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The Radiation-induced Oxidation of Hydroquinones in Aqueous Solutions[1]

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The oxidation of solutions of hydroquinones in 0.8 N sulfuric acid by Co^{60} gamma rays has been studied. The following G values (G = molecules converted/100 e.v.) in air-saturated solutions were obtained: $-G$ (2,5-dichloro-*p*-hydroquinone) = 1.42 ± 0.05; $-G$ (2,5-dimethyl-*p*-hydroquinone) = 3.36 ± 0.20; $-G$ (1,2,4-trihydroxybenzene) = 3.12 ± 0.18; $-G$ (2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone) = 7.68 ± 0.53. Mechanisms for these oxidations based upon these values and those for oxygen consumption, quinone and hydrogen peroxide formation, are discussed in terms of the primary decomposition products of water radiolysis.

Introduction

Numerous investigations[3-8] in recent years have led to the formulation of a radical diffusion model for radiation chemical reactions in aqueous solutions. According to this model radiation chemical reactions in aqueous solutions are initiated by radicals generated from water as a result of energy degradation processes. In studying the effect of Co^{60} gamma rays on ascorbic acid in aqueous solutions, Barr[8] was able to postulate a mechanism of oxidation consistent with this model. Investigation of the radiation-induced oxidation of a series of organic compounds in aqueous solutions was undertaken to test the general applicability of this model and to obtain information on the mechanism of oxidation of organic compounds in solution. Hydroquinones were selected not only because they undergo an oxidation reaction which may be conveniently studied but also because the kinetics of their oxidation by common oxidizing agents have been investigated.[9-15] It was felt that these studies would be helpful in the interpretation of the radiation-induced oxidations. 2,5-Dimethyl-*p*-hydroquinone, 2,5-dichloro-*p*-hydroquinone, 1,2,4-trihydroxybenzene and 2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone were selected since all are oxidized to the corresponding quinones.

Experimental

Irradiations.—Two cylindrical sources of Co^{60} gamma rays, which have been described previously,[16] were used. Energy absorption in solutions was determined periodically with the Fricke ferrous sulfate dosimeter.[17] Dose rate values for the two sources were 1.6×10^{21} e.v./l. hr. and 7.0×10^{21} e.v./l. hr. All irradiations were performed in pre-irradiated Pyrex glassware at temperatures between 25 and 30°. Distilled water and reagent grade inorganic chemicals were used throughout. 2,5-Dimethyl-*p*-benzoquinone, 2,5-dichloro-*p*-benzoquinone and 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone were purchased from the Eastman Kodak Company. 2,5-Dihydroxy-*p*-benzoquinone was obtained from the Edwal Laboratories, Inc. The method of Thiele and Winter[18] was used for the synthesis of 1,2,4-trihydroxybenzene; hydroxy-*p*-benzoquinone was prepared from this compound by silver oxide oxidation.[19] The hydroquinones were prepared by standard reduction procedures utilizing zinc and acetic acid and resublimed before use, with the exception of 2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone. 2,5-Dichloro-3,6-dihydroxy-*p*-hydroquinone decomposes over a broad temperature range and no melting point was obtained. In all other cases the melting points corresponded to those in the literature. Air-saturated solutions of the hydroquinones ($1-7 \times 10^{-3}$ M) in 0.8 N H_2SO_4 were studied in most cases. Solutions to be irradiated in the absence of oxygen were placed into an all-glass apparatus, sparged with nitrogen, evacuated and sealed off. Six individual irradiation tubes could be filled and sealed without exposure to air. The solutions were then irradiated and analyzed in the usual manner.

Analytical Methods.—The hydroquinones and quinones were determined spectrophotometrically, using a Beckman DU spectrophotometer with temperature controlled at 30.0 ± 0.2°. The measurements in the ultraviolet region were taken in 1 cm. quartz cells; 10 cm. Corex cells were used in the visible range. The extinction coefficients for the quinone compounds used in this study are given in Table I.

Dissolved oxygen was determined polarographically[8,20] in a bath thermostated to 30 ± 0.1°.

The determination of hydrogen peroxide in this study is based on the complex formation between hydrogen peroxide and titanium sulfate.[21] Since it had been observed that on addition of titanium sulfate to an irradiated hydroquinone solution, an oxidation reduction reaction is initiated between the peroxide and the hydroquinone, the analytical technique described by Eisenberg[21] was modified. The following method gave reproducible results for hydrogen peroxide formed during irradiation of hydroquinone solutions: equal aliquots of the irradiated solution and of titanium sulfate reagent were mixed. A timer was started at the moment of mixing, and optical density measurements were taken over a period of several minutes. The optical density measurements then were extrapolated to zero time (mixing time). The rates of hydrogen peroxide formation were obtained from plots of zero time values *versus* the time of irradiation.

Results and Discussion

It was found that 2,5-dichloro-*p*-hydroquinone, 2,5 - dimethyl - *p* - hydroquinone, 1,2,4-trihydroxybenzene and 2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone are sufficiently soluble to be studied under concentration-independent conditions and are oxidized to the corresponding quinones. Attempts

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TABLE I

EXTINCTION COEFFICIENTS OF HYDROQUINONES AND QUINONES STUDIED

Compound	Wave length, Å.	Slit width, mm.	Molar ext. coeff.
2,5-Dimethyl-*p*-hydroquinone	2570	0.8	343 ± 10
	2880	.6	3,265 ± 12
2,5-Dimethyl-*p*-benzoquinone	2570	.8	19,500 ± 500
	2880	.6	257 ± 10
2,5-Dichloro-*p*-hydroquinone	2720	.7	860 ± 20
	2980	.5	4,500 ± 50
2,5-Dichloro-*p*-benzoquinone	2720	.7	19,650 ± 300
	2980	.5	354 ± 30
1,2,4-Trihydroxybenzene	2570	.8	350 ± 10
	2880	.6	3,235 ± 25
Hydroxy-*p*-benzoquinone	2460	.9	10,800 ± 200
	2570	.8	14,200 ± 350
	2880	.6	450 ± 12
2,5-Dihydroxy-*p*-benzoquinone	2460	.9	1,285 ± 60
	2570	.8	4,680 ± 120
	2880	.6	21,180 ± 580
2,5-Dichloro-3,6-dihydroxy-*p*-hydroquinone	5120	.1	0
2,5-Dichloro-3,6-dihydroxy-*p*-benzoquinone	5120	.1	398 ± 12

to study durohydroquinone failed, due to the low solubility of this compound in aqueous solution. The rate of disappearance of hydroquinone and oxygen and the appearance of hydrogen peroxide and quinone were in all cases found to be independent of total dose, dose rate and initial concentration of hydroquinone.

The values of G were obtained in irradiation experiments in which the time of irradiation did not exceed 12 minutes and the conversion of hydroquinone to quinone was less than 2%. The values recorded in Table II represent data from at least 5 separate experiments where 5 points were taken in each experiment.

TABLE II

G VALUES FOR THE IRRADIATION OF HYDROQUINONES IN AIR-SATURATED 0.8 N SULFURIC ACID[a]

	Calcd.	Obsd.
G(−2,5-dichloro-*p*-hydroquinone)	1.47	1.42 ± 0.05
G(2,5-dichloro-*p*-benzoquinone)	1.47	1.42 ± .05
G(−oxygen)	1.84	1.82 ± .17
G(hydrogen peroxide)	2.62	2.38 ± .29
G(−2,5-dimethyl-*p*-hydroquinone)	3.30	3.36 ± .20
G(2,5-dimethyl-*p*-benzoquinone)	3.30	3.36 ± .20
G(−oxygen)	3.68	3.50 ± .21
G(hydrogen peroxide)	4.46	4.44 ± .09
G(−1,2,4-trihydroxybenzene)	3.30	3.12 ± .28
G(hydroxy-*p*-quinone)	3.30	3.07 ± .21
G(2,5-dihydroxy-*p*-benzoquinone)	..	0.09 ± .01
G(−oxygen)	3.68	3.43 ± .17
G(hydrogen peroxide)	4.37	4.17 ± .39
G(2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone)	7.75	7.68 ± .53

[a] Concentrations of the hydroquinone solutions range from 1×10^{-5} to 7×10^{-3} M.

The theoretical G values for the hydroquinone mechanisms were calculated on the basis of a G value for the ferrous–ferric system of 15.5[3] and a value for the ceric–cerous system of 2.33.[22] For the radical and molecular yields of Co^{60} gamma irradiated 0.8 N sulfuric acid solutions, the values used were

$$H_2O \xrightarrow[0.8\,N\,H_2SO_4]{Co^{60}\,\gamma} \cdot H + \cdot OH + H_2O_2 + H_2 \qquad (1)$$

$$G(-H_2O) = 4.48;\ G_H = 3.68;\ G_{OH} = 2.92;$$
$$G_{H_2O_2} = 0.78;\ G_{H_2} = 0.40$$

The G values for hydroquinone disappearance range from 1.4 to 7.7. G values for oxygen consumption and formation of products also differ widely for different hydroquinones. In spite of this, the fact that the G values are independent of the total dose and of initial hydroquinone concentration can perhaps be best interpreted on the basis that all these reactions are initiated by the above postulated set of radicals. In all cases it is assumed that the H atoms react with molecular oxygen to give HO_2 radicals

$$H\cdot + O_2 \longrightarrow HO_2\cdot \qquad (2)$$

In view of this assumption, there are three oxidative species formed during the radiolysis of air-saturated 0.8 N sulfuric acid solution, namely, $\cdot OH$, $HO_2\cdot$ and H_2O_2. The different yields, $G(-QH_2)$, are then explainable in terms of a selective reactivity which different hydroquinones show toward these oxidative species. Experimental evidence points toward three possibilities:

A. The hydroquinone reacts with OH radicals only.

B. The hydroquinone reacts with OH and HO_2 radicals.

C. The hydroquinone reacts with $\cdot OH$, $HO_2\cdot$ and H_2O_2.

For the system in which the hydroquinone acts as a scavenger for the OH radicals only, the reactions postulated after the initial steps 1 and 2 are

$$QH_2 + \cdot OH \longrightarrow QH\cdot + H_2O \qquad (3)$$
$$QH\cdot \longrightarrow {}^1/_2\,Q + {}^1/_2\,QH_2 \qquad (4)$$
$$HO_2\cdot \longrightarrow {}^1/_2\,O_2 + {}^1/_2\,H_2O_2 \qquad (5)$$

Using values for the individual radical and molecular yields, the sequence (1), (2), (3), (4) and (5) should give rise to these G values

$$G(-QH_2) = {}^1/_2\,G_{OH}$$
$$G(-O_2) = {}^1/_2\,G_{OH} + G_{H_2O_2} - G_{H_2}$$
$$G(H_2O_2) = {}^1/_2\,G_{OH} + 2\,G_{H_2O_2} - G_{H_2}$$

The experimental values for 2,5-dichloro-*p*-hydroquinone which are in reasonably good agreement with those calculated are given in Table II.

In the case where hydroquinone reacts with OH and HO_2 radicals we have the sequence (1), (2), (3), (6) and (4), where (6) is

$$QH_2 + HO_2\cdot \longrightarrow QH\cdot + H_2O_2 \qquad (6)$$

This mechanism predicts the G values

$$G(-QH_2) = G_{OH} + G_{H_2O_2} - G_{H_2}$$
$$G(-O_2) = G_{OH} + 2\,G_{H_2O_2} - 2\,G_{H_2}$$
$$G(H_2O_2) = G_{OH} + 3\,G_{H_2O_2} - 2\,G_{H_2}$$

The compounds which appear to fit these values (Table II) are 2,5-dimethyl-*p*-hydroquinone and 1,2,4-trihydroxybenzene.

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Finally, a hydroquinone which reacts in accordance with the third possibility, that is, it is oxidized by $\cdot OH$, $HO_2\cdot$ and H_2O_2, is 2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone. Since it is impossible at this stage to state what fraction of the formed semiquinone will interact with $\cdot OH$, $HO_2\cdot$ or H_2O_2, the order of reactions suggested is (1), (2), (3), (6), (4) and

$$QH_2 + H_2O_2 \longrightarrow Q + 2\,H_2O \qquad (7)$$

The experimental $G(-QH_2)$ value for this compound listed in Table II is within experimental error of that calculated from the above mechanism, $G(-QH_2)$ calculated $= 2G_{OH} + 4G_{H_2O_2} - 3G_{H_2}$.

According to the "equivalent redox potential" concept of Dainton and Collinson,[23] all of these hydroquinones should be oxidized. In the cases reported here, an apparent relationship exists between the standard oxidation–reduction potentials of the hydroquinone systems and the mechanism of the radiation-induced reaction. Thus data for 2,5-dichloro-*p*-hydroquinone with an E^0 of 0.720 v.[24] are consistent with the reaction scheme in which the HO_2 radical is incapable of oxidizing the hydroquinone. The fate of the HO_2 radical under these conditions is most probably a disproportionation to oxygen and peroxide, a reaction postulated previously.[3]

1,2,4-Trihydroxybenzene (E^0 = 0.596 v.)[24] and 2,5-dimethyl-*p*-hydroquinone (E^0 = 0.590 v.)[24] are subject to attack by both OH and HO_2 radicals. Effective scavenging of the HO_2 radical by the hydroquinone should result in a much higher yield of H_2O_2 as compared with the 2,5-dichloro-*p*-hydroquinone system. This has been verified experimentally. From the *G* values in Table II, it is evident that in the case of 1,2,4-trihydroxybenzene, hydroxylation of the ring took place, in addition to the oxidation reaction. The hydroxylation reaction of the ring also has been observed in a preliminary investigation of *p*-hydroquinone and toluhydroquinone. However, in experiments under deaerated conditions, hydroxylation was not observed, indicating that the hydroxylation may take place via the HO_2 radical.

The compound of the lowest standard oxidation–reduction potential, 2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone (E^0 = 0.420 v.)[25] was the most rapidly oxidized compound studied, and the results are consistent with the suggestion that both the HO_2 radical and the OH radical are capable of oxidizing the hydroquinone. In addition, the oxidation–reduction potential of hydrogen peroxide (0.699 v.) is sufficiently high to expect a quantitative oxidation of 2,5-dichloro-3,6-dihydroxy-*p*-hydroquinone. When hydrogen peroxide is added to a solution of the above hydroquinone, an immediate quantitative oxidation is observed. The *G* value for the radiation-induced oxidation of this compound to the quinone only is recorded in Table II, since the relatively high spontaneous rate of oxidation precluded precise measurements of the disappearance of the hydroquinone and oxygen.

On the basis of these experiments, it appears that the selective reactivity of hydroquinones toward the radicals formed by radiolysis of water provides a useful tool for the study of the properties of these radicals. The results suggest that it should be possible to study the relative oxidizing power of the HO_2 radical by measuring *G* values for a considerably more extensive series of hydroquinones of varying oxidation–reduction potentials.

The results of preliminary investigations in deaerated solutions indicate that the oxidative reactions of hydroquinones to quinones are accompanied by other reactions such that stoichiometric conversions could not be demonstrated. On the other hand, the reduction of quinones in deaerated solutions appears a system worthy of further investigation. In particular, under deaerated conditions it should be possible to study the reduction system over a *p*H range extending into the alkaline region. Data from such experiments will be reported elsewhere.

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