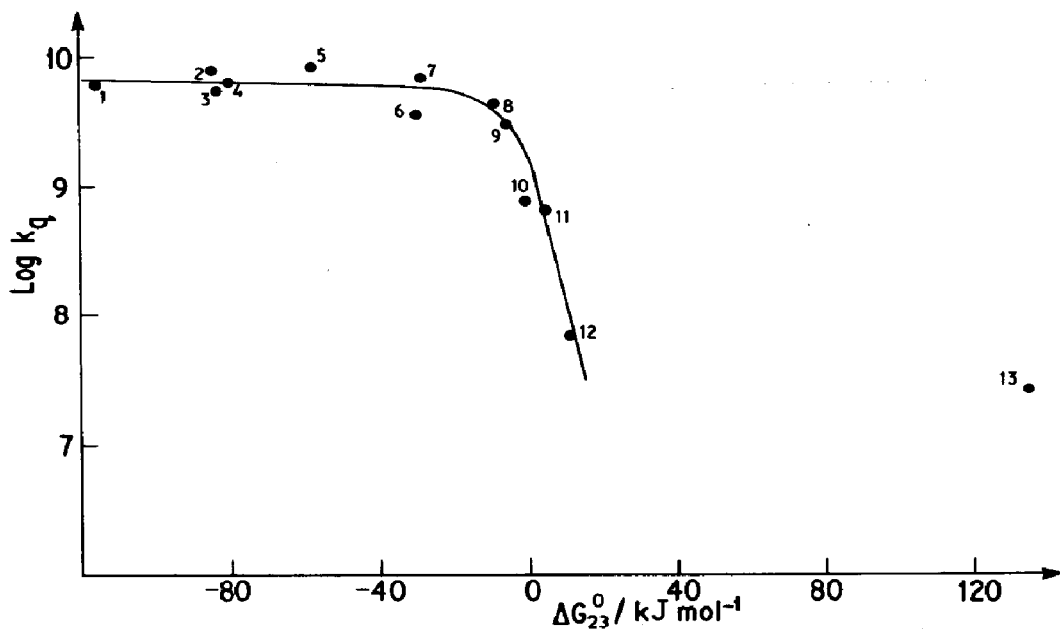
Fig. 1. log k_q vs. $\Delta G°_{23}$ for the reductive quenching of ^{1}(DCA)* by inorganic ions in MeOH–H$_2$O (1:1 by volume). The numbering of the quenchers is as in Table 2; ———, theoretical values derived from the Rehm–Weller treatment (for parameters see text).
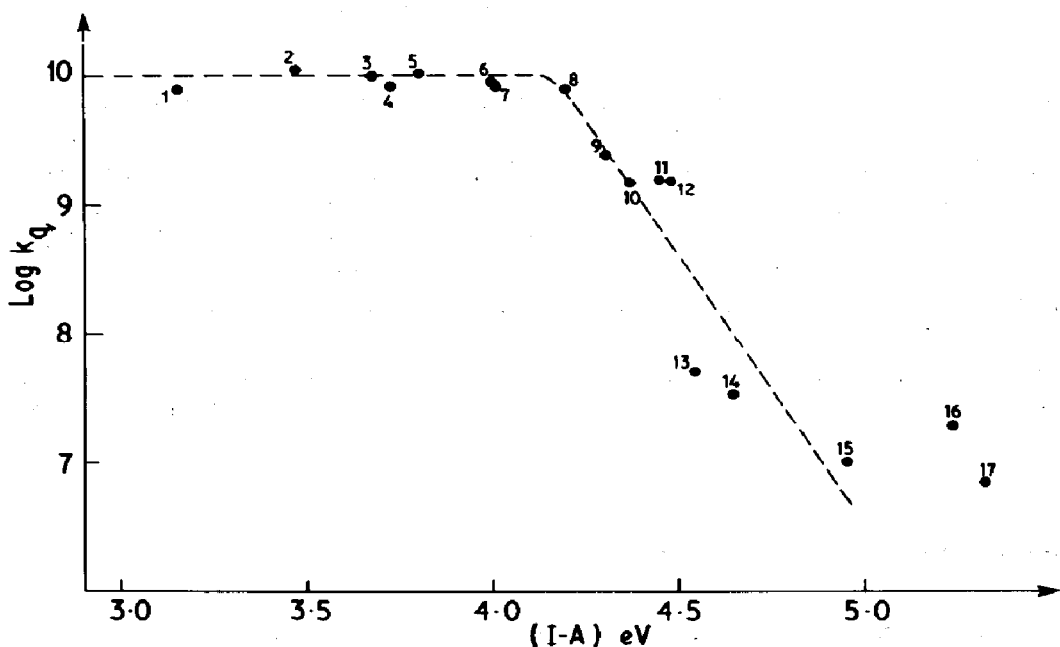

Fig. 2. log k_q vs. $I - A$ for the reductive quenching of ^{1}(DCA)* by organometallic compounds in cyclohexane solution. The numbering of the quenchers is as in Table 3; – – –, theoretical values derived from the Polanyi equation (for parameters see text). (A for ^{1}(DCA)* is estimated by us as 4.45 eV from $E_{1/2}$(DCA|DCA$^-$) = —0.98 V (SCE) [13], the correlation $A = 2.49 + E_{1/2}$ (V (SCE)) [32] and $\Delta^1 E_{0,0} = 2.945$ eV for ^{1}(DCA)* in cyclohexane.)
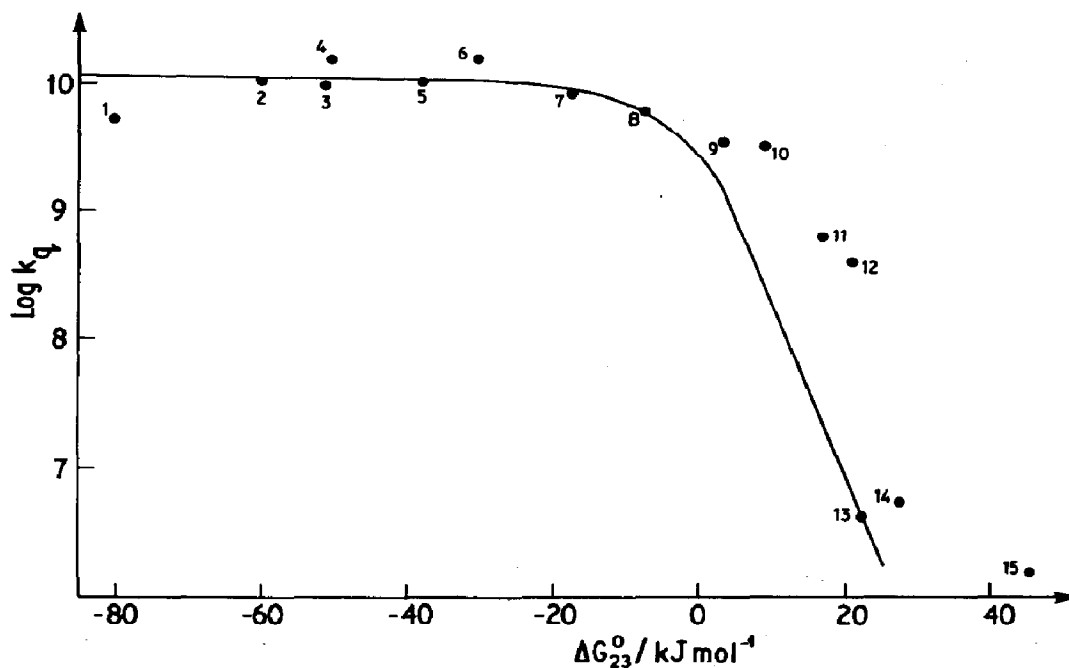
Fig. 3. log k_q vs. $\Delta G°_{23}$ for the oxidative quenching of ^{1}(DCA)* by organic electron accep-
tors in MeOH. The numbering of the quenchers is as in Table 4;————, theoretical values
derived from the Rehm–Weller treatment (for parameters see text).

7.11 kJ mol^{-1}, but even so the agreement in the endoergonic region is rather
poor; the observed quenching rates usually exceed those calculated by a
considerable factor, although the downward trend at higher $\Delta G°_{23}$ is of the
correct magnitude, implying the possibility of a small systematic error in a
thermochemical datum, probably the oxidation potential of DCA [33].
Interestingly, the fluorescence quenching of zinc octaethylporphin by elec-
tron donors in both MeCN and toluene solution also shows anomalously high
k_q at $\Delta G°_{23} > 0$ [36].

In conclusion, ^{1}(DCA)* is quenched by an electron transfer mechanism
by both donor and acceptor molecules in hydroxylic solvents and in cyclo-
hexane.

Acknowledgments

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