Semiquinone Free Radicals: Determination of Acid Dissociation Constants by Pulse Radiolysis

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Summary The acid dissociation constants of the semiquinone free radicals of 2,5-dimethyl-*p*-benzoquinone, tetramethylbenzoquinone, 1,4-naphthaquinone, 2-methyl-1,4-naphthaquinone, and anthraquinone-2,6-disulphonate, have been determined in water–isopropyl alcohol–acetone solutions (*ca.* 90% w/w water) by pulse radiolysis.

THE acid dissociation constants (pK_a) of several semiquinone free radicals have been determined by flash photolysis and pulse radiolysis techniques. In particular, for the semiquinones of *p*-benzoquinone in water,[1] tetramethylbenzoquinone (duroquinone) in water–ethanol,[2] anthraquinone-2-sulphonate in water,[3] and ubiquinone in methanol,[4] pK_a values of 4·0, 5·7, 3·25, and 6·5 respectively, have been reported.

Recently,[5,6] it has been shown that benzoquinone semiquinone radicals can be formed in isolation on pulse radiolysis of water–acetone–isopropyl alcohol solutions of the quinone (Q).

$$H_2O \rightarrow H, e^-_{aq}, OH \qquad (1)$$

$$CH_3COCH_3 + e^-_{aq} \rightarrow CH_3CO^-CH_3 \qquad (2)$$

$$CH_3CO^-CH_3 + H_2O \rightleftharpoons CH_3\dot{C}(OH)CH_3 \qquad (3)$$

$$CH_3\dot{C}H(OH)CH_3 + H \text{ or } OH \rightarrow CH_3\dot{C}(OH)CH_3 + H_2 \text{ or } H_2O \qquad (4)$$

$$CH_3\dot{C}(OH)CH_3 + Q \rightarrow Q^- + CH_3COCH_3 + H^+ \qquad (5)$$

$$\text{or } CH_3\dot{C}(OH)CH_3 + Q \rightarrow QH\cdot + CH_3COCH_3 \qquad (6)$$

$$Q^- + H_2O \rightleftharpoons QH\cdot + OH^- \qquad (7)$$

Thus, if (*a*) equilibrium (7) is established rapidly compared to reactions (5) and (6) and both QH· and Q^- decay relatively slowly, (*b*) A is the observed overall optical absorption at a wavelength where the extinction coefficient of QH and Q^- differ markedly and is equal to the sum of the separate absorbances of the conjugate forms, and (*c*) $A_{QH\cdot}$ and A_{Q}^{-} are the observed absorbance when $[QH]/[Q^-] \rightarrow \infty$ and 0 respectively, then a plot of A against pH should fit equation (8). In the case of benzoquinone, the experimental data fitted equation (8) for pK_a = 4·1, in good agreement with pK_a=4·0 determined previously.[1] Thus, the

$$A = A_{QH\cdot}/(1 + 10^{pH-pK_a}) + A_{Q}^{-}/(1 + 10^{pK_a-pH}) \qquad (8)$$

above system appeared to provide a convenient method for the determination of the acid dissociation constants of other semiquinones, particularly as the hydroquinone analogues are not required and the presence of acetone and isopropyl alcohol often facilitates solution preparation.

On pulse radiolysis of solutions of 2,5-dimethyl-*p*-benzoquinone, tetramethylbenzoquinone, 1,4-naphthaquinone, 2-methyl-1,4-naphthaquinone, and anthraquinone-2,6-disulphonate (10^{-4}M), containing acetone and isopropyl alcohol (1M) intense transient absorptions were observed in the region 300—600 nm. The absorptions, which formed over a period of 10—30 μs and decayed relatively slowly, varied markedly with pH and are attributed, in acid solution, to the corresponding semiquinone radicals and, in neutral solution, to the conjugate radical anions (Table). The spectra observed in neutral solutions of 2-methyl-1,4-naphthaquinone (menadione) were similar to those of the radical-anion, formed by direct electron attachment, reported previously.[7,8]

Semiquinone absorption maxima and acid dissociation constants

Quinone	λ_{max}/nm (pH 2)	λ_{max}/nm (pH 7)	pK_a*
2,5-Dimethyl-*p*-benzoquinone	415	440	4·6 (440 nm†)
Tetramethyl-*p*-benzoquinone	430	445	5·1 (450 nm)
1,4-Naphthaquinone	380	390	4·1 (400 nm)
2-Methyl-1,4-naphthaquinone	370	405	4·7 (410 nm)
Anthraquinone-2,6-disulphonate	390	395, 525	3·2 (390 nm)
			3·2 (525 nm)

* ±0·1 pK units. † All solutions contained phosphate buffer (4mM) and, where necessary, additional H_2SO_4.

The optical absorptions, measured at selected wavelengths, closely fitted equation (8). Acid dissociation constants for the best fit, at the wavelengths shown in parentheses, were derived from computed theoretical curves. With anthraquinone-2,6-disulphonate similar values were derived at 525 nm where the absorption increased and at 390 nm where the absorption decreased with increasing pH. The pK_a value for durosemiquinone (5·1) is lower than that determined by flash photolysis (5·7). However, the trend of an increasing acid dissociation constant of the benzosemiquinone radical with an increasing substitution of methyl-groups is supported by the intermediate value (4·6) determined for the 2,5-dimethyl-derivative. The value for 2-methyl-1,4-naphthasemiquinone (4·7) is higher than that for the unsubstituted radical (4·1)

Studies have also been made with anthraquinone-1,5-disulphonate. However, little change in the transient absorption spectrum (λ_{max} = 395 nm) was observed over the range pH 2—6. At pH 8 a similar absorption was observed initially, but this decayed slowly ($t_{\frac{1}{2}}$ *ca.* 60 μs) to form another absorption (λ_{max} 400 and 525 nm). Preliminary kinetic studies in the presence of t-butyl alcohol suggest that the initial absorption is that of the semiquinone radical which dissociates according to equation (7) with pK_a *ca.* 7. This marked variation in the acid dissociation constants of the semiquinone radicals of the anthraquinone-1,5- and -2,6-disulphonate may be related to the observed differences in their photosensitising abilities.

The technical assistance of Mr. K. Patel is gratefully acknowledged.

(*Received, July 12th,* 1971; *Com.* 1184.)

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