Pulse Radiolysis Study of some Radical Protonation Reactions

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The rates of establishment of the acid-base equilibria for the radical anions of benzaldehyde, benzamide, benzonitrile, benzophenone, *p*-cyanoacetophenone and fluorenone have been studied by pulse radiolysis. In each case a first order rate of reaction was observed with $k_{obs} = k' + k''$ [H⁺], the constants having values of $k' = (0.3 - 7.8) \times 10^4 \text{ s}^{-1}$ and $k'' = (0.7 - 2.5) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These rate constants are associated with the reaction of the radical anion with water (k') and H⁺ (k''). The nature of the radical ions involved is discussed.

Many radicals exhibit acid-base properties, and a large number of acid dissociation constants have been reported.¹ Under certain circumstances a non-equilibrium mixture of radicals may be formed, as has been observed following pulse radiolysis of aqueous solutions of benzonitrile^{2, 3} and benzophenone,⁴ or flash photolysis of duroquinone.⁵ If the lifetime of the radicals is sufficiently long, the rate of establishment of equilibrium can, in principle, be determined. We describe here some such measurements with radicals produced by the hydrated electron reduction of benzalde-hyde, benzamide, benzonitrile, benzophenone, *p*-cyanoacetophenone and fluorenone.

EXPERIMENTAL

MATERIALS

All solutions were prepared from triply distilled water. Benzonitrile was purified by distillation and benzaldehyde by distillation under reduced pressure. Fluorenone (Fluka, puriss), *p*-cyanoacetophenone (Ega), benzamide (Aldrich, zone refined), benzophenone (Baker, photosensitizer), and t-butanol (Merck, p.a.) were used without further purification. The pH of the solutions was adjusted by addition of HClO₄ or NaOH, and was measured in unirradiated solutions. A small correction (always $\leq 10\%$) has been applied to this to take into account the H⁺ ions produced by the radiation [reaction (1)]. All experiments were performed at $22\pm 2^{\circ}$ C.

APPARATUS

Pulse radiolysis experiments were carried out using $0.5-1.0 \mu$ s pulses of 1.6 MeV electrons from a Van de Graaff accelerator. Doses of ~0.5-1.0 krad per pulse were used. The optical system consisted of a 15 mm path length cell, a Zeiss MQ4 III prism monochromator, and an EMI 9558 QB photomultiplier. Other details of apparatus and technique were as described elsewhere.⁶⁻⁸

RESULTS AND DISCUSSION

The radicals were produced by the pulse radiolysis of deaerated aqueous solutions containing 10^{-3} mol dm⁻³ S, where S = benzaldehyde, benzamide, benzonitrile,

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benzophenone, p-cyanoacetophenone or fluorenone. The reactions occurring following a pulse of radiation can be described by (1) and (2). t-Butanol was added to scavenge the hydroxyl radicals :

$$H_2O \longrightarrow e_{aq}, H, OH, H_2, H_2O_2, H^+$$
(1)

$$e_{aq}^- + S \to S^- \tag{2}$$

$$S^- + H^+ \rightleftharpoons SH.$$
 (3)

The absorption spectra of the acid and base forms of the radicals have been shown to differ, and the pK_3 values measured.^{2-4, 9-12} At pH values above pK_3 or less than ≈ 4 , the radicals were observed to decay by second order kinetics (the half life was inversely dependent on dose). At pH values between ≈ 4 and pK_3 , however, there was a rapid decay to a plateau. Under these conditions the absorption spectrum at the end of the pulse was similar to that at much higher pH (S⁻), whilst that of the plateau was practically identical to the absorption found at much lower pH (SH). The initial absorption decayed exponentially (plots of $\ln(D_t - D_{\infty})$ against time were linear over three half lives) at pH values $\sim 4-5$. The observed rate constant, k_{obs} , was found to vary with [H⁺] according to eqn (4) (see fig. 1).

$$k_{\text{obs}} = k' + k''[\text{H}^+] \tag{4}$$

Values of the constants k' and k'' for the various compounds studied were estimated from the intercepts and slopes respectively of plots such as shown in fig. 1, and are collected together in table 1.



FIG. 1.—Plot of k_{obs} against [H⁺] for the protonation of some radical anions. (a) for benzophenone (○), benzaldehyde (□), and fluorenone (△) in deaerated solutions containing 10⁻³ mol dm⁻³ of the solute and 0.1 mol dm⁻³ t-butanol (2.5 mol dm⁻³ for fluorenone). (b) for benzonitrile (10⁻³ mol dm⁻³) containing 0.1 (○), 1.0 (□), and 2.5 (△) mol dm⁻³ t-butanol.

These observations can be understood in terms of the protonation of S^- to give SH. The reactions to be considered are (3) and (5):

$$S^- + H_2 O \rightleftharpoons SH + OH^-. \tag{5}$$

The rate of conversion of S^- to SH is given therefore by (6).

$$-d[S^{-}]/dt = k_{3}[H^{+}][S^{-}] - k_{-3}[SH] + k_{5}[S^{-}][H_{2}O] -k_{-5}[SH][OH^{-}].$$
(6)

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No simple solution exists for this equation (with similar expressions for d[SH]/dt and d[OH⁻]/dt). Under the conditions of these experiments equations (3) and (5) initially lie 100% to the left, whilst at equilibrium they are strongly to the right ([SH]/ $[S^-] \ge 10$). Over the first three half lives of the decay of S⁻, the rates of the reverse reactions, (-3) and (-5), are negligibly small, and (6) simplifies to (7),

$$-d[S^{-}]/dt = k_{3}[H^{+}][S^{-}] + k_{5}[S^{-}][H_{2}O]$$
(7)

$$= (k_3[H^+] + k'_5)[S^-]$$
(8)

where $k'_5 = k_5[H_2O]$. Hence the experimentally determined rate constants, k' and k", can be identified with k'_5 and k_3 respectively. The values found are similar to those for stable species of about the same size measured by conventional relaxation

solute (S) ^a	[t-butanol]/ mol dm ⁻³	$\frac{10^{-4}k'}{s^{-1}b}$	$\frac{10^{-10}k''}{\mathrm{dm^3 \ mol^{-1} \ s^{-1} \ c}}$	pK ₃
benzaldehyde	0.1	5.0	0.9	8.4, ^d 10.5 ^e
benzamide	0.1	2.3	0.55	7.75
benzonitrile	0.1	3.0	1.6	7.2, ^g 7.4 ^h
	1.0	2.5	1.1	
	2.5	2.0	0.7	
benzophenone	2.5	7.8	1.2	9.2, ⁱ 9.25 ^f
p-cyanoacetophenone	0.1	1.2	2.5	6.95 ^j
fluorenone	2.5	≤0.3	0.9	6.3 ^f

^a [S] = 10^{-3} mol dm⁻³ in all cases; ^b rate constant for S⁻+H₂O, ±50%; ^c rate constant for S⁻+H⁺, ±20%; ^d from ref. (11); ^e from ref. (10); ^f from ref. (4); ^e from ref. (2); ^h from ref. (3); ⁱ from ref. (9); ^j from ref. (12).

methods.¹³ The values of k_3 fall into the group described by Eigen *et al.*¹³ as "normal"; that is, they are near the diffusion controlled limit and ~ 10 times smaller than $k(H^++OH^-)$. Rate constants for SH+OH⁻ (*i.e.*, k_{-5}) calculated from the experimentally determined values of k'_5 and literature data on pK_3 (see table 1) fall in the range $(0.5-13) \times 10^{10}$ dm³ mol⁻¹ s⁻¹, and we conclude that this reaction is diffusion-controlled in the cases studied.

With benzophenone and fluorenone it was found necessary to add a concentration of t-butanol of 2.5 mol dm⁻³ (i.e., $\approx 25 \% v/v$) to aid solubility. In the former case the experimental value of k' is, therefore, an underestimate of k'₅. Also the reduction in the dielectric constant and the diffusion coefficients, especially that of H⁺, caused by the use of high t-butanol concentrations leads to underestimation of k_3 relative to that in dilute aqueous solutions. Some experiments on the effect of [t-butanol] in the benzonitrile system were performed (table 1), and give an indication of the magnitude of the reductions involved.

The benzonitrile results at [t-butanol] = 0.1 mol dm⁻³ are slightly at variance with those of Holcman and Sehested,³ who found $k_3 = 3.5 \times 10^{10}$ dm³ mol⁻¹ s⁻¹, a factor of two greater than our value, and no acid independent pathway. We have no entirely satisfactory explanation for these discrepancies.

For benzaldehyde, benzamide, benzophenone and fluorenone the radical anion, S⁻, is of the ketyl type, $R_1CO^-R_2$. With benzonitrile the radical anion has been assigned ² the structure $C_6H_5C = N^-$. We have been able to confirm that the radical exists as an anion at pH 9.85, and as a neutral species at pH 3.9 by measuring the a.c. conductivity ¹⁴ following pulse radiolysis of benzonitrile solution. With the *p*-cyanoacetophenone radical Adams and Willson ¹² have stated that the unpaired electron density is associated predominantly with the carbonyl function. We suggest,

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however, that it resides mainly on the cyano group, on the grounds that the pK of the radical is 6.95,¹² close to that of the radical derived from benzonitrile (pK = 7.2),² but well below that of other acetophenones (pK = 9.2-9.7).¹²

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