thiazine, thionol, with the values given by Clark[3] for two other thiazines, Lauth's violet and methylene blue. At *p*H 7 the E_0' for thionol is 0.158, for methylene blue 0.011, and for Lauth's violet 0.062 at *p*H 6.967, and 0.045 at *p*H 7.517, which gives 0.061 at *p*H 7 by interpolation. These values place thionol appreciably closer to the oxygen electrode than the other two thiazines, being about midway between 1-naphthol-2-sulfonate-indophenol and 2,6-dichlorophenol-indo-*o*-cresol. This is in agreement with the observation that spontaneous oxidation of leuco thionol exposed to air occurs more slowly than is the case with methylene white at the same *p*H. Likewise, the reducing power of a given sample of urine is more readily demonstrated with thionol than with methylene blue.

Summary and Conclusions

1. The potentiometric characteristics of thionol have been determined.

2. Colorimetric evidence for the existence of a semiquinone has been submitted.

3. The three thiazines, methylene blue, Lauth's violet and thionol have been compared with regard to their position on the oxidation–reduction scale.

SAN FRANCISCO, CALIF. RECEIVED JUNE 15, 1938

[COMMUNICATION NO. 675 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XII.[1] The Autoxidation of Hydroquinone and of the Mono-, Di- and Trimethylhydroquinones

BY T. H. JAMES, J. M. SNELL AND A. WEISSBERGER

A study of the primary reaction in the autoxidation of hydroquinone is severely complicated by the presence of secondary reactions involving nuclear hydrogens. In order to avoid such complications, we investigated the autoxidation of durohydroquinone.[1] In this compound, the four nuclear hydrogens of hydroquinone are replaced by methyl groups. This prevents secondary reactions, which complicate the hydroquinone autoxidation. Hydrogen peroxide and duroquinone could be shown to be the reaction products, and it was further observed that duroquinone exerts a marked catalytic effect upon the reaction. In order to apply these results to the autoxidation of hydroquinone, we have investigated the autoxidation of the intermediate members of the homologous series, namely, toluhydroquinone, the three xylohydroquinones, and ψ-cumohydroquinone(trimethylhydroquinone)and we have extended previous observations on the oxidation of hydroquinone itself.

Materials[2]

***p*-Benzoquinone**, twice sublimed; m. p. 116°.

Hydroquinone, recrystallized from benzene, or three times from water slightly acidified with hydrochloric acid; m. p. 172°. No kinetical difference between these samples and the original material was detected.

Toluquinone, recrystallized from ligroin (b. p. 70–90°), and sublimed at 100°.

Toluhydroquinone, recrystallized from toluene; m. p. 127–128°.

Dimethylquinones were made from the corresponding xylidines, as follows.

The xylidine (61 g., 0.5 mole) was dissolved in 200 ml. of concentrated sulfuric acid and 1000 ml. of water, and a solution of 60 g. of sodium bichromate in 150 ml. of water was slowly run in, with stirring, at a temperature below 10°. The mixture was left standing in a cool place for twenty-four hours, and then 80 g. of bichromate in 240 ml. of water was added in the same manner. After another twenty-four hours, the precipitate was collected, washed with water, and the filtrate extracted with ether. The combined precipitate and ether solution was steam distilled. The distillate was half saturated with sodium chloride, cooled, the quinone collected, and the filtrate extracted with ether. The combined precipitate and ether extract residue was recrystallized from petroleum ether or ligroin and sublimed.

2,5-Dimethylquinone.—Yield 40%; m. p. 124–124.5°.

2,5-Dimethylhydroquinone was prepared according to Conant and Fieser[3]; recrystallized from ethanol, yield 46%; m. p. 210–212°.

2,6-Dimethylquinone.—Yield 10%; m. p. 72–73°.

2,6-Dimethylhydroquinone was prepared analogously to the 2,5-dimethylhydroquinone;[2] recrystallized from water (Norite), yield 60%; m. p. 153–154°.

2,3-Dimethylquinone.—From 3-amino-1,2-dimethylbenzene; yield 8%; m. p. 59–60°.

2,3-Dimethylhydroquinone.—The solution of the quinone (0.6 g.) in 25 ml. of 25% ethanol was reduced at 0° with sulfur dioxide for one hour; yield 17%; m. p. 224–225°.

(1) Part XI: T. H. James and A. Weissberger, THIS JOURNAL, **60**, 98 (1938).

(2) All materials the origin of which is not stated are Eastman grades.

(3) Conant and Fieser, THIS JOURNAL, **45**, 2199 (1923).

3-Amino-1,2-dimethylbenzene.[4]—Forty-eight grams of 3-nitro-1,2-dimethylbenzene was reduced with 56 g. of iron powder in 150 ml. of water containing 10 ml. of concentrated hydrochloric acid, followed by stirring and heating on the steam-bath for three hours, followed by steam distillation: yield 70%; b. p. 109–111° at 22 mm. The acetyl derivative was recrystallized from toluene; m. p. 133–134°.

3-Nitro-1,2-dimethylbenzene.—*o*-Xylene (100 g.) was run slowly into a mixture of 600 g. of fuming nitric acid (sp. gr. 1.52) and 200 g. of glacial acetic acid, with rapid stirring, at 20–25°. Stirring was continued at this temperature for one hour, the mixture poured into water, extracted with benzene and washed.

The isomers were separated by fractional distillation through a 17-cm. Widmer column at 12 mm. Fractions were collected at intervals of 3–4°, between 113 and 126°, cooled in an ice–salt bath and crystals collected. The filtrates were refractionated; yield of 3-nitro-1,2-dimethylbenzene, b. p. (12 mm.) 113–116°, 48 g., 37%; 4-nitro-1,2-dimethylbenzene, b. p. (12 mm.) 125–126°, 35 g., 27%.

2,3,5-Trimethylquinone (ψ-Cumoquinone).—The method of L. I. Smith[5] was not used because no pseudocumidine of satisfactory quality was available. Instead, isoduridine was oxidized with elimination of the methyl group[6] in the para position to the amino group. Isoduridine was prepared from isodurene through the monobromo derivative.[7]

Bromoisodurene was prepared closely following the procedure for the bromination of durene[4]; yield, 61 g., 77%; b. p. 148–149° at 30 mm.

Nitrobromoisodurene.—Sixty-one grams of bromoisodurene in 280 g. of chloroform was added to 226 g. of concentrated sulfuric acid, cooled to 0°, and, with rapid stirring, a mixture of 22 g. of fuming nitric acid (sp. gr. 1.52) and 55 g. of chloroform was run in from a dropping funnel, at about 5°. After stirring had been continued for five minutes, 500 ml. of chloroform was added to dissolve the solid reaction product. The chloroform layer was separated and washed with sodium carbonate and with water, and the chloroform distilled off until the residue (about 125 cc.) started to crystallize. An equal volume of methyl alcohol was added, the mixture was cooled in ice and the crystals were filtered off and washed with methyl alcohol; yield, 49 g., 66%; m. p. 168–173°. Calcd. for $C_{10}H_{12}NO_2Br$: N, 5.44; Br, 31.0. Found: N, 5.35; Br, 31.4.

2-Amino-1,3,4,5-tetramethylbenzene (Isoduridine).—The method employed by Willstätter and Kubli[4] for the preparation of duridine did not eliminate the halogen from the isodurene derivative. To crude nitrobromoisodurene (49 g.) in 600 ml. of boiling glacial acetic acid and 100 ml. of concentrated hydrochloric acid was added, with boiling and stirring, 50 g. of zinc dust in small portions. When the reaction slowed down, an additional 50 g. of zinc dust and 50 ml. of hydrochloric acid were added, and boiling and stirring continued for one hour. The solution was cooled, the crystals filtered off, the filtrate concentrated until crystals formed (about 150 ml.) diluted with water and hydrochloric acid and the resulting precipitate combined with the main product.

The crude bromoisodurene hydrochloride was debrominated with a solution of 160 g. of potassium hydroxide in 375 ml. of water and 600 ml. of 95% ethyl alcohol, with 125 g. of zinc dust and 1 g. of mercuric chloride with boiling and stirring overnight. This was usually sufficient for reduction, but in one case it was necessary to continue boiling for an additional twenty-four hours, adding more alkali (100 g.), water (250 ml.), and zinc (50 g.), with 1 g. of mercuric chloride.

The reaction mixture was steam distilled and the distillate, which contained insoluble oil, was collected. The amine was salted out and extracted with ether. The yield of isoduridine, b. p. (16 mm.) 134–136°, was 18.5 g., 66%, based on the nitrobromoisodurene. The acetyl derivative was recrystallized from alcohol, m. p. 219–220°.[8]

2,3,5-Trimethylquinone (ψ-Cumoquinone).—Isoduridine (18.5 g.) in 1500 ml. of water and 170 ml. of concentrated sulfuric acid was oxidized below 5° with 44 g. of sodium bichromate crystals in 150 ml. of water, added slowly from a dropping funnel with rapid stirring. After one hour, the mixture was kept in a cool place for twenty hours. Then an additional 34 g. of sodium bichromate in 80 ml. of water was added as before at 5° and the mixture stirred at room temperature for twenty-four hours. It was worked up as mentioned; yield of pure quinone 1.27 g., m. p. 28.5–29.5°.

2,3,5-Trimethylhydroquinone (ψ-Cumohydroquinone) was prepared analogously to the 2,5-dimethylhydroquinone,[3] using the residue of the petroleum ether filtrate from the quinone purification. About 3 g. was warmed on the steam-bath with a solution of 5 g. of stannous chloride in 45 ml. of 2 *N* hydrochloric acid. The colorless solution was cooled, filtered, and the product recrystallized from 30% ethanol and from toluene; colorless needles, m. p. 171–173°, 1.86 g.; combined yields of pure quinone and hydroquinone, 17%, based on the isoduridine.

Tetraethylquinone.—We are indebted to Professor L. I. Smith, of the University of Minnesota, for a sample of this material; m. p. 58–59°.

Tetraethylhydroquinone.—The quinone (1.14 g.) was reduced in alcohol (15 ml.) with stannous chloride (25 g.) in concentrated hydrochloric acid (6 ml.) on the steam-bath. Water (30 ml.) was added to the colorless solution, cooled, and the crystals washed with a little water; recrystallized from toluene; yield 0.8 g., 67%; m. p. 170.5–171.5°.

Durohydroquinone Monomethyl Ether.—Durohydroquinone (3.2 g.) was heated in a nitrogen-filled sealed tube with 4.6 g. of methyl iodide and 50 cc. of absolute ethanol, in which 0.46 g. of sodium had been dissolved, for two hours in a steam-bath. The contents were poured into 100 ml. of water, filtered, and the precipitate extracted with 75 ml. of boiling benzene. The insoluble material consisted of 0.8 g. of durohydroquinone. The residue of the solution was stirred under nitrogen with 50 cc. of warm (2 *N*) sodium hydroxide, and cooled and filtered. Hydrochloric acid precipitated colorless crystals which were recrystallized from ligroin: yield, 0.7 g., 19.5%; m. p. 115–116°. The alkali-insoluble material consisted of durohydroquinone dimethyl ether and a little duroquinone.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.9. Found: C, 73.1; H, 8.8.

(4) Noelting and Forel, *Ber.*, **18**, 2611 (1885).
(5) Smith, THIS JOURNAL, **56**, 472 (1934).
(6) Noelting and Baumann, *Ber.*, **18**, 1152 (1885).
(7) Willstätter and Kubli, *ibid.*, **42**, 4157 (1909).
(8) Noelting and Baumann give 210–211°, *ibid.*, **18**, 1149 (1885).

TABLE I

Chemical	Amount, mmol.	Solution	Time of oxidation, min.	Ml. O_2 abs.	Ml. O_2 ev.	100 O_2 ev. / O_2 abs.
Hydroquinone	0.5	Water	50	5.3	0.9	17
	.5	Water[a]	46	5.2	3.1	60
Toluhydroquinone	.25	20% ethanol	50	4.8	2.4	50
o-Xylohydroquinone	.25	20% ethanol-water	16	3.6	3.3	92
	.25		60	5.6	4.6	82
m-Xylohydroquinone	.25	20% ethanol		5.8	3.8	66
p-Xylohydroquinone	.25	20% ethanol	50	6.0	4.3	70
ψ-Cumohydroquinone	.125	20% ethanol	30	2.9	2.5	86

[a] Oxidation in presence of 0.2 g. of 2-methylbenzothiazole-metho-*p*-toluenesulfonate.

The other materials were identified with or prepared according to the same methods as those described in the preceding paper of this series.[1]

Reaction Products

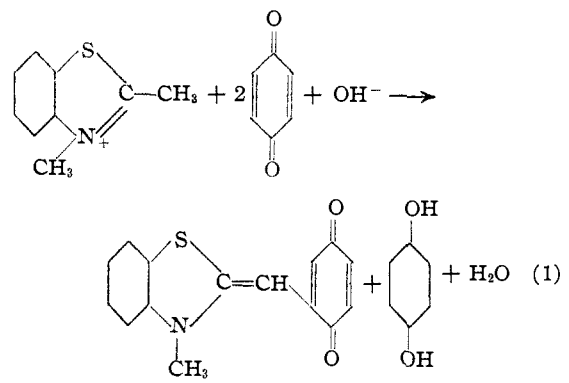
Tests for hydrogen peroxide in the autoxidized solutions were positive. With the xylohydroquinones and ψ-cumohydroquinone, the procedure described for durohydroquinone was used. This method failed in the case of hydroquinone itself, supposedly because the reaction between peroxide and quinone[9] was too rapid. The test was therefore carried out after hydroquinone (0.11 g.) had been oxidized in aqueous borate buffered solutions (50 ml.) containing 2-methylbenzothiazole-metho-*p*-toluenesulfonate (0.3 g.). The latter acted as a quinone acceptor (see formula (1)), forming a water-insoluble reaction product, and the filtered solution gave a positive peroxide test (perchromate reaction).

Peroxide was determined quantitatively by measuring the oxygen evolved when aqueous 0.1 *M* potassium permanganate solution was added in excess to the autoxidized solutions buffered at *p*H 7.6–8.0. Acidulated permanganate could not be used in many cases, since carbon dioxide was formed in the reaction between the acid permanganate and the quinone. Control experiments showed that neutral permanganate did not cause evolution of gas on addition to the buffered (*p*H 7.8–8.0) solutions of hydroquinone, quinone, or hydroxyquinone.

A representative example of the results of the peroxide tests is given in Table I.

ψ-Cumoquinone and the *xyloquinones* were extracted from the oxidized solutions of the corresponding methylhydroquinones with benzene and identified by melting point determinations.

Proof that *quinone* was formed in the autoxidation of *hydroquinone* itself was obtained by making use of the reaction of quinone with 2-methylbenzothiazole - metho - *p* - toluenesulfonate. According to our colleague Dr. L. G. S. Brooker,[10] these substances react in alkaline solution with formation of [(3-methyl-2(3)-benzothiazolylidene)-methyl]-*p*-benzoquinone



(1)

This is in agreement with our observation that the addition of 2-methylbenzothiazole-metho-*p*-toluenesulfonate to an alkaline solution of hydroquinone increases the oxygen absorption through the regeneration of hydroquinone. In the case of ψ-cumohydroquinone, the total oxygen absorption increased from 1 to 2 moles. The experiments were carried out in aqueous borate buffered solutions (50 cc.) at *p*H 8.2.

(1) Hydroquinone (0.25 mmol.), oxidized in the presence of an excess of 2-methylbenzothiazole - metho - *p* - toluenesulfonate (1.0 mmol.), yielded a blue-violet precipitate.

(2) Quinone, added to a buffered 2-methylbenzothiazole-metho-*p*-toluenesulfonate solution, yielded a blue-violet precipitate.

(3) Hydroquinone which had absorbed 1 mole of oxygen yielded, on addition of methylbenzothiazole-metho-*p*-toluenesulfonate, a green solution without a precipitate.

(4) Quinone, which had stood for some time in the alkaline solution in the presence of excess hydrogen peroxide, yielded, on addition of methylbenzothiazole-metho-*p*-toluenesulfonate, a green solution without a precipitate.

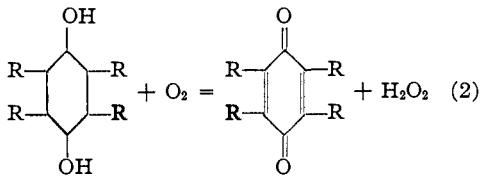
(5) Hydroxyquinone, added to the methylbenzothiazole-metho-*p*-toluenesulfonate solution, yielded a green solution of the same appearance.

(9) Reinders and Dingemans, *Rec. trav. chim.*, **53**, 209 (1934).

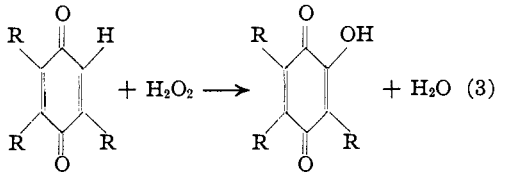
(10) Private communication; see also F. Kröhnke and H. Schmeiss, *Ber.*, **70**, 1728 (1937).

Precipitates (1) and (2) were filtered off, washed, dried, and dissolved in ethanol. The absorption spectra of the resulting solutions were measured.[11] They were identical, having a maximum absorption at 620 mμ and a minimum at 420–460 mμ. A solution prepared from hydroxyquinone and methylbenzothiazole - metho - *p* - toluenesulfonate gave an entirely different spectrum with a maximum absorption at 450–460 mμ, a small minimum at 540–550 mμ, and another slight maximum at 620–630 mμ.

The analogy between hydroquinone and its homologs makes it unlikely that the *formation* of quinone and hydrogen peroxide with the former is due to an interference of the methylbenzothiazole - *p* - toluenesulfonate. These experiments therefore generalize the results reported in the preceding paper and show that the *first products in the autoxidation of hydroquinone and its homologs are the corresponding quinones and hydrogen peroxide.* The general equation for the first step in the autoxidation of hydroquinone and its mono-, di, tri-, and tetramethyl homologs can thus be written



where R represents alkyl groups or hydrogen. The experiments (3–5) show further that quinone reacts with the hydrogen peroxide with formation of hydroxyquinone. It appears safe to generalize that if at least one of the R's is hydrogen, the further reaction



(3) takes place, and polymerization of the hydroxyquinone provides for the formation of "humic acids."[12]

Kinetics

The apparatus and general procedure employed in the study of the kinetics were those described in the preceding papers of this series. All experiments, unless otherwise specified, were carried out at 20.00 ± 0.03°, and with a total solution volume of 50.0 ml. The aqueous buffers were prepared from 25.0 ml. of 0.15 *M* borax plus 0.8 *M* boric acid, or 25.0 ml. of 0.5 *M* disodium phosphate and 0.2 *M* monosodium phosphate. Because of the slight solubility of some of the compounds in water, 20% ethanol solutions were used in some of the experiments. In these experiments the buffer was prepared from 10.0 ml. of 0.2 *M* disodium phosphate and sufficient 0.1 *M* hydrochloric acid to give the desired *p*H value. Measurements of *p*H were made on the completed solutions by means of a calibrated glass electrode.

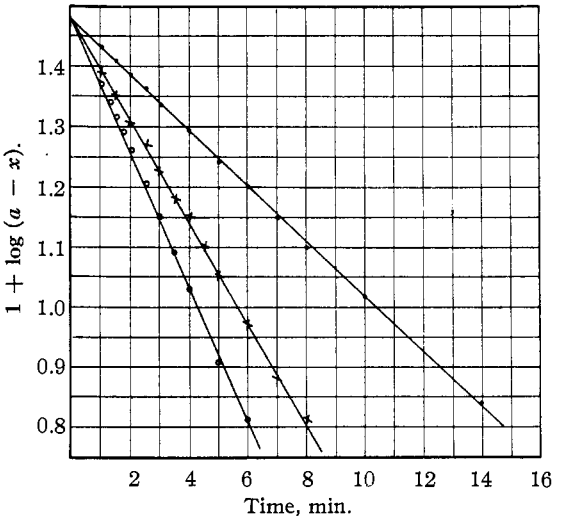


Fig. 1.—Oxidation of xylohydroquinone phosphate buffer, *p*H 7.75: —·—·— *o*-xylohydroquinone; —x—x— *p*-xylohydroquinone; —o—o— *m*-xylohydroquinone.

The data were analyzed as follows: log $(a - x)$ was plotted against t for each set of data (a is the theoretical oxygen uptake if 1 mole of oxygen is absorbed per mole of the hydroquinone; x, the volume absorbed at time t (minutes)). The slope of the resulting curve was then determined for various values of x. If the rate of oxygen uptake is governed by a first-order equation, the slope will be independent of x, and its value, k_{10}, multiplied by 2.3, will give the first-order reaction constant (k). In the case of the xylohydroquinones, k_{10} was constant throughout the greater part of the reaction (Fig. 1). The autoxidation of toluhydroquinone and of hydroquinone likewise follows the first-order equation for oxygen uptakes to 50–70% mole. Beyond this, compli-

(11) We are indebted to Mr. E. Richardson for the absorption measurements.

(12) Eller and Koch, *Ber.*, **53**, 1469 (1920).

cations arise which are due to further oxidation of the primary reaction products.

The use of the theoretical oxygen uptake a is suggested by the results with durohydroquinone in combination with the observations about the reaction products reported above. After 1 mole of oxygen has been absorbed, further uptake is much slower with ψ-cumohydroquinone and the dimethyl hydroquinones so that a break in the ml. O_2/t curve occurs. (For *m*-xylohydroquinone, the character of this subsequent reaction was substantiated by the fact that a mixture of equal molecular portions of the quinone and of hydrogen peroxide absorbed oxygen at the same rate as the oxidized solution of the hydroquinone at the same *p*H.) The oxygen values where the breaks in the ml. O_2/t curves occur check well with the theoretical values. This is shown in Table II.

TABLE II

TOTAL AMOUNTS OF OXYGEN ABSORBED (N. T. P.)

Compound	O_2 Absorbed	Theoretical
ψ-Cumohydroquinone	5.45	5.6
p-Xylohydroquinone	2.75	2.8
m-Xylohydroquinone	2.7	2.8
o-Xylohydroquinone	2.7	2.8

The differences between observed and theoretical values obviously are caused by the action of hydrogen peroxide on the hydroquinones. With toluhydroquinone and with hydroquinone itself, the difference in the reaction rates between the initial and the subsequent reaction is less pronounced. It is sufficient, however, as mentioned above, to produce a straight line on our plots for about 70 and 50%, respectively, of an oxygen uptake of one mole.

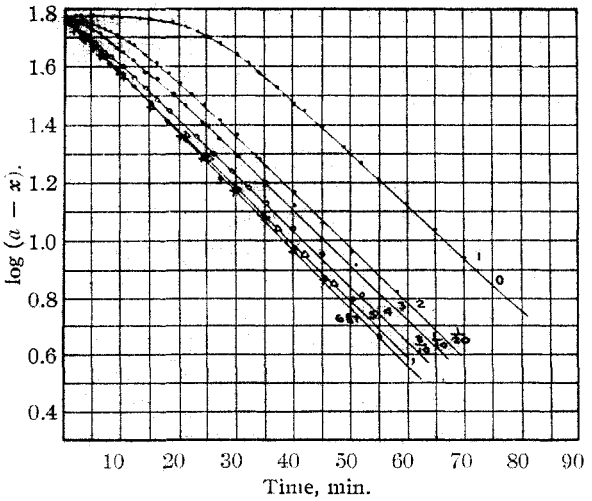


Fig. 2.—Oxidation of ψ-cumohydroquinone. Effect of added ψ-cumoquinone on $^1/_4$ *M* mol. of ψ-cumohydroquinone: Curve 1, no added ψ-cumoquinone; Curve 2, $^1/_{80}$ *M* mol.; Curve 3, $^1/_{40}$ *M* mol.; —o—o— 4. $^3/_{40}$ *M* mol.; —Δ—Δ— 5. $^3/_{20}$ *M* mol.; ——— 6. $^1/_4$ *M* mol.; —x—x— 7. $^1/_2$ *M* mol.

For **the autoxidation of cumohydroquinone,** which will be considered first, 20% ethanol was used as solvent because of the low solubility of the material. A phosphate buffer was employed for most of the work, although check runs were made in a buffered borate solution. The buffers used kept the *p*H of the solutions constant within 0.02 unit throughout the entire course of the oxidation.

The reaction exhibits a pronounced *induction period*, as shown in curve 1 of Fig. 2. The slope of the curve attains a maximum, and this constant value is maintained throughout the remainder of the oxidation, in conformity with the kinetics of a first-order reaction.

The induction period does not appear to be due to the presence of an inhibitor. Successive purifications of the ψ-cumohydroquinone gave no significant change, and identical oxidation curves were obtained when the ethanol normally used was replaced by a sample obtained from an entirely different source and purified according to the method of Danner and Hildebrand.[13] Moreover, the induction period persisted if the solutions were prepared, mixed, and stored for one hour in an atmosphere of pure nitrogen before oxidation was begun.

The induction period is shortened by the addition of ψ-cumoquinone to the reaction mixture at the start of the oxidation, and it is eliminated completely if about 0.15 mmol. of *ψ-cumoquinone* is added to the 0.25 mmol. of ψ-cumohydroquinone used in these experiments Thus, it appears that the ψ-cumoquinone formed during the autoxidation acts as a catalyst. Other quinones, phenosafranin and indophenol, also eliminate the induction period.

In Fig. 3, values of k_{10} obtained from curve 1 of Fig. 2 are plotted against the corresponding amounts of oxygen absorbed. In the same figure, the initial values of k_{10} obtained from curves 2–7 (Fig. 2) are plotted against the amounts of ψ-cumoquinone added. The close similarity of the curves confirms the fact that the governing factor in the acceleration is the ψ-cumoquinone. The slight difference between the two curves is

(13) Danner and Hildebrand, THIS JOURNAL, **44**, 2827 (1922).

explained by the action of the hydrogen peroxide upon the ψ-cumoquinone in the experiments recorded by curve 2.

The dependence of k_{10} upon the initial amounts of ψ-cumohydroquinone present is given in Table III.

TABLE III

DEPENDENCE OF k_{10} UPON THE INITIAL CONCENTRATION OF ψ-CUMOHYDROQUINONE; PHOSPHATE BUFFER, *p*H 7.40

Total volume of solution	50.0	50.0	100.0	50.0
Mmol. ψ-cumohydroquinone	0.50	0.25	0.25	0.125
Mmol. O_2 absorbed	k_{10}	k_{10}	k_{10}	k_{10}
0.005	0.0014	0.0014	..	0.0012
.010	.0028	.0026	0.0012	.0025
.015	.0042	.0044	.0020	.0044
.020	.0057	.0058	.0026	.0052
.040	.0102	.0100	.0046	.0110
.060	.0135	.0133	.0065	.0145
.080	.0170	.0170	.0094	.0172
.100	.0175	.0176	.0110	.0175
.200	.0175	.0176	.0170	..

With a constant volume of solution, the induction period disappears in all cases after the *same amount* of oxygen has been absorbed. The elimination of the induction period does not depend upon the ratio of ψ-cumoquinone to ψ-cumohydroquinone, but it depends either on the absolute amount or on the concentration of the ψ-cumoquinone. The data obtained when a total volume of 100 ml. was employed instead of the customary 50 ml. showed that the *concentration* of the ψ-cumoquinone is the essential factor.

The observation that the quinone eliminates the induction period in the autoxidation of ψ-cumohydroquinone is analogous to our results with durohydroquinone.[1] At variance with the case of durohydroquinone, however, an initial velocity which might be interpreted as that of the uncatalyzed reaction, is not indicated by the curves in Fig. 3 which go through the origin. A more important difference consists in the dependence of the reaction velocity on the concentration of the quinone. With durohydroquinone, the reaction rate rises linearly with the concentration of the quinone; *with ψ-cumohydroquinone, however, the catalytic influence drops with increasing concentration of the quinone until a further addition becomes irrelevant* (see Fig. 3).

Duroquinone, upon standing in an alkaline solution, gradually loses its power of catalyzing the autoxidation of durohydroquinone. The rate of this loss, which is probably due to self condensation of the quinone, is too low to be of significance in the experiments recorded in the previous paper.[1] In order to determine whether a similar, but more rapid, loss occurring in the case of ψ-cumoquinone could account for the fact that its catalytic effect reaches a limiting value, experiments were carried out where the mixture of ψ-cumohydroquinone and ψ-cumoquinone was allowed to stand for varying times in an atmosphere of pure nitrogen before oxidation was started. Some of the results are recorded in Table IV.

TABLE IV

1/8 mmol. ψ-Cumohydroquinone, 1/8 mmol. ψ-Cumoquinone

Time elapsing before start of oxidation	Volume oxygen absorbed, 20°, 760 mm.				
Oxidation time, min.	15 sec.	30 min.	74 min.	75 min.[a]	0[b]
2	0.40	0.40	0.40	0.40	..
4	.80	.75	.70	.70	0.03
7	1.22	1.10	1.00	1.13	.10
12	1.80	1.52	1.45	1.70	.40
15	2.02	1.80	1.68	1.95	.68
20	2.35	2.10	2.00	2.30	1.13
75	2.95	2.95	2.95	..	2.90

[a] Quinone alone stood in alkaline solution. [b] No quinone added.

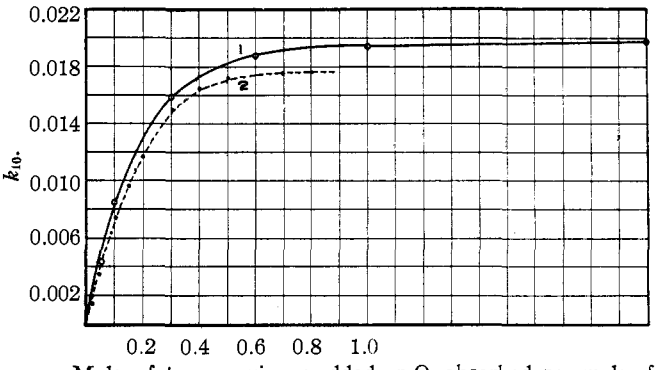


Fig. 3.—Quinone catalysis of the autoxidation of ψ-cumohydroquinone: —o—o— 1, ψ-cumoquinone added; — —·— —·— — 2, from oxidation curve.

Only very little loss occurred in the catalytic activity of ψ-cumoquinone which stood in alkaline solution for the length of time required for completion of the normal autoxidation of ψ-cumohydroquinone. The peculiar behavior of ψ-cumoquinone is therefore due to other causes.

The dependence of the maximum value of k_{10} upon the pH of the solution is shown in Table V. The maximum velocity of the reaction varies with the square of the hydroxyl-ion concentration, and plot

of log k_{10} against pH gives a straight line of slope 2.0.

TABLE V

DEPENDENCE OF k_{10} UPON THE HYDROXYL-ION CONCENTRATION; 0.25 MMOL. ψ-CUMOHYDROQUINONE

pH	k_{10}	$2+\log k_{10}$
7.84	0.140	1.15
7.64	.056	0.75
7.48	.0252	.40
7.40	.0180	.26

The pH values given in the first column were measured by means of a glass electrode placed in solutions of the buffer which contained all the ingredients of the solution used in oxidation measurements except the ψ-cumohydroquinone and alcohol. The latter was replaced by an amount of water sufficient to give the same total volume. The pH values may therefore be wrong in their absolute amounts, but their gradation is right, since no significant effect on the oxidation velocity is observed when successive amounts of water are replaced by alcohol in experiments with hydroquinone, using the same phosphate buffer as that employed in the present case (see page 2091).

Table VI shows the *variation of* k_{10} *with the partial pressure of oxygen* for three pH values.

TABLE VI

0.25 MMOL. ψ-CUMOHYDROQUINONE. DEPENDENCE OF k_{10} UPON PARTIAL PRESSURE OF OXYGEN

O_2 abs./ψ-Cumohydroquinone	pH 7.84		pH 7.64		pH 7.40	
	O_2	Air	O_2	Air	O_2	Air
0.02	0.016	0.013	0.0030	0.0026	0.0014	0.0012
.05	.034	.022	.0090	.0075	.0035	.0024
.10	.060	.028	.0175	.0107	.0070	.0040
.15	.076	.032	.0250	.013	.0095	.0046
.20	.090	.034	.0325	.0144	.0118	.0052
.30	.110	.035	.0425	.0135	.0150	.0048
.40	.126	.035	.0480	.0135	.0163	.0046
.50	.130	.035	.0520	.0135	.0172	.0046

Although the accuracy with which k_{10} can be determined in the early stages of the oxidation is low, the data show that the dependence of the rate of autoxidation upon the oxygen pressure increases as the reaction progresses. It did not quite attain a direct proportionality, however, in these experiments.

The autoxidation of the xylohydroquinones, toluhydroquinone, and hydroquinone itself follows the first-order law with respect to the concentration of the dihydroxy compound. This is demonstrated both by the straight line obtained in a log $(a-x)$, t plot and by the independence of the reaction constant upon the initial concentration of the hydroquinone over tenfold variations in concentration. The autoxidation rate varies linearly with the concentration of the oxygen (Table VII).

TABLE VII

DEPENDENCE OF k UPON PARTIAL PRESSURE OF OXYGEN

Borax buffer, 0.25 mmol. hydroquinone, 20% ethanol

	o-Xylohydroquinone	*m*-Xylohydroquinone	*p*-Xylohydroquinone
Pure oxygen	0.024	0.045	0.042
Air	.0051	.0095	.0089
Ratio	4.71	4.73	4.72

The dependence of the rate of autoxidation upon the hydroxyl-ion concentration of the solution has been a subject of some dispute. Euler and Brunius, and Reinders and Dingemans observed a dependence upon the square of the hydroxyl-ion concentration. La Mer and Rideal found a relationship between the first power of the reaction rate and the 1.5 power of the hydroxyl-ion concentration. St.-Maxen claimed a first-power relationship.[1] We have found a dependence upon the square of the hydroxyl-ion concentration for the following materials: durohydroquinone, ψ-cumohydroquinone, *o*-, *m*-, and *p*-xylohydroquinone, toluhydroquinone, and hydroquinone.

These data are summarized in Fig. 4, in which log k is plotted against pH. The slope of each line is very nearly 2.0. All data given are for aqueous solutions. Two series of buffers were used, phosphate and borate. The ionic strengths were kept as nearly as possible constant in each series. Measurements of pH were made on the complete solutions with a glass electrode. The fact that, in every case, the slope measured is slightly less than 2.0 can be understood on the assumption that the singly charged hydroquinonate ion is also oxidizing, but at a much lower rate than the doubly charged ion.

This assumption gains support from the fact that monomethyl ethers undergo autoxidation, albeit at a very low rate, as exemplified in Table VIII; this is parallel with the autoxidation of benzoin methyl ether.[14]

TABLE VIII

AUTOXIDATION OF MONOMETHYL ETHERS

Monomethyl ethers of	Amount mmol.	1.0 *M* KOH ml.	Rate, ml./min.	Solution
Durohydroquinone	1/8	2.0	0.003	45 cc. 30% ethanol
Hydroquinone	1/2	0.4	.002	50 cc. water
Hydroquinone	1/2	4.0	.002	50 cc. water

The addition of hydrogen peroxide at the start of the oxidation has no measurable effect upon

(14) James and Weissberger, THIS JOURNAL, **59**, 2040 (1937).

the initial rate of autoxidation. As the oxidation proceeds, however, the oxidation of the hydroquinone by the peroxide becomes appreciable and the total oxygen uptake decreases. This action of the hydrogen peroxide accounts for the fact that the observed "end" volumes of oxygen absorbed (see page 2089) are somewhat less than 1 mole in the cases of durohydroquinone, ψ-cumohydroquinone, and the xylohydroquinones. With toluhydroquinone and hydroquinone itself, the subsequent reactions prevent the determination of "end" volumes.

An apparent slight induction period was noted in several experiments in the autoxidation of the xylohydroquinones, but in no case was the existence of such an induction period established beyond doubt. *No catalysis was observed when the corresponding quinone was added to the oxidation mixture at the start of the experiments with these compounds.*

Benzoquinone itself autoxidizes at a rate which, at the maximum, is roughly 0.01 of that of hydroquinone under the conditions of our experiments. It therefore can be neglected here.

Effect of Alcohol upon the Rate of Oxidation.—Inasmuch as the low solubility of ψ-cumoquinone and the xylohydroquinones made it necessary to use alcohol–water mixtures as solvent, it was desirable to know to what extent the change of solvent influenced the rate of oxidation. A borate buffer could not be used for this purpose, since the rapid reaction between borate and alcohol affects the hydroxyl-ion concentration of the solution. A phosphate buffer of the following composition was therefore employed: 0.2 *M* Na_2HPO_4, 10 ml.; 0.067 *M* NaH_2PO_4, 1 ml.: total volume of solution, 50 ml. The results obtained are recorded in Table IX.

TABLE IX

EFFECT OF ETHANOL ON THE RATE OF OXIDATION OF HYDROQUINONE

Ethanol, %	k_{10}	$k_{10}/[O_2]$
0	0.0172	14.6
1	.0176	14.9
5	.0173	15.0
20	.0162	15.2

In the last column, a correction has been made for the change in solubility of oxygen in the ethanol solution. The variation in the oxidation rate observed scarcely exceeds the limits of experimental error.

Effect of Substitution.—From the data given in Fig. 4, the relative rates of oxidation of hydroquinone and its mono- and dimethyl homologs can be calculated. The figures obtained are given in Table X (aqueous solution, phosphate buffer). In addition, the maximum rate of oxidation of ψ-cumohydroquinone relative to hydroquinone in 20% ethanol solution is added. No corresponding value can be stated, of course, for durohydroquinone, for which the rate of the uncatalyzed reaction is given for comparison.

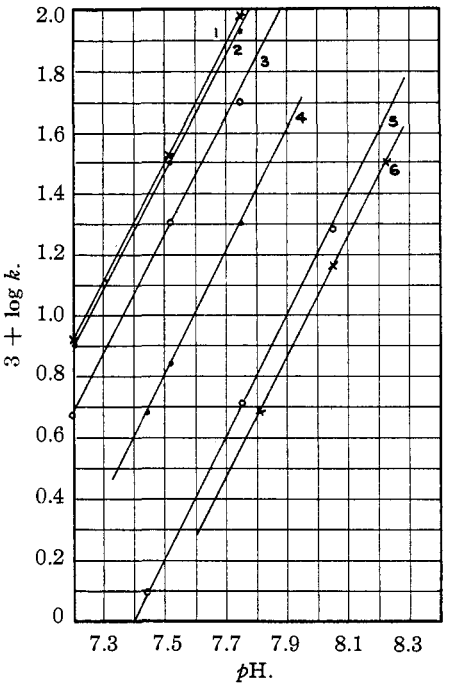


Fig. 4.—*p*H dependency: 1, *m*-xylohydroquinone, phosphate buffer, slope 1.95; 2, *p*-xylohydroquinone, phosphate buffer, slope 1.96; 3, *o*-xylohydroquinone, phosphate buffer, slope 1.96; 4, toluhydroquinone, phosphate buffer, slope 1.97; 5, hydroquinone, phosphate buffer, slope 1.98; 6, hydroquinone, borate buffer, slope 1.98.

TABLE X

Compound	Relative rate of oxidation
Hydroquinone	1.00
Toluhydroquinone	3.9
o-Xylohydroquinone	10.5
m-Xylohydroquinone	18.2
p-Xylohydroquinone	17.0
ψ-Cumohydroquinone (max. value 20% ethanol)	31.0
Durohydroquinone (uncatalyzed reaction)	1.00

It appears that substitution by methyl groups raises the rate of autoxidation. This can be due to an increase in the dissociation constants, or to other factors. The reaction rate of durohydroquinone may be low by reason of steric hindrance. It might be, however, that the correct value for comparison would be that of a quinone-catalyzed

reaction of this compound. This raises the question of whether the values given for hydroquinone, toluhydroquinone, and the xylohydroquinones belong to the uncatalyzed reaction or are maximum values of quinone-catalyzed reactions to be compared with the value given for ψ-cumohydroquinone.

Discussion of Results

The qualitative and quantitative analyses of the *autoxidation products* of hydroquinone, toluhydroquinone, the xylohydroquinones and ψ-cumohydroquinone show that the reaction products are analogous to those of durohydroquinone, *i. e.*, the corresponding quinones and hydrogen peroxide. The *kinetics* of the oxidation are identical with regard to the dependency of the reaction rate on the hydroxyl-ion concentration. This is in the *p*H range 7.2–8.2 very nearly proportional to the square of the hydroxyl-ion concentration. This reveals that the reaction is controlled by the concentration of the doubly charged ion. A slight deviation from the second power may be due to some reactivity of the monovalent ion.

Durohydroquinone, on the one hand, however, and *hydroquinone*, *toluhydroquinone* and the *xylohydroquinones*, on the other, differ essentially with regard to the directly observed existence of an induction period, and with regard to the catalytic influence of quinones which may be added or formed during the reaction. The autoxidation of *durohydroquinone* is catalyzed by duroquinone, whereas the addition of quinones to *hydroquinone* and its lower homologs is without effect on their autoxidation velocities. The rate of the uncatalyzed oxidation of *durohydroquinone* under the conditions of our experiments is proportional to the oxygen concentration, whereas the quinone-catalyzed reaction is unaffected by the latter. The autoxidation rate of *hydroquinone*, *toluhydroquinone* and the *xylohydroquinones* is proportional to the oxygen concentration.

The autoxidation of *ψ-cumohydroquinone* furnishes the transition between the two types. It shows an induction period and a strong catalysis by small amounts of quinone. (The rate of the uncatalyzed reaction in the absence of quinone could not be determined.) The reaction rate, however, does not increase linearly with the concentration of the quinone, but increases at a slower and slower rate until a further addition of the quinone remains without effect. The oxygen dependency in the region of the strong quinone catalysis resembles that of the quinone-catalyzed autoxidation of *durohydroquinone*. The oxygen dependency in the region where further addition of quinone is without effect corresponds to the behavior of *hydroquinone* and its lower homologs. It may be suggested, therefore, that our observations with durohydroquinone correspond to that autoxidation of ψ-cumoquinone which is represented by the lower portion of the curve in Fig. 3, whereas the autoxidation which we observe with hydroquinone and its lower homologs corresponds to the type of reaction represented by the section of the curve with slope zero. In other words, we suggest that *the autoxidation of the lower members of the series is catalyzed by traces of the quinone too small to be ascertained*. This assumption fits in with the observations recorded in Table X. It offers further an interesting aspect of various photographic problems, of which only the following will be mentioned here.

The catalytic effect of the oxidation products may be significant for the photographic behavior of developers, since this catalysis enhances the differentiation between parts of the emulsion where reaction has started and those which are unattacked.

The quinone catalysis throws new light on the problem of the induction period of hydroquinone developers, since, as far as has been tested, those substances (quinone, phenosafranin, indophenol) which cut down the latter,[15] also remove the induction period in the autoxidation processes.

Sodium sulfite inhibits the autoxidation of hydroquinone and its methyl homologs with the exception of durohydroquinone, *i.e.*, it acts in those cases where it can form hydroquinone sulfonates with the quinone and not in the case where this action is impossible. It may be, therefore, that the inhibiting action of sodium sulfite is due to the removal of the catalyzing quinone.

The probable mechanism of the quinone catalysis of the autoxidation of durohydroquinone has been suggested in the preceding paper. A semiquinone is formed by the interaction of the divalent ion and the quinone, and this semiquinone is oxidized rapidly. If the formation of the semiquinone is the rate-controlling reaction and the subsequent interaction with oxygen proceeds smoothly at a comparatively high rate, the kinet-

(15) Frötschner, *Phot. Ind.*, **35**, 801 (1937).

ics observed with durohydroquinone are those to be expected.

The fact that, with ψ-cumohydroquinone, the quinone catalysis reaches a saturation value is open to various interpretations and further work must, therefore, be done on the investigation of this problem.

Summary

1. Hydroquinone, toluhydroquinone, the three xylohydroquinones, and ψ-cumohydroquinone are oxidized in alkaline solution by molecular oxygen with the formation of hydrogen peroxide and the corresponding quinones. This is followed by a reaction between the hydrogen peroxide and the quinones.

2. The high rate of the reaction between benzoquinone and hydrogen peroxide made it necessary to use an acceptor (2-methylbenzothiazole-metho-*p*-toluenesulfonate) for the quinone to protect the hydrogen peroxide and to make it available for analysis.

3. The quinones were, in general, identified after isolation. In the case of the autoxidation of hydroquinone, the condensation product with the acceptor was identified spectroscopically and through it the quinone.

4. The formation of hydroxyquinone by reaction of quinone and hydrogen peroxide in the autoxidation of hydroquinone was confirmed by spectroscopic analysis of the condensation products with 2-methylbenzothiazole-metho-*p*-toluenesulfonate.

5. Very close dependency of the autoxidation rate of hydroquinone and its homologs upon the square of the hydroxyl-ion concentration in the *p*H range 7.2 to 8.2 shows that the oxidation involves mainly the doubly charged hydroquinone anion.

6. A slight deviation from the second power may be due to a comparatively slow oxidation of the monovalent ion, suggested by the autoxidation of monomethyl ethers of hydroquinone and of durohydroquinone.

7. The oxidation of ψ-cumohydroquinone is strongly catalyzed by small amounts of quinones. This catalytic action approaches a maximum.

8. In the maximum, the autoxidation rate is proportional to the concentration of the ψ-cumohydroquinone.

9. The rate of reaction of ψ-cumohydroquinone is independent of the oxygen concentration with low amounts of quinone as a catalyst. As the quinone catalysis reaches its maximum, the reaction rate becomes almost proportional to the oxygen concentration.

10. In the presence of small amounts of the quinone, the kinetics of the autoxidation of ψ-cumohydroquinone resemble those of the quinone-catalyzed durohydroquinone reaction; as the quinone concentration increases, the kinetics pass over into those of the autoxidation of the lower members of the hydroquinone series.

11. The rates of oxidation of hydroquinone, toluhydroquinone, and the xylohydroquinones vary directly with the concentrations of oxygen and of the hydroquinones.

12. No quinone catalysis was detected in the autoxidation of hydroquinone, toluhydroquinone, and the xylohydroquinones. However, on the basis of the transition which ψ-cumohydroquinone affords between the kinetics of the oxidation of durohydroquinone and the lower members of the series, it is suggested that quinone catalysis exists for the latter, and that the maximum value is reached at quinone concentrations sufficiently low to escape detection.

13. Sodium sulfite inhibits the autoxidation of hydroquinone, toluhydroquinone, the xylohydroquinones, and ψ-cumohydroquinone.

14. Suggestions are made for the interpretation of the inhibition of the oxidation of hydroquinones by sulfite and of the action and the nature of the induction period of photographic developers.

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