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Oxidation Processes. XI.[1] The Autoxidation of Durohydroquinone

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Introduction

The methods employed in previous papers of this series are now applied to the investigation of photographic developers. Some of the substances which have been dealt with hitherto, such as furoin, are developers when used at suitable hydrogen-ion concentration and, preferably, in an atmosphere of nitrogen. They fog, however, badly—which may be due, in part at least, to hydrogen peroxide action upon the silver halide.[2]

Study of the oxidation by molecular oxygen of photographic developing agents is partly suggested by interest in the fate of that part of the agent which does not reduce silver halide but is oxidized by air. Better knowledge of this, however, will also bring information on the activity of developers and, perhaps, on the mechanism by which they act on the silver halide—particularly if the investigation is extended to the action of other oxidizing agents, such as Fehling's solution,[3] and to silver halide itself.[4]

The hydroxybenzene series of developers and of these the *p*-dihydroxybenzenes will be dealt with first.

Previous Work.—The autoxidation in alkaline solution of the chief representative of the *p*-dihydroxybenzene developers, hydroquinone, is a complicated process. Eller and Koch[5] established the formation of a humic acid $(C_6H_4O_3)_x$ as the *oxidation product*. If this was formed according to (1)

$$xC_6H_6O_2 + xO_2 \longrightarrow (C_6H_4O_3)_x + xH_2O \qquad (1)$$

the *total oxygen uptake* should be 1 mole of oxygen per mole hydroquinone. La Mer and Rideal,[6] however, found that, at *p*H 8.56, more than 1 mole of oxygen per mole of hydroquinone was absorbed in ten minutes, and that slow absorption continued until nearly 2 moles had been absorbed at the end of two days. Harger[7] reported the uptake of 1.85 moles of oxygen and the isolation of brown needles, which, however, were not identified. On the other hand, Reinders and Dingemann[8] oxidized hydroquinone in buffered solutions "as far as possible." The oxygen uptake at *p*H 7.86 was somewhat less than 1 mole. The reaction products were: at *p*H 7.86, almost only humic acid; at *p*H 7.37, both humic acid and quinone; at *p*H 6.93, quinone, no humic acid.

The first complete step in the reaction according to various investigators[6,9,10,11] is the formation of *quinone*. As an intermediate step, Schilow and Fedotoff,[12] Lehmann and Tausch,[11] and others postulated a *hydroquinone peroxide*. Manchot[13] and La Mer and Rideal[6] assume direct formation of quinone and *hydrogen peroxide* without demonstrating their presence, and tests made by several investigators, notably von Euler and Brunius,[10] Reinders and Dingemann[8] and Sym[14] have failed to reveal hydrogen peroxide. Its formation was shown only in the *enzymatic* oxidation in neutral solution by Wieland and Fischer,[15] using a catalase-free oxidase. Reinders and Dingemann assume that, in the non-enzymatic reaction, hydroquinone is directly oxidized to *hydroxyquinone*, and that quinone, when it arises, does so by way of a secondary reaction.

The *velocity* of the oxidation of hydroquinone by molecular oxygen is directly proportional to the partial pressure of the oxygen,[8,10] and to the hydroquinone concentration.[6,8,10] The temperature coefficient between 20 and 40° is about 3.5.[8] Data on the dependence on the *hydroxyl-ion concentration* are conflicting. La Mer and Rideal,[6] using a manometric procedure, found proportionality between the reaction velocity and the 3/2 power of the hydroxyl-ion concentration over a *p*H range of 7.56–8.56. Von Euler and Brunius,[10] using Knecht and Hibbert's[16] titanium chloride method for titrating quinone, found a proportionality to the square of the hydroxyl-ion concentration over the *p*H range 7.08–8.16. Reinders and Dingemann,[8] using a volumetric method, checked this latter result for the *p*H range 7.003–7.880. Lastly, Saint-Maxen,[17] working with a manometric method, concludes from his results that a first power proportionality holds over a wide *p*H range.

Sodium sulfite markedly inhibits the autoxidation of hydroquinone in alkaline solution.[18,19] On the other hand, hydroquinone inhibits the autoxidation of sulfite.[20] In the

(1) T. H. James and A. Weissberger, THIS JOURNAL, **59**, 2040 (1937).

(2) A. Weissberger, H. Mainz, and E. Strasser, *Ber.*, **62**, 1942 (1929).

(3) A. Weissberger, W. Schwarze, and H. Mainz, *Ann.*, **481**, 68 (1930).

(4) R. Luther and A. Leuber, *Brit. J. Phot.*, 632, 653, 673, 692, 710, 729, 747 (1912).

(5) W. Eller and K. Koch, *Ber.*, **53**, 1469 (1920).

(6) V. K. La Mer and E. Rideal, THIS JOURNAL, **46**, 223 (1924).

(7) R. N. Harger, *ibid.*, **46**, 2540 (1924).

(8) W. Reinders and P. Dingemann, *Rec. trav. chim.*, **53**, 209 (1934).

(9) J. Pinnow, *Z. wiss. Phot.*, **11**, 289 (1913).

(10) H. v. Euler and E. Brunius, *Z. physik. Chem.*, **139**, 615 (1928).

(11) E. Lehmann and E. Tausch, *Phot. Korr.*, **71**, 17 (1935); E. Tausch, "Zur Chemie der photographischen Entwickler," Dissertation, Berlin, 1934.

(12) N. Schilow and S. Fedotoff, *Z. Elektrochem.*, **18**, 929 (1912).

(13) W. Manchot, *Ann.*, **314**, 177 (1901).

(14) E. A. Sym, *ibid.*, **487**, 174 (1931).

(15) H. Wieland and F. G. Fischer, *Ber.*, **59B**, 1180 (1926).

(16) E. Knecht and E. Hibbert, *ibid.*, **43**, 3455 (1910); E. Knecht, *J. Chem. Soc.*, **125**, 1537 (1924).

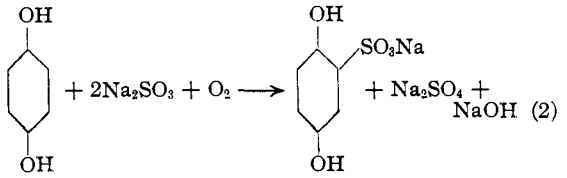
(17) A. Saint-Maxen, *J. chim. phys.*, **32**, 161 (1935).

(18) H. B. Berkeley, *Phot. News*, 41 (1882); *Phot. Korr.*, 47 (1882).

(19) A. L. Lumière and A. Seyewetz, *Bull. soc. chim.*, [3] **33**, 444 (1905).

(20) H. Bäckström and H. N. Alyea, THIS JOURNAL, **51**, 90 (1929); K. K. Jeu and H. N. Alyea, *ibid.*, **55**, 575 (1933).

presence of sufficient sulfite, the autoxidation of hydroquinone follows (2)



The relative amounts of hydroquinone and sulfite used up during the oxidation, and the amounts of sulfate and free alkali formed, are in good agreement with (2).[9,11,21] Sodium hydroquinone monosulfonate has been isolated from the reaction mixture to the extent of 73% of the theoretical amount.[22]

Data by Pinnow[9] and Lehmann and Tausch[11] indicate that sodium hydroquinone monosulfonate in its turn undergoes an analogous autoxidation. Storch,[23] Kauffmann[24] and many subsequent investigators have isolated sodium hydroquinone disulfonate from oxidized developers.

Side reactions to the extent of a few per cent. in both phases of the autoxidation of hydroquinone in the presence of sulfite, are assumed to occur by Pinnow and by Lehmann and Tausch.

The oxidation rates of aqueous hydroquinone–sulfite mixtures increase with increasing *p*H over the range tested (7.35–8.18).[25] The rate is higher with a borate buffer than with a phosphate buffer of equal *p*H.[25] For a fixed sulfite concentration, the oxidation rate (cc. O_2/time) is approximately proportional to the hydroquinone concentration.[25] Cupric salts catalyze the reaction,[25] and alter the ratio of hydroquinone consumed:sulfite consumed:sulfate formed.[21]

Various substances catalyze the autoxidation of hydroquinone. 1 Part of copper (introduced as cupric ion) per 1000 parts of hydroquinone increases the oxidation velocity 11-fold at a *p*H of 6.86.[8] The reaction velocity is approximately proportional to the oxygen pressure, the amount of cupric ion added, the hydroxyl-ion concentration, and the square root of the hydroquinone concentration. The temperature coefficient varies from 1.7 to 2.0 over a 20–40° range. The effect of manganous ion[8] is also approximately proportional to the amount added,[14] but much smaller than that of copper. Both Reinders and Dingemann and Sym assume a metal–hydroquinone complex as the seat of the metal catalyzed oxidation. The action of iron salts was studied by Wieland and Franke.[26]

Catalytic action is further reported for vanadium, uranium, and cobalt ion, alkali or alkaline earth peroxides,[27] yttrium, and lanthanum hydroxides,[17] hydrolyzed nickel acetate,[28] platinum black,[29] colloidal silver,[30] and carbon.[31,32]

(21) J. Pinnow, *Z. wiss. Phot.*, **27**, 344 (1930).
(22) J. Pinnow, *ibid.*, **13**, 41 (1913).
(23) L. Storch, *Ber. österreich Ges. Förderung Chem. Ind.* (1893).
(24) H. Kauffmann, *Ber.*, **40**, 4550 (1907).
(25) W. Reinders and P. Dingemann, *Rec. trav. chim.*, **53**, 231 (1934).
(26) H. Wieland and W. Franke, *Ann.*, **464**, 110 (1928).
(27) J. Aloy and V. Valdignic, *Bull. soc. chim.*, **35**, 792 (1924). The activity of these substances may be due to their alkalinity.
(28) Job, *Compt. rend.*, **144**, 1266 (1907); A. Saint-Maxen, *J. chim. phys.*, **32**, 410 (1935).
(29) F. Wöhler, *Ann.*, **51**, 153 (1844).
(30) M. Volmer, *Z. wiss. Phot.*, **20**, 189 (1921).
(31) M. Matsui, *Mem. Col. Sci. Eng. Kyōtō*, **1**, 386 (1909).
(32) A. Gandini, *Gazz. chim. ital.*, **63**, 9 (1933).

No kinetic work on the autoxidation of hydroquinone homologs and derivatives is reported in the literature.

It is obvious that the complicated course of the autoxidation of hydroquinone is largely due to the reactivity of the hydrogen atoms attached to the benzene nucleus. To get simpler conditions, it seemed to be advisable, therefore, to substitute these by other atoms or groups. Halogens are not very suitable for this purpose since they rather readily split off in alkaline solution. We therefore chose *tetramethylhydroquinone, durohydroquinone*, as a model.

Materials

Duroquinone.—We are indebted to Prof. L. I. Smith, Minneapolis, Minn., for a sample of duroquinone, m. p. 111–113°. More of the material was prepared according to this author, m. p. 112–113°.[33]

Durohydroquinone.—Eleven grams (0.067 mole) of duroquinone is dissolved in 300 cc. of hot glacial acetic acid and is reduced by adding, in small portions, about 12 g. of zinc dust until the solution is colorless. Then it is filtered while hot and the residue is extracted with another 100 cc. of hot glacial acetic acid. The filtrate crystallizes on cooling, the precipitate is collected at the pump, washed with glacial acetic acid, and then water, and dried in a vacuum desiccator over sodium hydroxide. It is then sublimed *in vacuo* 190–200° (2 mm.), m. p. 239–240°; yield, 8 g., which is 72.7% of the theoretical yield. Repeated recrystallization from glacial acetic acid and sublimation does not change the product in its appearance, melting point, and reactivity.

Disodium Phosphate and Sodium Tetraborate.—Baker and Adamson, Reagent Quality.

Hydrochloric Acid.—de Häens "Fixanal."

Potassium Hydroxide.—de Häens "Fixanal."

Alcohol.—95% C. P. Ethanol.

Reactions.—The reaction products of the autoxidation of durohydroquinone in moderately alkaline solution are *duroquinone* and *hydrogen peroxide* in molar proportion.

$$C_{10}H_{12}(OH)_2 + O_2 \longrightarrow C_{10}H_{12}O_2 + H_2O_2 \qquad (3)$$

Duroquinone was identified by melting point and mixed melting point. *Hydrogen peroxide* was identified as follows: 0.05 g. of durohydroquinone was dissolved in 4 cc. of ethanol, 4 cc. of half saturated aqueous barium hydroxide solution added, the mixture agitated with air for five minutes, and the precipitate filtered off and extracted with 2 *N* sulfuric acid. The solution gave a strongly positive reaction for hydrogen peroxide in the perchromate test.

It was determined as follows: 0.25 m*M* of durohydroquinone was oxidized in 20 cc. of saturated aqueous barium hydroxide solution; 6.15 cc. of oxygen was absorbed at 20° (746 mm.). The theoretical value of 1 mole of oxygen is 6.2 cc. Then 10 cc. of 0.1 *M* potassium permanganate plus 10 cc. of 2 *M* sulfuric acid were added: 6.5 cc. of gas was evolved. A control yielded a blank of 0.4 cc. Hence, 6.1 cc. of oxygen was evolved by the reaction between permanganate and barium hydroxide. *The oxida-*

(33) L. I. Smith, *Org. Syntheses*, **10**, 40 (1930).

tion of durohydroquinone is thus attended by quantitative formation of hydrogen peroxide.

The rate of oxygen uptake was determined by the volumetric method used previously.[2,1] The temperature was 20.00 ± 0.02°. The shaker rates used were always well above those which preliminary tests showed to be the minimum required to maintain saturation of the solution with oxygen. (Higher rates effected no change in the rate of oxygen uptake.)

The upper part of the reaction vessel employed in the experiments requiring preparation and mixing of the solutions under exclusion of oxygen was constructed similar to the apparatus used by Weissberger, Schwarze, and Mainz[34] and consisted of two compartments as illustrated in Fig. 1.

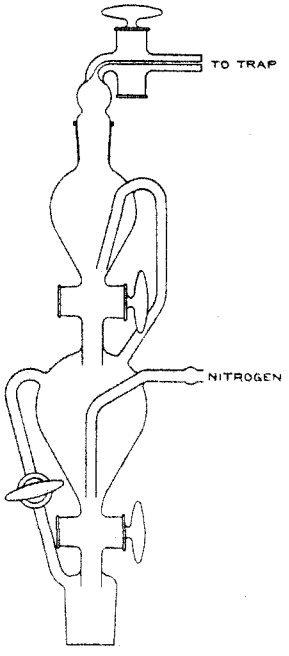


Fig. 1.

The acid and alkaline solutions thus could be prepared separately in an atmosphere of nitrogen, and the resulting solutions mixed and stored for any desired time in a nitrogen atmosphere. The lower reaction chamber was as usual.

Durohydroquinone is too insoluble in water to allow the use of pure aqueous solutions. On the other hand, it was essential that the solutions have a closely controlled and reproducible *p*H. The solvent finally chosen was 50% aqueous ethyl alcohol. Even in this solution, the solubility of durohydroquinone is small.

The durohydroquinone was dissolved in ethanol to which 2 cc. of 0.1 *N* hydrochloric acid was added for protection. This solution, contained in the reaction vessel proper, was made up to 40 cc. of 50% ethanol by addition of water and 0.1 *M* hydrochloric acid. The buffer salt and additional hydrochloric acid, dissolved in 50% ethanol, were contained in the upper vessel.

As buffer salt, 4 cc. of 0.2 *M* disodium phosphate or 5 cc. of 0.15 *M* sodium tetraborate was employed, and the *p*H adjusted to the desired value by addition of 0.1 *N* hydrochloric acid. In the following, therefore, the buffer will be characterized by "Borate" or "Phosphate" and the amount of acid used.

At the start of the experiment the solutions were mixed. Unless otherwise specified the total solution volume was 60 cc.

For the buffer most frequently used borate, 1.2 mMol. of hydrochloric acid, the *p*H values were measured potentiometrically by Dr. A. E. Cameron:[35] calibrated glass electrode, *p*H 9.37, hydrogen electrode, *p*H 9.41. Relative *p*H values were obtained by comparison with the oxidation velocities of hydroquinone in the various solutions (see section on variation of oxidation rate with *p*H).

(34) A. Weissberger, W. Schwarze, and H. Mainz, *Ann.*, **481**, 69 (1930).

(35) The authors wish to thank Dr. Cameron for this work.

Treatment of Data

For each run, the volume of oxygen absorbed was plotted against the time required (time readings were in general made for each 0.1 cc. uptake). The oxidation rate at any time was determined as the tangent of the smoothed curve at the point in question.

The oxidation rates were in general reproducible within ± 5%. The error in some initial rate determinations (see above) may be higher. This size of possible error is due to the low durohydroquinone concentration and the low buffering capacity of the solutions which it was necessary to use and to the autocatalytical nature of the reactions. With the same method when applied to hydroquinone in aqueous solution the limit of error does not exceed ± 2%.

All oxidation rates are expressed in cc. of O_2 (N. T. P.) uptake per minute.

The Oxidation Curve. Dependence on the Concentration of Duroquinone.—A typical example of the general form of the oxidation curve of durohydroquinone is given in Fig. 2. The rate

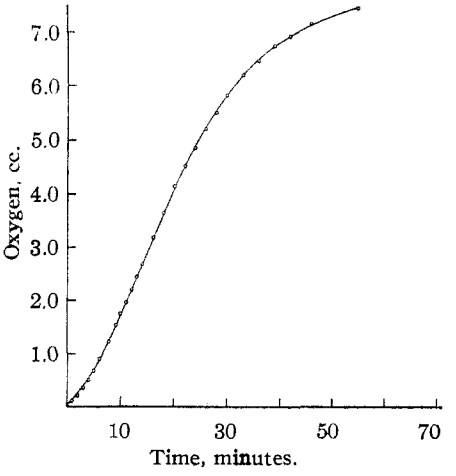


Fig. 2.—One-third mMol. of durohydroquinone, phosphate buffer, 0.02 mMol. of HCl.

of oxygen uptake at first increases with time, then attains a fairly constant value, and finally decreases. The same type of curve is obtained in phosphate and in borate buffers, and no change was noted when the solutions were made up with conductivity water instead of ordinary distilled water, with ethanol purified by the method of

Danner and Hildebrand,[36] and with durohydroquinone which had undergone further recrystallizations and sublimations. When the solutions were prepared, mixed, and stored for one hour in an atmosphere of nitrogen before exposure to oxygen, an extension of the toe of the curve and a decrease in the initial rate was observed. The addition of duroquinone in various amounts revealed the reason for the course of the reaction. *Duroquinone catalyzes the reaction* in proportion to its concentration as shown in Fig. 3. For a given *p*H the rate is well represented by the equation

$$R_s = R_0 + K_c[\text{duroquinone}] \qquad (4)$$

where R_s is the total rate, R_0 the rate in the absence of duroquinone, and K_c a constant characteristic for the duroquinone catalyzed reaction.

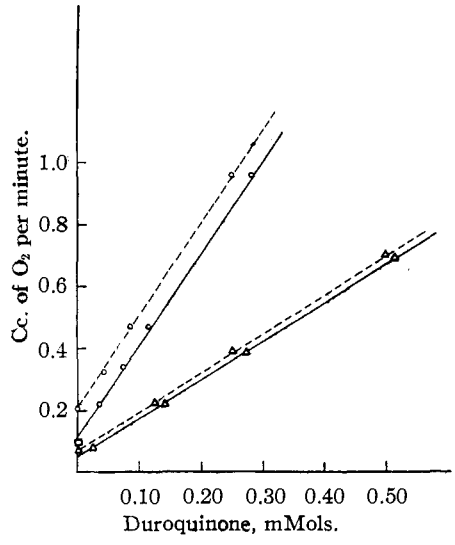


Fig. 3.—Borate buffer: OOO, 1.2 mMol. of HCl; □, point obtained with 2,4-dinitrophenylhydrazine (1.2 mMol. of HCl); ΔΔΔ, 1.3 mMol. of HCl.

R_0, the rate of the reaction of durohydroquinone with oxygen which is not catalyzed by duroquinone, should be obtained as the intercept value with the ordinate in Fig. 3. Values obtained from a direct plot of the experimental data (broken lines), however, are too high.

The total oxygen uptake was always 4–8% below the theoretical. This deficiency could be due to the interaction of hydrogen peroxide with durohydroquinone, or to preliminary oxidation occurring during the preparation of the solutions. The first effect is negligible with reactions of the velocity in question, since separate runs with the addition of hydrogen peroxide showed no appreciable change in the total uptake of oxygen. Therefore, allowance was made for the formation of duroquinone by preliminary oxidation and the full-line curves in Fig. 3 were obtained. They yield intercept values R_0 considerably smaller than those obtained without the correction.

This correction is justified by the fact that solutions prepared in nitrogen atmosphere (see page 100) showed nearly the theoretical total oxygen uptake, and initial rates in agreement with those obtained after the correction. The maximum velocities were unchanged. Furthermore, when the durohydroquinone solutions were prepared with the addition of dimethyldihydroresorcinol or of 2,4-dinitrophenylhydrazine and kept for about one-half hour before adding the alkaline solution, the initial rates obtained (□ in Fig. 3) also agreed with the corrected values. Both of the added substances form compounds with the quinone. Since these compound formations are, however, slow in comparison with the autoxidation of durohydroquinone, the oxidation rates show soon the action of the quinone produced.

The value for R_0 also can be obtained for individual runs if $\frac{\text{oxidation rate}}{\text{concentration of durohydroquinone}}$ is plotted against the oxygen uptake (duroquinone, ordinate). The rate of the uncatalyzed reaction is then again given by the intercept with the ordinate. Figure 4 gives an example of this treatment. As before, allowance is made for preliminary oxidation.

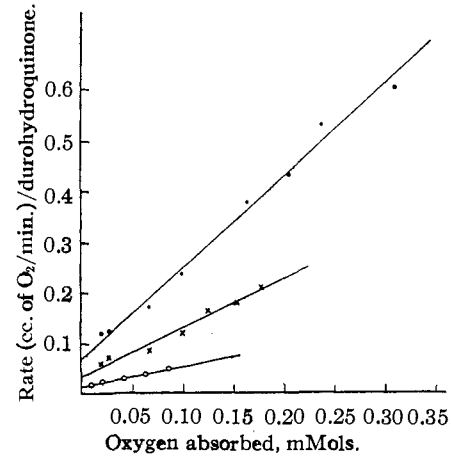


Fig. 4.—Borate buffer: 1.35 mMol. of HCl; ●-●-●, 0.5 mMol. of durohydroquinone; ×-×-×, 0.25 mMol. of durohydroquinone: O-O-O, 0.083 mMol. of durohydroquinone.

(36) P. S. Danner and J. H. Hildebrand, THIS JOURNAL, **44**, 2827 (1922).

On the basis of Equation (4) and Fig. 3 (values of R_0 and R_c), and with the knowledge that in the presence of a fixed amount of duroquinone the oxidation rate of durohydroquinone is proportional to its concentration (Table III), the reaction velocities R_s under given conditions (pH, O_2) can be calculated for any time during an individual reaction. The results of such a calculation are given in Table I.

TABLE I

BORATE BUFFER, 1/2 MMOL. OF DUROHYDROQUINONE

% oxidized[a]	$R_{s\,obsd.}$	$R_{s\,calcd.}$
0.0	0.12	0.12
8.3	.16	.18
16.7	.20	.22
25.0	.25	.27
33.3	.30	.29
41.6	.28	.30
50.0	.30	.30
58.3	.26	.28
75.0	.16	.21

[a] Calculated from oxygen uptake, without correction for preliminary oxidation.

This and several other data show that during the first half of the oxidation the calculated values agree well with the observed ones. Beyond this, the observed values fall off slightly. This is probably due to formation of acetic acid by the action of hydrogen peroxide on alcohol and the so-caused drop of the pH in the weakly buffered reaction mixtures. If sodium sulfite is added to the reaction mixture as an acceptor of the hydrogen peroxide (Table II), the calculated and observed values agree over the whole course of the reaction. Equally good agreements between observed and calculated rates were obtained for higher durohydroquinone concentrations.

TABLE II

1/12 MMOL. OF DUROHYDROQUINONE, 1/12 MMOL. OF Na_2SO_3

% oxidized[a]	$R_{s\,obsd.}$	$R_{s\,calcd.}$
0	0.022	0.022
10	.022	.023
20	.023	.023
40	.020	.021
50	.021	.019
60	.018	.017
80	.010	.010
90	.0045	.005

[a] Calculated from oxygen uptake, without correction for preliminary oxidation.

Action of Sodium Sulfite.—No inhibiting action is exerted by sulfite on the autoxidation of durohydroquinone except when sulfite is added to the acidified durohydroquinone solution and this is allowed to stand for some time. The then observable slight decrease of the initial oxidation rate is obviously due to reduction of duroquinone formed by preliminary oxidation. This is in contrast to the hydroquinone autoxidation where sulfite markedly decreases the rate of reaction.

Dependence on the Concentration of Durohydroquinone.—If a considerable amount of duroquinone is added to the mixture, the reaction starts without appreciable induction period and in this case the initial rates R_i can be calculated in the usual way (tangent to the cc./time curve through the origin). The results of a series of experiments with varying concentrations of durohydroquinone are given in Table III.

TABLE III

BORATE BUFFER, 1.3 MMOL. OF HCl, 0.25 MMOL. OF DUROQUINONE

Durohydroquinone mMols.	R_i/N. T. P.	Durohydroquinone/R_i
0.0625	0.09	0.69
.125	.18	.69
.250	.34	.73
.50	.71	.70

The constancy of the values in the third column shows that under these circumstances the rate of oxygen uptake is proportional to the concentration of durohydroquinone.

The rates of the reaction which is *not catalyzed by duroquinone* (obtained as the intercept values with the ordinate from Fig. 3) are given in Table IV.

TABLE IV

BORATE, 1.35 MMOL. of HCl

Durohydroquinone mMols.	R_0	R_0/Durohydroquinone
0.5	0.070	0.14
.25	.035	.14
.083	.014	.17

It follows from these data that both the uncatalyzed reaction and the duroquinone catalyzed reaction are of the first order with respect to the durohydroquinone.

Dependence on the Concentration of the Hydroxyl Ions.—For the determination of the influence of the pH on the rate of reaction, it is necessary to know exactly the variation in the pH of the solutions. Since electrometric determinations of the alcoholic solutions meet with considerable difficulties, an indirect method was used. The suggestion of various authors that the autoxidation rate of hydroquinone varies with the

square of the hydroxyl-ion concentration has been contested by other authors (see page 98). It is, however, valid according to our own measurements which will be given in a subsequent paper. This dependency, which has been confirmed for aqueous solutions, can be assumed to hold also for an aqueous alcoholic medium. If, therefore, the quotient, autoxidation rate of durohydroquinone/autoxidation rate of hydroquinone, is constant, it is established that the rate of autoxidation of durohydroquinone, too, is proportional to the square of the hydroxyl-ion concentration. Table V shows by columns 6 and 7 that this is the case as well for the initial reaction as for the duroquinone catalyzed reaction.

TABLE V

VARIATION OF RATE WITH HYDROXYL ION CONCENTRATION. BORATE BUFFER, 0.25 MMOL. OF DUROHYDROQUINONE

HCl	R_H Hydroquinone	R_0	R_s[b]	R_c[b]	R_0/R_H	R_c/R_H
1.40	0.0125	0.0125	0.054	0.0415	1.00	3.3
1.30	.049	.051	.204	.153	1.04	3.0
1.20	.115	.11	.49	.38	0.95	3.4
2.20[a]	.20	.20	.90	.70	1.00	3.5

[a] 10 cc. Borax, 40% ethanol.

[b] In the presence of 1/8 mMol. of duroquinone.

Dependency on the Concentration of Oxygen.—In the curves where oxygen uptake per minute/concentration of durohydroquinone (ordinate) is plotted against concentration of duroquinone, the intercept with the ordinate as shown above (page 101) gives the rate of the reaction which is uncatalyzed by duroquinone, whereas an identical slope of the curves shows identity of the rate of the duroquinone-catalyzed part. Various reactions run with oxygen and with air showed proportionality of the rate of the uncatalyzed reaction to the concentration of oxygen, and practical independency of the duroquinone-catalyzed reaction. This is illustrated by Table VI.

TABLE VI

VARIATION OF RATE WITH OXYGEN PRESSURE: BORATE BUFFER, 1/4 MMOL. OF DUROHYDROQUINONE

HCl, mMols.	Additions	After formation of 1/8 mMol. duroquinone: R_0 Oxygen	R_0 Air	R_c Oxygen	R_c Air
1.25	.....	0.09	0.02	0.33	0.32
1.15	.....	.135	0.03	.47	.45
1.3	1/8 mMol. duroquinone	...	..	.135[a] (.18)	.14[a] (.15)
Hydroquinone					
1.3	.....	0.105	0.022		

[a] Values calculated from measured initial rates (given in parentheses) on assumption that R_0 is proportional to the oxygen concentration.

As a test for the method, a value of hydroquinone is given. The result is further confirmed by reactions with addition of duroquinone, where again only the uncatalyzed part is susceptible to a change in the oxygen concentration.

Catalysis by Copper.—Copper sulfate exerts a marked catalytic effect upon the autoxidation of durohydroquinone.

TABLE VII

BORATE BUFFER, 0.25 MMOL. OF DUROHYDROQUINONE, 1.3 MMOL. OF HCl

$CuSO_4$, mg.	R_i (O_2)	$R_{i\ Air}$
0.0	0.065	..
.2	1.1	..
.5	2.4	..

BORATE BUFFER, 0.25 MMOL. OF DUROQUINONE, 1.5 MMOL. OF HCl

3.0	0.26	0.06

The rate of the reaction is proportional to the oxygen concentration.

Dependence on Light.—No photochemical sensitivity was detected by exposure to a General Electric high-pressure mercury vapor lamp. The tests would not, however, have revealed a *small* photochemical effect, particularly on the duroquinone uncatalyzed reaction.

Autoxidation of Duroquinone.—The autoxidation of durohydroquinone practically stops in moderately alkaline solutions with the absorption of 1 mole of oxygen per mole of durohydroquinone. In strongly alkaline solution (*p*H 12–14), however, a further absorption of oxygen follows at a measurable rate, which is due to the autoxidation of duroquinone.

This reaction is so much slower (0.4 mMol. absorb 0.06 cc. of oxygen/minute in 0.16 *N* 50% alcoholic potassium hydroxide) than the autoxidation of the durohydroquinone that it does not interfere with the latter and it will, therefore be dealt with separately later on. It may be mentioned, however, that the stability of duroquinone and the ease with which durohydroquinone is oxidized might give substances of this type the characteristics important for the Vitamin E.[37]

Interpretation of Results

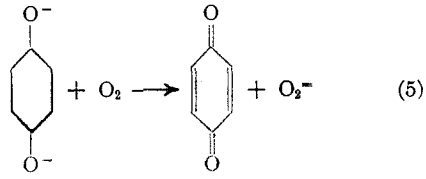
The kinetical results reported in the previous

(37) E. Fernholz, THIS JOURNAL, **59**, 1154 (1937); A. R. Todd, F. Bergel, H. Waldmann and T. S. Work, *Nature*, **140**, 361 (1937). Similarity in the oxidation of α-ketoles to that of Vitamin C, see A. Weissberger, *Ber.*, **65**, 1820 (1932).

pages elucidate the mechanism by which Equation (3) is fulfilled.

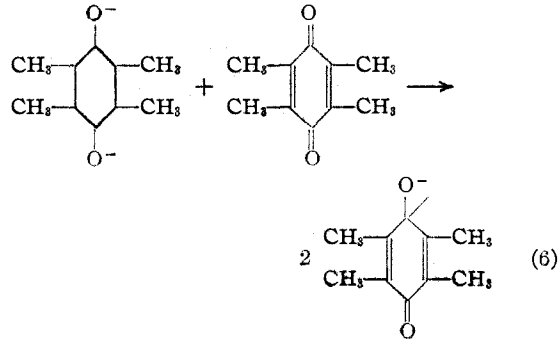
The dependency on the hydroxyl-ion concentration shows that the first step of the reaction consists in the formation of the doubly-charged anion of durohydroquinone

This ion reacts with oxygen with formation of duroquinone and hydrogen peroxide at a rate R_0 which is proportional to its concentration and to the concentration of the oxygen (5).



(5)

The catalytical effect of duroquinone shows that there exists a second way from the doubly-charged durohydroquinone ion to the final product, duroquinone. The rate of this reaction is directly proportional to the concentration of the ion and to the concentration of the duroquinone. It is, however, independent of the concentration of the oxygen under the conditions of our experiments (constant concentration of oxygen at partial pressures of 153 to 760 mm.). This shows that the speed-limiting phase of the reaction is not the final step of the interaction with the oxygen, but some other reaction preceding this. The conditions are similar to those of the autoxidation of α-hydroxy and α-amino ketones. There, the speed-limiting phase of the reaction was shown to be an enolization. In the present case it is the interaction of the doubly-charged durohydroquinone ion with 1 molecule of duroquinone with the formation of a highly oxidizable product, most likely a charged radical.



(6)

The kinetical establishment of this reaction deserves particular interest in view of the electrometric work of L. Michaelis and his collaborators[38] on the two-step oxidation of compounds of the type in question.

The quantitative yield of hydrogen peroxide obtained shows that both the catalyzed and the uncatalyzed reaction result in formation of one mole of hydrogen peroxide per mole of duroquinone.

Summary

1. Durohydroquinone is oxidized in alkaline solution by molecular oxygen with quantitative formation of duroquinone and hydrogen peroxide.

2. The dependency of the reaction rate upon the square of the hydroxyl-ion concentration shows that the first step in this reaction is the formation of the doubly charged durohydroquinone anion.

3. The reaction then splits up into two processes: (a) The ion can interact with the oxygen without kinetically detected complication. The rate of this reaction is proportional to the oxygen concentration, and to the concentration of the durohydroquinone.

4. (b) In the presence of duroquinone, further reaction takes place. The rate of this reaction is proportional to the concentrations of the duroquinone, and the durohydroquinone, and is independent of the oxygen pressure over the tested range (0.2 to 1 atmosphere).

5. It is assumed that the rate-controlling phase of the reaction catalyzed by duroquinone is the formation of a highly oxidizable charged radical in the interaction of the doubly charged durohydroquinone ion and duroquinone.

6. Sodium sulfite shows no inhibitory action on the autoxidation of durohydroquinone.

7. The autoxidation of durohydroquinone is catalyzed by copper sulfate. The rate of this reaction is proportional to the oxygen pressure.

8. Duroquinone autoxidizes at high alkalinity at a measurable rate which is several orders of magnitude lower than the rate of autoxidation of durohydroquinone.

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(38) L. Michaelis, *Chem. Rev.*, **16, 243 (1935).**