Linear Free Energy Relationships in the Electron-transfer Reactions between $Ph_2\dot{C}OH$ and Electron Acceptors

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The rates of the electron-transfer reaction between $Ph_2\dot{C}OH$ and 40 electron acceptors (π) have been determined by ns laser flash photolysis to give a uniquely comprehensive set of such data for an important transient organic radical. The rate data have been correlated successfully with various measures of the electron-accepting power of π, depending on the availability of thermodynamic data, *viz.* the redox potential at pH 7 in water (E_7^1), the polarographic half-wave potential in MeCN ($E_{\frac{1}{2}}$), the Hammett σ constant, and the energy of the lowest unoccupied MO (E_{LUMO}); thus the rate of reduction of $XC_6H_4CO_2H$ by $Ph_2\dot{C}OH$ varies 10^3-fold with change in X, yielding ρ 3.11 ± 0.21.

SEVERAL studies have been reported on the one-electron reducing properties of 1-hydroxyalkyl radicals,[1] for example, $Me_2\dot{C}OH$ produced by pulse radiolysis of aqueous propan-2-ol reduces nitro-compounds,[2] aromatic ketones,[3] halogeno-compounds,[4] and protonated acridine.[5] Despite some mechanistic work, based on e.s.r. spectroscopy and product analysis,[6,7] concerning the reducing ability of the $Ph_2\dot{C}OH$ radical (I) towards protonated heteroaromatic bases, absolute kinetic data for the one-electron oxidation of (I) are virtually non-existent, which is surprising in view of its central role in the classical problem of benzophenone photochemistry. Radical (I) can be generated in different ways, either by irradiation of benzophenone in reducing solvents [8] or by oxidative decarboxylation of benzilic acid in the presence of a suitable photoexcited transition-metal ion [9] and its characterization effected by e.s.r. and optical spectroscopy. While one major product from (I) is benzpinacol, it has become clear that the course of photoreaction in the benzophenone–propan-2-ol system is rather more complex than simple radical recombination and a number of light-absorbing transients have been reported.[10,11] Radical (I) also interacts with additives such as O_2, vinyl monomers,[12] and metal ions.[13-15] The electron-donating capacity of a radical $R^1R^2\dot{C}OH$ depends upon its structure as reflected in the stability of the conjugate carbonium ion [16] $R^1R^2\overset{+}{C}OH$, and it is expected that (I) might participate in one-electron transfer reactions rather than addition to the acceptor as established for $\dot{C}H_2OH$ [3,17] in certain cases.

In the present work we have determined the absolute rate constants for the one-electron transfer from (I) to a large number of organic electron acceptors (π) in acetone solution (or in some cases 25% v/v aqueous acetone), in order to study systematically the effect of structural variation in π on the reactivity of (I). The resulting rate constants were successfully correlated with different molecular parameters of π (Hammett substituent constant σ, energy of the lowest unoccupied MO,E_{LUMO}, polarographic half-wave reduction potential, $E_{\frac{1}{2}}$, and equilibrium redox potential, E_7^1). The relative Marcus theory for outer-sphere electron transfer is invoked to explain trends observed in the latter two correlations.

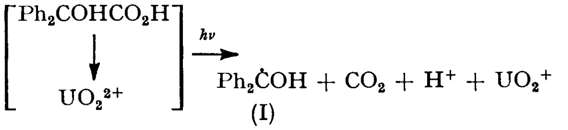
EXPERIMENTAL

Materials.—The purification of acetone (Fisons; AnalaR) and water (doubly distilled) followed the literature procedure.[18] Other chemicals were of the highest purity commercially available and most of them were used without further purification. However, their u.v.–visible spectra conformed with those published. Argon (high purity B.O.C.) was used throughout this work to deoxygenate solutions before irradiation.

Methods.—All samples were prepared immediately before use and deoxygenated by bubbling with argon for 15 min, special care being taken to avoid evaporation of acetone. Samples were subjected to the analysing light for the minimum possible time before laser photolysis. The laser flash photolysis assembly has been fully described elsewhere [19a] except with replacement of the doubling crystal by one of rubidium dihydrogenarsenate. 50-ns pulses of moderate intensity from a frequency doubled Q-switched ruby laser (347.1 nm) were used for excitation of the sensitiser, uranyl nitrate (see below). The transient absorption of (I) was monitored with a 250-W xenon arc lamp and monochromator system. The signal from a Hamamatsu R666S photomultiplier tube was terminated in 50Ω and then displayed on a Tektronix 7623 storage oscilloscope. The samples were never pulsed more than twice to minimise secondary reactions. All measurements were performed at 293 K.

RESULTS

Laser flash photolysis of a solution of uranyl nitrate (3.28×10^{-2} mol dm^{-3}) and benzilic acid (1.07×10^{-1} mol dm^{-3}) in acetone leads to the generation of (I),[9, 14] which is completely formed within the duration of the laser pulse. Its spectrum was determined by the point-to-point procedure and shown to be identical with that obtained on μs flash photolysis of benzophenone in propan-2-ol,[8] with $\lambda_{\text{max.}}$ 542 ± 2 nm. Our method, represented by reaction (1), is a convenient way of producing radical (I) in high yield for reasons pointed out previously.[14] Radical (I), monitored at λ 542 nm,



$$\left[\begin{array}{c} Ph_2COHCO_2H \\ \downarrow \\ UO_2^{2+} \end{array}\right] \xrightarrow{h\nu} \underset{\text{(I)}}{Ph_2\dot{C}OH} + CO_2 + H^+ + UO_2^+ \quad (1)$$

$$Ph_2\dot{C}OH \xrightarrow{k_0} \text{products} \quad (2)$$

$$Ph_2\dot{C}OH + \pi \xrightarrow{k_2} Ph_2CO + H^+ + \pi^{\cdot -} \quad (3)$$

TABLE 1

Absolute rate constants for reaction of $Ph_2\dot{C}OH$ with organic electron acceptors, in acetone

Acceptor	$10^{-6}k_2$/dm^3 mol^{-1} s^{-1}	E_7^1 †/V	$E_{\frac{1}{2}}$‡/V	E_{LUMO}*/β units
Nitrobenzene (1)	0.262 ± 0.018	−0.486 [a]	−1.147 [e]	−0.3787
3-Nitrotoluene (2)	0.288 ± 0.027		−1.170 [f]	
3-Nitroacetophenone (3)	0.548 ± 0.013	−0.437 [a]	−1.042 [e]	−0.3741
3-Nitrobenzaldehyde (4)	0.572 ± 0.019		−1.016 [e,g]	−0.3740
3-Nitrobenzoic acid (5)	0.601 ± 0.012	−0.433 [b]		
Methyl 3-nitrobenzoate (6)	0.712 ± 0.014		−1.045 [e,h]	
3-Nitrobenzonitrile (7)	0.736 ± 0.049		−0.938 [e,g]	−0.3771
4-Nitrobenzyl bromide (8)	0.912 ± 0.005		−1.090 [f]	
2-Nitrobenzoic acid (9)	1.00 ± 0.12 [m]	−0.412 [b]		
4-Nitrobenzoic acid (10)	1.13 ± 0.09	−0.396 [b]		
Methyl 4-nitrobenzoate (11)	1.21 ± 0.04		−0.947 [e]	
4-Nitrobenzamide (12)	1.28 ± 0.03		−1.014 [e]	
1,3-Dinitrobenzene (13)	1.28 ± 0.12 [m]	−0.345 [b]	−0.910 [i,j]	−0.3447
Tetrachlorophthalic anhydride (14)	1.36 ± 0.34		−0.860 [k]	
4-Nitroacetophenone (15)	1.61 ± 0.05	−0.358 [a]	−0.925 [e]	−0.2946
4-Nitrobenzaldehyde (16)	1.75 ± 0.07		−0.863 [e,g]	−0.2929
3,5-Dinitrobenzoic acid (17)	3.76 ± 0.04	−0.344 [b]		
2,4-Dinitrobenzoic acid (18)	3.79 ± 0.13	−0.345 [b]		
1-Fluoro-2,4-dinitrobenzene (19)	4.22 ± 0.10		−0.880 [i]	
1,2-Dinitrobenzene (20)	4.36 ± 0.13	−0.287 [b]	−0.830 [i]	−0.2031
4-Nitrobenzonitrile (21)	4.38 ± 0.11		−0.875 [e,g]	−0.3403
3,4-Dinitrobenzoic acid (22)	6.49 ± 0.20	−0.271 [b]		
1,4-Dinitrobenzene (23)	9.04 ± 0.04	−0.257 [b]	−0.700 [i]	−0.1997
2,5-Dinitrobenzoic acid (24)	10.40 ± 0.20	−0.272 [b]		
5-Nitro-2-furoic acid (25)	11.60 ± 0.90	−0.317 [a]		
anti-5-Nitro-2-furaldoxime (nifuroxime) (26)	21.60 ± 0.90	−0.253 [a]		
1,1′-Azobis-(*NN*-dimethylformamide) (diamide) (27)	27.50 ± 1.60			
2,3,5,6-Tetramethyl-1,4-benzoquinone (duroquinone) (28)	32.70 ± 1.10	−0.235 [c]	−0.840	
2-Methyl-1,4-naphthoquinone (menadione) (29)	72.20 ± 2.00	−0.203 [c]	−0.770 [l]	
2,5-Dimethyl-1,4-benzoquinone (30)	200.0 ± 11.0	−0.065 [d]	−0.670 [l]	
9,10-Phenanthraquinone (31)	228.0 ± 10.0		−0.660 [l]	
1,2-Naphthoquinone (32)	253.0 ± 21.0		−0.560 [l]	
Phenyl-1,4-benzoquinone (33)	257.0 ± 12.0		−0.500 [l]	
1,4-Benzoquinone (34)	263.0 ± 12.0	+0.099 [d]	−0.510 [l]	
5-Hydroxy-1,4-naphthoquinone (juglone) (35)	318.0 ± 20.0		−0.520 [l]	

† One-electron redox potential in aqueous solution, at pH 7, *versus* n.h.e. ‡ One-electron half-wave reduction potential in MeCN *versus* s.c.e., using 0.1N-NEt_4ClO_4, or -NPr_4ClO_4, as supporting electrolyte. * Energy of the lowest unoccupied MO in terms of the bond integral of benzene, β, as calculated in ref. 19*b*.

[a] Values from ref. 20. [b] Values from ref. 2. [c] Values from ref. 21. [d] Values from ref. 22. [e] Values from ref. 23. [f] Values from ref. 24. [g] Values from ref. 25. [h] Value from ref. 26. [i] Values from ref. 27. [j] Value from ref. 28. [k] Value from ref. 29. [l] Values from ref. 30. [m] Values from ref. 14.

decays relatively slowly (reacting with $[UO_2]^{2+}$), $k_{01} = (1.3 \pm 0.04) \times 10^5$ dm^3 mol^{-1} s^{-1}, and with Ph_2COHCO_2H, $k_{02} = (1.07 \pm 0.06) \times 10^4$ dm^3 mol^{-1} s^{-1}, with a total pseudo-first order rate constant, denoted by k_0 and given by equation (4), which has the experimental value $k_0 = (5.50 \pm 0.20) \times 10^3$ s^{-1} for the concentrations given above.

$$k_0 = k_{01}[UO_2^{2+}] + k_{02}[Ph_2COHCO_2H] \qquad (4)$$

$$k_{expt} = k_0 + k_2[\pi] \qquad (5)$$

Addition of a suitable of one-electron π-acceptor, π, accelerates the decay of (I) in such a way that from the dependence of the pseudo-first-order rate constant, k_{expt}, upon [π] the second-order rate constant, k_2, in reaction (3) could be determined. Kinetic analysis of the mechanism, represented by reactions (1)—(3), gives equation (5) for k_{expt} and values of k_2 were extracted from plots of $(k_{expt} - k_0)$ *versus* [π]; the first-order dependence of k_{expt} on [π] was observed up to at least three times k_0. For each acceptor the maximum concentration used was such that its absorbance at 347 nm was lower than that of the sensitiser, $[UO_2]^{2+}$. The thermal stability of benzilic acid in the presence of each acceptor was confirmed by u.v.–visible spectrometry. Non-first-order behaviour in the decay of (I) at 542 nm was found for solutions containing tetrahalogeno-1,4-benzoquinone for which no second-order rate constants could therefore be determined. Addition of water, up to 25% v/v, decreases the value of k_0 to $(2.80 \pm 0.20) \times 10^3$ s^{-1} and increases the value of k_2, the effect being more pronounced for the more reactive acceptors. Our values for k_2 for reaction of (1) with a large number of

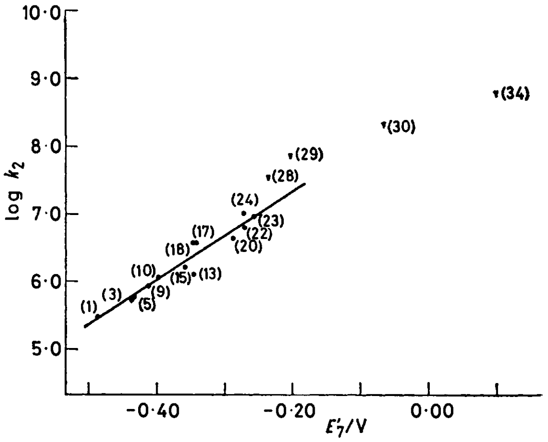


FIGURE 1 Dependence of log k_2, the second-order rate constant for electron transfer from (I) to nitroaromatic compounds (●) and quinones (▼), upon the equilibrium redox potential of the acceptor (numbering as in Table 1). The straight line refers to a least-squares analysis for the data for nitroaromatic compounds only, with a slope of (6.60 ± 0.54) V^{-1}

TABLE 2

Absolute rate constants for reaction of $Ph_2\dot{C}OH$ with nitrobenzenes and nitrobenzoic acids; Hammett σ values

(a) $XC_6H_4NO_2$

X	$10^{-5}k_2$/dm^3 mol^{-1} s^{-1}	σ	σ^-	Ref.
H	2.62 ± 0.18	0.00		*a*
m-CH_3	2.88 ± 0.27	-0.07		*a*
m-$COCH_3$	5.48 ± 0.13	0.38		*a*
m-CHO	5.72 ± 0.19	0.35		*a*
m-CO_2H	6.01 ± 0.12	0.37		*a*
m-CO_2CH_3	7.12 ± 0.14	0.37		*a*
m-CN	7.36 ± 0.49	0.56		*a*
p-CH_2Br	9.12 ± 0.05	0.18		*b*
p-CO_2H	11.30 ± 0.90	0.45		*a*
p-CO_2CH_3	12.10 ± 0.40	0.45		*a*
m-NO_2	12.80 ± 1.20	0.71		*a*
p-$CONH_2$	12.80 ± 0.30		0.62	*a*
p-$COCH_3$	16.10 ± 0.50	0.50		*a*
p-CHO	17.50 ± 0.70	0.43		*c*
p-CN	43.80 ± 1.10	0.66	0.90	*a*
p-NO_2	90.40 ± 0.40	0.78	1.24	*a*

(*b*) $XC_6H_4CO_2H$

X	$10^{-4}k_2$/dm^3 mol^{-1} s^{-1}	σ	Ref.
H	0.33 ± 0.06	0.00	*a*
p-F	0.67 ± 0.02	0.06	*a*
p-Cl	2.26 ± 0.24	0.23	*a*
m-Cl	3.00 ± 0.17	0.37	*a*
m-CF_3	4.06 ± 0.42	0.42	*d*
m-NO_2	60.10 ± 1.20	0.71	*a*
p-NO_2	113.0 ± 9.0	0.78	*a*

[a] Values from ref. 31. [b] Value from ref. 32. [c] Value from ref. 33. [d] Value from ref. 34.

organic acceptors are collected in Table 1, together with literature values for three different molecular parameters which are widely used as a measure of the electron affinity of π. Although two of these are somewhat solvent-dependent, we can nevertheless draw useful qualitative conclusions as to the efficiency of each one-electron acceptor in oxidising (I). In Figures 1 and 2 it is demonstrated that a linear relation exists between log k_2 and either $E_7{}^1$ or $E_{\frac{1}{2}}$ for a number of nitroaromatic compounds. It is also clear that those quinones studied do not adhere to the same correlation, the discrepancy being especially marked for $E_{\frac{1}{2}}$. A similar linear dependence is found between log k_2 and the energy of the lowest unoccupied MO with log $k_2 = (5.85 \pm 1.33) E_{\mathrm{LUMO}} + (8.02 \pm 0.43)$. Table 2 presents data for acceptors for which electrochemical data are lacking, giving k_2 together with relevant values of Hammett substituent constants for (a) monosubstituted nitrobenzenes and (b) monosubstituted benzoic acids. The resulting Hammett plots (Figures 3 and 4) yield ρ 1.13 ± 0.39 for mono-

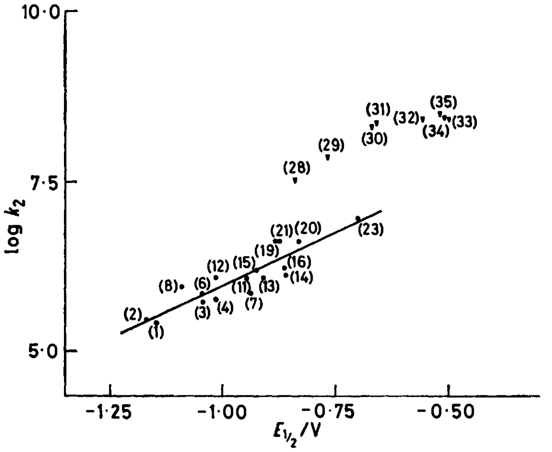


FIGURE 2 Dependence of log k_2 (see Figure 1) upon the half-wave reduction potential $E_{\frac{1}{2}}$ for some nitroaromatic compounds (●) and quinones (▼) (numbering as in Table 1). The straight line represents a least-squares analysis for nitroaromatic compounds only, with a slope of (3.14 ± 0.39) V^{-1}

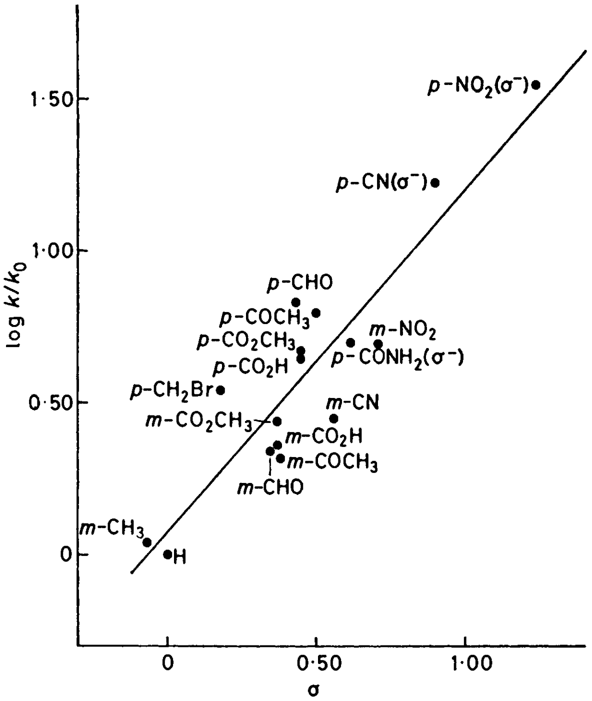


FIGURE 3 Hammett plot for reaction (3) for a series of nitrobenzenes (ρ 1.13 ± 0.39)

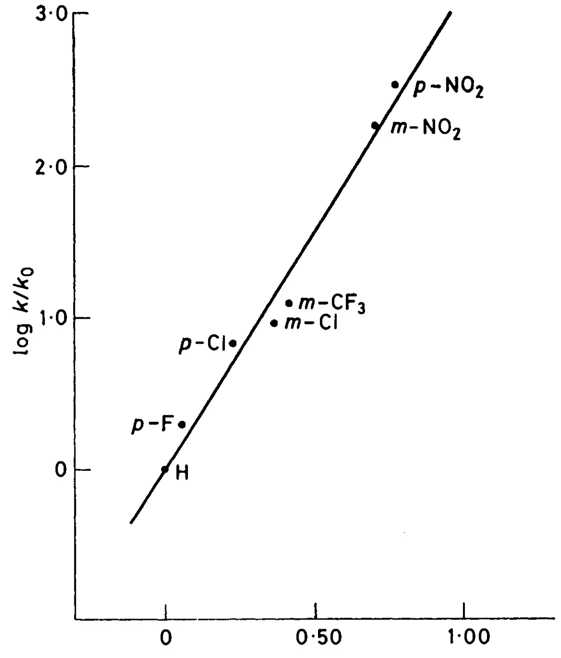


FIGURE 4 Hammett plot for reaction (3) for a series of benzoic acids (ρ 3.11 ± 0.21)

substituted nitrobenzenes and ρ 3.11 ± 0.21 for monosubstituted benzoic acids.

DISCUSSION

Because of their relative ease of reduction, nitroaromatic and nitroheterocyclic compounds have been used as efficient one-electron acceptors in the oxidation of both neutral free radicals and radical anions both of chemical and radiation-biological interest.[2,3,22,35-42] A similar application has been found for quinones.[39] Rates of reaction for the one-electron oxidation of $Me_2\dot{C}OH$ and $CO_2^{\cdot -}$, in aqueous solution, by nitrobenzoic acids, nitrobenzenes and di- and tri-nitrobenzoic acids have been reported [2] and are in the range 2×10^8—4×10^9 dm^3 mol^{-1} s^{-1} as determined by the pulse-radiolysis technique. Several 2- and 5-nitroimidazole radical anions transfer one electron to *p*-nitroacetophenone with rates lower than $(4.0 \pm 0.2) \times 10^7$ dm^3 mol^{-1} s^{-1} in aqueous solution.[38] The radical anion $CO_3^{\cdot -}$ is oxidised by duroquinone, in aqueous solution, with a rate of 2.0×10^9 dm^3 mol^{-1} s^{-1} which was measured by laser flash photolysis.[40] Semiquinone radical anions are reversibly oxidised by substituted 2-, 4-, and 5-nitroimidazoles [41] and by quinones [22] with rates in the range 7×10^5—1.5×10^8 dm^3 mol^{-1} s^{-1} and 0.5—2×10^8 dm^3 mol^{-1} s^{-1} respectively, in aqueous solution. 1-Hydroxy-radicals of propan-1-ol and butan-1-ol generated on pulse radiolysis of aqueous solutions are oxidised by nitroaromatic compounds with rates between 3×10^8 and 1.6×10^9 dm^3 mol^{-1} s^{-1}.[42]

TABLE 3

Absolute rate constants for the reaction of $Ph_2\dot{C}OH$ with nitroaromatic compounds in 25% (v/v) aqueous acetone

	$10^{-5}\ k_2$/dm^3 mol^{-1} s^{-1}	
Acceptor	Acetone	25% (v/v) Aqueous acetone
Nitrobenzene	2.62 ± 0.18	3.50 ± 0.25
3-Nitrobenzoic acid	6.01 ± 0.12	11.0 ± 0.8
1,3-Dinitrobenzene	12.8 ± 1.2 [a]	41.9 ± 3.7
3,4-Dinitrobenzoic acid	64.9 ± 2.0	371.0 ± 24
1,4-Dinitrobenzene	90.4 ± 0.4	378.0 ± 41

[a] Value from ref. 14.

The ability of the acceptor to take up an electron has been related to its electron affinity as measured by various parameters. For example, correlations of rate constants with polarographic half-wave reduction potentials, $E_{\frac{1}{2}}$, have been reported for the electrochemical one-electron reduction of nitroaromatic compounds in aprotic solvents,[43,44] and with equilibrium redox potentials, $E_7{}^1$, for the single electron reduction of quinones determined by pulse radiolysis, in aqueous solution at pH 7.[39] Unfortunately no electrochemical potentials are available in acetone with the exception of 1,2- and 1,4-naphthoquinone, the half-wave reduction potentials of which have been measured in different dipolar aprotic solvents,[45] including acetone. Values of $E_{\frac{1}{2}}$ so obtained, with the conditions used, are presented in Table 4 for acetone and acetonitrile from which a close similarity is apparent. It seems reasonable therefore to use $E_{\frac{1}{2}}$ values determined in MeCN to correlate with our rate constants, measured in acetone. Indeed a good linear dependence is found for nitroaromatic compounds, with $\log k_2 = 3.1 E_{\frac{1}{2}} + 9.1$, as illustrated in Figure 2. Moreover the rates for the reactions with quinones do not adhere to the same correlation found for nitroaromatic compounds. Because the values of $E_{\frac{1}{2}}$ used were measured in reversible conditions,[30,46] we conclude that the rates for the oxidation of (I) by quinones are higher by a factor of 10 than those by nitroaromatic compounds involving a similar change of standard free energy, ΔG^0. This result recalls a previous observation that in the oxidation of some nitroaromatic radical anions, in water, by O_2 [41] and quinones [20] with similar ΔG^0, the rates are 10^2—10^3 higher for the latter. In both cases the difference in reaction rates can be accounted for in terms of the Marcus theory for outer-sphere electron-transfer reactions[47] which predicts a different intercept, of 0.5 $(\Delta G_{11}{}^* + \Delta G_{22}{}^*)$, in a plot of the type $\Delta G_{12}{}^*$ *versus* ΔG^0 [here $\Delta G_{11}{}^*$, $\Delta G_{22}{}^*$, and $\Delta G_{12}{}^*$ refer to changes in the free energies of activation of the self-exchange reactions of (I) and the acceptors and of cross-reactions between (I) and acceptor] since the self-exchange reaction rates k_{22} are known to be different for nitroaromatic compounds and quinones. k_{22} Is higher for quinones [22] than for nitroaromatic compounds [48,49] with respective rates of 5×10^7 and 10^5 dm^3 mol^{-1} s^{-1} in aqueous solution, and 4—5×10^8 and 3—9×10^7 dm^3 mol^{-1} s^{-1} in aprotic solvents. One might expect, on the basis of Marcus theory, a larger difference in rate constants for electron-transfer reactions in aqueous solution than in aprotic solvents, for reactions with nitroaromatics and quinones involving similar ΔG^0. Radical (I) displays a low rate for the self-exchange of one electron in acetone since it is probably of the same order of

TABLE 4

Half-wave reduction potentials of naphthoquinones in Me_2CO and MeCN

Acceptor	Solvent	Dielectric constant of the solvent	10^{-3} Solvent viscosity/ poise	$E_{\frac{1}{2}}$/V, *vs.* s.c.e.	Concentration of the supporting electrolyte/ mol dm^{-3}
1,2-Naphthoquinone	Me_2CO	21.3	3.23	−0.57 [a]	0.05
	MeCN	37.5	3.45	−0.58 [a]	0.05
	MeCN			−0.56 [b]	0.10
1,4-Naphthoquinone	Me_2CO			−0.69 [a]	0.05
	MeCN			−0.70 [a]	0.05
	MeCN			−0.57 [b]	0 10

[a] Values from ref. 45. [b] Values from ref. 30.

magnitude of the reaction rate of (I) with benzophenone, which we found to be 3×10^5 dm^3 mol^{-1} s^{-1} in acetone. This rate is much lower than that for the self-exchange of $Ph_2CO^{\cdot -}$, of 1.1—1.6 $\times$ 10^8 dm^3 mol^{-1} s^{-1} measured in aprotic solvents by e.s.r.,[50] and could reflect geometrical changes accompanying the electron transfer.

In a recent publication[51] the one-electron reduction potentials of a number of acceptors, measured in dimethylformamide by cyclic voltammetry, were correlated with the equilibrium redox potentials, E_7^1, determined in aqueous solution by pulse radiolysis. This prompted us to attempt the correlation of our rate constants with E_7^1 values shown in Figure 1. A good linear relationship is found for nitroaromatic compounds, while a different correlation is apparent for quinones, a dichotomy which parallels that in the correlation with $E_{\frac{1}{2}}$ values (Figure 2). Even the fastest rates (with the quinones) are somewhat below the diffusion control limit, indicating that in these reactions the limiting rate is controlled by an orientation, or entropy, factor as are the slow reactions of e_{aq}^- with metal ions.[52]

For a number of acceptors no electrochemical potentials were available and consequently, following other groups, we have employed other parameters as a measure of the electron affinity of the acceptor such as the Hammett substituent constant, σ,[53-56] and the energy of the lowest unoccupied MO (LUMO).[43] From our data we found good linear correlations with the substituent σ constants for the oxidation of (I) by monosubstituted nitrobenzenes, with ρ 1.13, and by monosubstituted benzoic acids, with ρ 3.11 (Figures 3 and 4). The latter figure indicates a considerable sensitivity of the transition state to removal of charge from the ring, and recalls the ρ value of 4.80 found for the one-electron reduction of monosubstituted benzenes by e_{aq}^-.[53] The much smaller value of ρ for the reaction of the nitrobenzene series with (I) simply reflects the depletion of ring charge by the NO_2 group which results in much faster rates for the whole series with (I), with a resulting reduced response to further removal of charge. This situation parallels that found for the rates of electron transfer from $(CNS)_2^{\cdot -}$ and $Br_2^{\cdot -}$ to a series of *p*-substituted phenols, which show little sensitivity to substituent effects with reaction constants, ρ, of 1.2 and 1.1 respectively.[56] The dominant effect of the NO_2 group as the main repository of charge in the resulting radical anion relates to the requirement to use σ^- values in accounting for the effects of additional NO_2 and CN groups on the rate of reaction with nitrobenzene. In general, σ^- values are appropriate when there is direct conjugation between the substituent group (NO_2 and CN) and the site of reaction (NO_2), the so-called 'polarisability effect'[57] or 'through-conjugation.'[58]

In terms of simple MO theories, the electron affinity can be equated to the negative of the energy of the lowest unoccupied MO, E_{LUMO}.[59] Values for these have been calculated for a series of nitrobenzenes using the Hückel LCAO theory and the approximate configuration interaction treatment of McLachlan[19b] with γ_{CN} 1.2, γ_{NO} 1.67, δ_N 2.2, and δ_O 1.4. The correlation of log k_2 with these values is represented by the equation log $k_2 = 5.9\ E_{LUMO} + 8.0$. Energies for LUMOs were calculated for some quinones[61] by a self-consistent procedure with γ_{CO} 1.0 and δ_O 1.3, and are in the order $-E_5(b_{2g})$ 1,4-benzoquinone $> -E_7(b_1)$ 1,2-naphthoquinone $> -E_9(b_1)$ 9,10-phenanthraquinone; rate constants with these quinones are in the same order, as may be seen from Table 1.

The conclusion to be drawn is that the rate constants for the single-electron oxidation of (1) by suitable acceptors are linearly dependent upon various parameters used as a measure of the electron affinity of these acceptors, and this is in agreement with previous observations,[39,44] made on a smaller number of acceptors. Regrettably, the lack both of reliable reversible reduction potentials for the vast majority of our acceptors and of (I) itself in acetone solution, made a full Marcus treatment of our results impossible, but this may be only a temporary situation in view of the interest in establishing such data.[62]

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