The Radiation-induced Oxidation of Aqueous Solutions of Hydroquinone

By **T. J. Fellows** and **G. Hughes,*** Donnan Laboratories, The University, Liverpool L69 3BX

The radiation-induced oxidation of hydroquinone in aqueous solution has been investigated. The products are hydrogen peroxide, *p*-benzoquinone, and 2-hydroxy-*p*-benzoquinone. The yields are pH-dependent and *G*(2-hydroxy-*p*-benzoquinone) decreases to zero at low pH. The effect of solutes on *G*(*p*-benzoquinone) has also been investigated and a mechanism suggested for the reactions occurring.

IN the radiolysis of aqueous solutions of some compounds *e.g.* propan-2-ol [1] and *p*-nitrosodimethylaniline,[2] these solutes can apparently react with the hydroxyl radical (or its equivalent) even under conditions where all hydroxyl radicals might be expected to react with added scavengers. This has been interpreted as indicating that there is some precursor of the hydroxyl radical which reacts preferentially with these solutes. However the evidence is somewhat sparse and it seems desirable to study scavenger effects in other systems. It is claimed [3] that the oxidation yields in the radiolysis of aqueous solutions of some substituted hydroquinones can be related simply to the hydroxyl radical yield and it appeared that such systems would be suitable for a further investigation of scavenger effects. There are few data on the radiation-induced oxidation of aqueous solutions of hydroquinone itself and this paper reports first on a study of hydroquinone solutions and secondly on the effect of scavengers.

EXPERIMENTAL

Triply distilled water was used in making all solutions. Solutions were irradiated with a 90 Ci ^{137}Cs source at 20 ± 2 °C at dose rates 0·6—2 × 10^{16} eV cm^{-3} min^{-1}. The irradiation facility has been described.[4] Chemicals were AnalaR grade where possible. *p*-Benzoquinone was laboratory grade and was recrystallised twice from hot aqueous ethanol. 2-Hydroxy-*p*-benzoquinone was prepared from 1,2,4-trihydroxybenzene by oxidation in ethereal solution under strictly anhydrous conditions with Ag_2O.

p-Benzoquinone was determined spectrophotometrically (Unicam SP500). Its extinction coefficient at its absorption maximum of 246 nm was determined to be 2·14 × 10^4 l mol^{-1} cm^{-1}. At this wavelength the extinction coefficient of hydroquinone was 205 l mol^{-1} cm^{-1} and is thus negligible. However, 2-hydroxy-*p*-benzoquinone absorbs at 246 nm (ε 1·05 × 10^4 l mol^{-1} cm^{-1}). The amount of 2-hydroxy-*p*-benzoquinone could be determined from its absorption peak at 360 nm (ε 1·60 × 10^3 l mol^{-1} cm^{-1}), at which wavelength neither *p*-benzoquinone nor hydroquinone absorb. Its contribution to the absorption at 246 nm could therefore be calculated.

Great difficulty was experienced in analysing for hydrogen peroxide either by the potassium iodide [5] or titanium sulphate [6] method in the presence of hydroquinone which led to a decrease in the optical density with time. Extrapolation to zero time of mixing was not very satisfactory though an approximate value could be obtained by the potassium iodide method by diluting the irradiated solutions such that [hydroquinone] < 5 × 10^{-5}M.

RESULTS AND DISCUSSION

Radiation-induced Oxidation of Hydroquinone.—When a solution of 10^{-3}M-hydroquinone (HQ) in oxygen-saturated 0·05M-H_2SO_4 was irradiated, absorption maxima developed in the irradiated solution at 246

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[1] G. Hughes and H. A. Makada, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 325.

[2] S. Shah, C. N. Trumbore, B. Geissner, and W. Park, ' Radiation Chemistry,' Advances in Chemistry Series, American Chemical Society, 1968, vol. 81, p. 321.

[3] B. H. J. Przybielski-Bielski and R. R. Becker, *J. Amer. Chem. Soc.*, 1960, **82**, 2164.

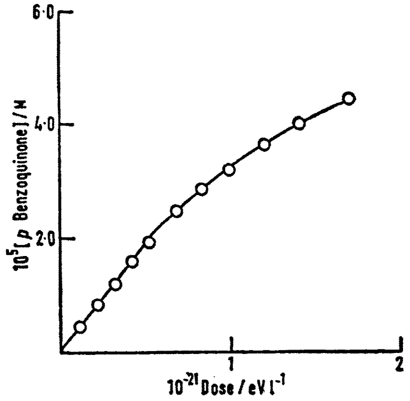
[4] G. Dobson and G. Hughes, *Trans. Faraday Soc.*, 1961, **57**, 1117.

[5] C. J. Hochanadel, *J. Phys. Chem.*, 1952, **56**, 587.

[6] G. M. Eisenberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 327.

and 360 nm, these being characteristic of *p*-benzoquinone (BQ) and 2-hydroxy-*p*-benzoquinone (HBQ) respectively. Moreover the spectrum of the irradiated solution corresponded to the sum of the individual spectra of benzoquinone and 2-hydroxybenzoquinone.

The Figure shows that the rate of production of benzoquinone is constant at low doses but decreases at higher doses, presumably because BQ reacts with radiolytic intermediates. The yields reported are in all cases initial yields and were independent of dose. The dependence of the yields of benzoquinone and 2-hydroxybenzoquinone on hydroquinone concentration in oxygen-saturated solution is shown in Table 1.



Production of *p*-benzoquinone in 4 × 10^{-3}M-hydroquinone in oxygen-saturated 0·05M-H_2SO_4

TABLE 1

Product yields in 0·05M-sulphuric acid

10^4[Hydroquinone]/M	*G*(*p*-Benzoquinone)	*G*(2-Hydroxy-*p*-benzoquinone)
2·0	1·13	1·00
4·0	1·37	1·23
5·0	1·24	1·22
6·0	1·38	1·35
8·0	1·62	0·96
10·0	1·80	0·85
30·0	2·28	0·55
40·0	2·46	0·50
65·0	2·62	0·46
80·0	2·62	0·42
100·0	2·64	0·40

Whereas *G*(BQ) increases with hydroquinone concentration, *G*(HBQ) decreases. Tables 2 and 3 present data for 0·5, 1·0, and 2·0M-H_2SO_4. At higher acidities, *G*(BQ) increases to a limiting yield and there is a corresponding decrease in *G*(HBQ) which falls to zero at the highest hydroquinone concentrations in [H_2SO_4] > 1M. At [H_2SO_4] ⩾ 1M there is no effect of increasing acidity. Table 3 shows that there is no effect of oxygen concentration in the range 2 × 10^{-4}—10^{-3}M. The limiting values of *G*(BQ) were also shown to be independent of dose rate in the range 0·6—2·0 × 10^{16} eV cm^{-3} min^{-1}.

TABLE 2

Product yields in 0·50M-sulphuric acid

10^4[Hydroquinone]/M	*G*(*p*-Benzoquinone)	*G*(2-Hydroxy-*p*-benzoquinone)
2·0	1·30	1·30
5·0	1·96	1·21
10·0	2·20	1·02
22·5	2·38	1·04
40·0	2·98	0·64
54·0	2·96	0·60
60·0	3·01	0·50
80·0	2·99	0·31
100·0	3·02	0·22

TABLE 3

Product yields in 1·0 and 2·0M-H_2SO_4

10^4[Hydroquinone]/M	*G*(*p*-Benzoquinone)		*G*(2-Hydroxy-*p*-benzoquinone)	
	1·0M	2·0M	1·0M	2·0M
10·0	2·94	2·95	0·47	0·41
10·0 *	2·96	2·91		
20·0	3·11	3·15		
40·0	3·20	3·32	0·30	0·20
40·0 *	3·27	3·28		
60·0	3·21	3·31		
80·0	3·19	3·32	0	0
100·0	3·24	3·28	0	0
100·0 *	3·34	3·31		

* Air-saturated solution.

$$H_2O \rightsquigarrow H,\ e^-_{aq},\ H^+,\ OH,\ H_2,\ H_2O_2 \qquad (1)$$

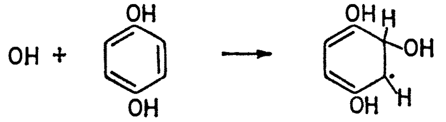
$$e^-_{aq} + O_2 \rightarrow O_2^- \qquad (2)$$

$$e^-_{aq} + H^+ \rightarrow H \qquad (3)$$

$$H + O_2 \rightarrow HO_2 \qquad (4)$$

$$O_2^- + H^+ \rightleftharpoons HO_2 \qquad (5)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \qquad (6)$$



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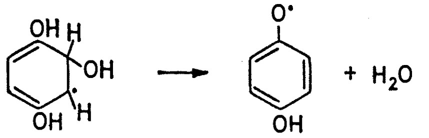
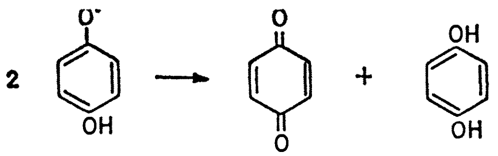


(8)

By analogy with the reaction scheme suggested by Bielski and Becker,[3] reactions (1)—(8) might be expected to occur in the radiolysis of oxygenated hydroquinone solutions. If the only fate of the semiquinone radical was the disproportionation (9), then benzoquinone would be the only organic oxidation product



(9)

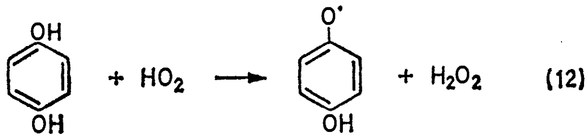
and oxidation yields would be given by equations (10) and (11). It is clear however that *G*(BQ) > $\frac{1}{2}G_{OH}$.

$$G(BQ) = \tfrac{1}{2}G_{OH} \qquad (10)$$

$$G(H_2O_2) = \tfrac{1}{2}(G_e + G_H) + G_{H_2O_2} \qquad (11)$$

Although it was difficult to measure *G*(H_2O_2) accurately, an approximate value of *G*(H_2O_2) = 4·0 ± 0·5 was obtained for 10^{-3}M-hydroquinone in 1·0M-H_2SO_4. This is clearly in excess of that predicted by equation (11).

These higher yields could arise if HO_2 reacts (12)



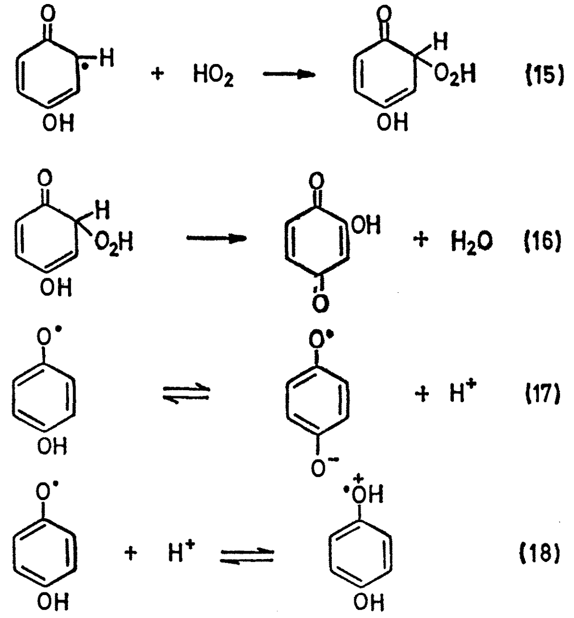
with hydroquinone. If all HO_2 reacts *via* (12) then equations (13) and (14) should hold. From accepted

$$G(BQ) = \tfrac{1}{2}(G_e + G_H + G_{OH}) \quad (13)$$

$$G(H_2O_2) = G_e + G_H + G_{H_2O_2} \quad (14)$$

values of the primary yields,[7] the predicted values of $G(BQ)$ and $G(H_2O_2)$ are 3·30 and 4·35 respectively.

The limiting value of $G(BQ)$ observed at the higher hydroquinone concentrations in $[H_2SO_4] \geqslant 1M$ is in good agreement with the predicted value. At lower hydroquinone concentrations and at lower acidities, $G(BQ)$ is less than the predicted value and production of 2-hydroxybenzoquinone is observed. A possible mechanism for the production of 2-hydroxybenzoquinone involves ring addition of the HO_2 radical to the semiquinone radical[8] although it is likely that addition (15) takes place *via* the resonance form in which the free electron is delocalised on the benzene ring followed by reaction (16). Insofar as reaction (15) is in competition with reaction (12), $G(HBQ)$ would decrease with increasing hydroquinone concentration. The effect of acidity would indicate an acid–base equilibrium (17)



involving the semiquinone radical. Ionisation of this radical has been observed.[9] However at pH 2 all the semiquinone is present in its un-ionised form and $pK_a = 4·0$ so that this equilibrium cannot be responsible for the changes observed. There does not appear to be any information on the effect of high acid concentrations on the semiquinone radical, although the protonated species would be expected to be resonance-stabilised.

The equivalent protonated resonance structure would not be expected to undergo radical addition as readily as its unprotonated equivalent insofar as the electron density on the 2-position is likely to be less. Addition of HO_2 then, and consequently production of 2-hydroxybenzoquinone only takes place at low acidity and at low hydroquinone concentration.

Although estimates of the spin distribution of the protonated form of the semiquinone radical in nitromethane indicate that the distribution may not be very different from that in the unprotonated form,[9] it is not clear that this would necessarily be the case in the aqueous system. If this proved to be so for the aqueous system, then the effect of acidity may well reflect the acid-catalysed nature [10,11] of reaction (8).

Effect of Added Scavengers.—It was of interest to investigate the effect of hydroxyl radical scavengers on the oxidation of hydroquinone. $4 \times 10^{-3}M$-Hydroquinone was used in oxygen-saturated $1·0M-H_2SO_4$. When methanol, ethanol, and propan-2-ol were used as scavengers, it was found that they had no effect on $G(BQ)$; see Table 4. The rate constants for the reaction of the OH radical with hydroquinone, methanol, ethanol, and propan-2-ol are $1·2 \times 10^{10}$, 3×10^8, 3×10^8, and $9·6 \times 10^8$ l mol^{-1} s^{-1} respectively,[12,13] so that at the highest concentrations of alcohols used most, if not all, OH radicals are scavenged by the alcohol.

TABLE 4

Effect of alcohols on G(*p*-benzoquinone) in $4 \times 10^{-3}M$-hydroquinone in oxygen-saturated $1·0M-H_2SO_4$

	G(*p*-Benzoquinone)		
100[Alcohol]/M	Methanol	Ethanol	Propan-2-ol
0	3·20	3·20	3·20
5·0	3·18	3·20	3·22
10·0	3·14	3·16	3·14
25·0	3·27	3·18	3·20
50·0	3·24	3·18	3·24
100	3·21	3·20	3·29

It is likely that if reaction (12) occurs, then other peroxy-radicals may be able to react similarly. Thus the alcohol will scavenge hydroxyl radicals or hydrogen atoms to give peroxy-radicals in the presence of oxygen. These may then react in a similar manner to reaction (12). If RH represents the alcohol, the overall reaction will be (19)—(22). $G(BQ)$ is given by equation (13)

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[7] G. V. Buxton, ' Radiation Research,' ed. G. Silini, North Holland Publishing Co., Amsterdam, 1967, p. 235.

[8] B. H. J. Bielski and J. M. Gebicki, ' Advances in Radiation Chemistry,' eds. M. Burton and J. L. Magee, Wiley-Interscience, New York, 1970, p. 177.

[9] P. D. Sullivan, J. R. Bolton, and W. E. Geiger, *J. Amer. Chem. Soc.*, 1970, **92**, 4176.

[10] R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1967, 926.

[11] G. E. Adams, B. D. Michael, and E. J. Land, *Nature*, 1966, **211**, 293.

[12] G. E. Adams and B. D. Michael, *Trans. Faraday Soc.*, 1967, **63**, 1171.

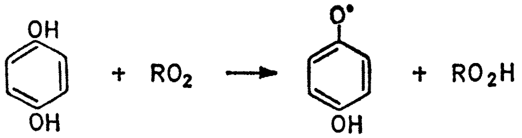
[13] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1965, **16**, 227.

and should be independent of alcohol concentration, as observed.

$$\mathrm{OH} + \mathrm{RH} \longrightarrow \mathrm{R} + \mathrm{H_2O} \qquad (19)$$

$$\mathrm{H} + \mathrm{RH} \longrightarrow \mathrm{R} + \mathrm{H_2} \qquad (20)$$

$$\mathrm{R} + \mathrm{O_2} \longrightarrow \mathrm{RO_2} \qquad (21)$$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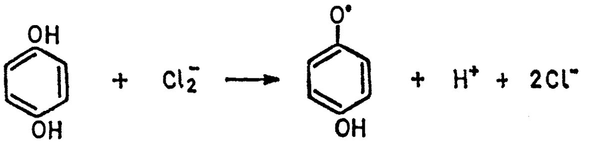
(23)

When sodium chloride was used as a hydroxyl scavenger, there was an increase in G(BQ) at high chloride ion concentrations (Table 5). This increased yield can be attributed to spur scavenging of molecular hydrogen peroxide by chloride ion and subsequent reaction (23) of the $\mathrm{Cl_2^-}$ ion-radical with hydroquinone.

TABLE 5

Effect of $\mathrm{Cl^-}$ on G(*p*-benzoquinone) in 4×10^{-3}M-hydroquinone in oxygen-saturated 1·0M-$\mathrm{H_2SO_4}$

[Cl⁻]/M	G(*p*-benzoquinone)	[Cl⁻]/M	G(*p*-benzoquinone)
0	3·20	0·8	3·47
0·2	3·28	1·2	3·63
0·4	3·35	1·6	3·71
0·6	3·40		

Since alcohol scavengers do not affect G(BQ), it is clear that the hydroquinone system cannot be used in a manner analogous to the propan-2-ol system.[1] Bielski and Becker[3] suggested that some substituted hydroquinones do not react with peroxy-radicals so that these would be potentially simpler systems and attention has been turned to these and will be reported later.

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