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Oxidation Processes. XIX.[1] Quinone Catalysis in the Autoxidation of Hydroquinones

By J. E. LuValle and A. Weissberger

The autoxidation of durohydroquinone is catalyzed by duroquinone, which is formed in the reaction or added to the mixture.[2] Similar autocatalysis and catalysis take place with pseudo-cumohydroquinone, but here the reaction rate does not always increase in proportion to the amount of quinone added.[3] If pseudo-cumoquinone is added or formed in higher concentrations, the catalytic effect of additional quinone appears to decrease until it becomes negligible, *i.e.*, it reaches saturation. The expression "quinone catalysis" is used as a brief term for the designation of the catalysis of the oxidation of a compound, R, by the bivalently oxidized product, T, or by a similar compound. It is a special case of the equilibrium

$$R + T \rightleftarrows 2S \qquad (1)$$

Quinone catalysis and its saturation at rather low quinone concentrations appear to be of fundamental importance in the autoxidation of enediols of hydroquinones and of related compounds.[2,3,4]

The quinone acts as a catalyst through the formation of highly reactive semiquinones.[2] The saturation of the quinone catalysis is explained with the attainment of a steady state by the semiquinone.[1,5] The attainment of saturation by the quinone catalysis should depend upon the ratio of (T)/(R)[1] rather than upon the concentration of T. Dependency on the latter had been surmised by James, Snell and Weissberger.[3] They also found some indications, but no definite proof, that the xylohydroquinones might exhibit an autocatalytic period. Both observations needed checking, and the present paper gives new data on pseudo-cumohydroquinone, 2,5-dimethylhydroquinone, toluhydroquinone, and hydroquinone, and a discussion which is based on the preceding paper.

Experimental

Materials and Techniques

Reagents, unless noted otherwise, and techniques for the measurement of oxygen absorption and *p*H were identical with those described in preceding papers of this series.[3,4b,6] The temperature of the kinetic experiments was 19.97 ± 0.02°. Buffers were present in a concentration of 0.20 *M*, and the solutions were 0.004 *M* in potassium cyanide and potassium thiocyanate, respectively, in order to inhibit heavy metal catalysis.[4d]

A very useful and clean method for the reduction of quinones is the treatment with hydrazine.

2,5-Xylohydroquinone.[6a]—Eastman Kodak Co. *p*-xyloquinone (13.6 g.; 0.1 mole) was dissolved in 100 ml. of hot 95% alcohol, and the solution cooled to 50°. Successive small portions of a mixture of 85% hydrazine hydrate solution with an equal volume of water were then added until the solution was almost colorless. Nine to ten ml. of the hydrazine solution was required. The temperature was kept at 50° during the addition. The alcohol solution was then heated to boiling, 100 ml. of boiling water was added, and the mixture cooled to 0°. The hydroquinone was filtered off, washed with water and dried in the air; yield was 11.4 g. (81%). Recrystallized from 40% alcohol, it melted at 213–215°.

Pseudo-cumohydroquinone.[6a]—Pseudo-cumohydroquinonewas prepared from pseudo-cumenol-6 by the method of Smith[7a] and co-workers. The over-all yield of quinone was 76%, based on the pseudo-cumenol-6 used.

The pseudo-cumoquinone was reduced to the hydroquinone by the hydrazine hydrate method; yield was 76%. After sublimation, followed by two recrystallizations from toluene, the pseudo-cumohydroquinone melted at 169–170°.

Calculations

In the preceding papers of this series, it was frequently found that the total amount of oxygen absorbed was greater or smaller than that calculated for

$$R + O_2 \longrightarrow T + H_2O_2 \qquad (2)$$

where R is the substrate, *e.g.*, hydroquinone, and T is the oxidation product, *e.g.*, quinone. The deviations are caused by side reactions and subsequent reactions, respectively. For instance, reactions of R and of the semiquinone with hydrogen peroxide diminish the total oxygen uptake, whereas reactions of the quinone, or of a reaction product of the quinone, with oxygen increase the oxygen uptake. The choice of the proper volume of absorbed oxygen at t_∞ is therefore often difficult and may even be arbitrary. Such a choice is avoided by Guggenheim's method[8] for the analysis of rate measurements. In this method, two sets of data are recorded, a set, X_i, at time, t_i, and another X'_i at time, t'_i, where $t'_i = t_i + \tau$. The accuracy of the method increases with τ. Values of $\log (X'_i - X_i)$ are then plotted against t_i. The resulting curve is a straight line for first-order reactions. The rate constant, k, is proportional to the slope, s, of this line, $k = -2.30s$.

It may be recalled that in terms of the traditional way of calculating rate constants of first-order reactions, $k = 2.30s'$, where s' is the slope of the plot of $\log (a - x)$ against t, a being

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(1) Part XVIII, LuValle and Weissberger, This Journal, **69**, 1567 (1947).

(2) James and Weissberger, *ibid.*, **60**, 98 (1938).

(3) James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938).

(4) (a) James and Weissberger, *ibid.*, **61**, 442 (1939); (b) Weissberger and Thomas, *ibid.*, **64**, 1561 (1942); (c) Weissberger, Thomas, and LuValle, *ibid.*, **65**, 1489 (1943); (d) Weissberger, LuValle and Thomas, *ibid.*, **65**, 1934 (1943).

(5) Kornfeld and Weissberger, *ibid.*, **61**, 360 (1939).

(6) Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929).

(6a) For these preparations, we are indebted to Mr. E. C. Armstrong.

(7) Smith and co-workers, *J. Org. Chem.*, **4**, 318 (1939).

(8) Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

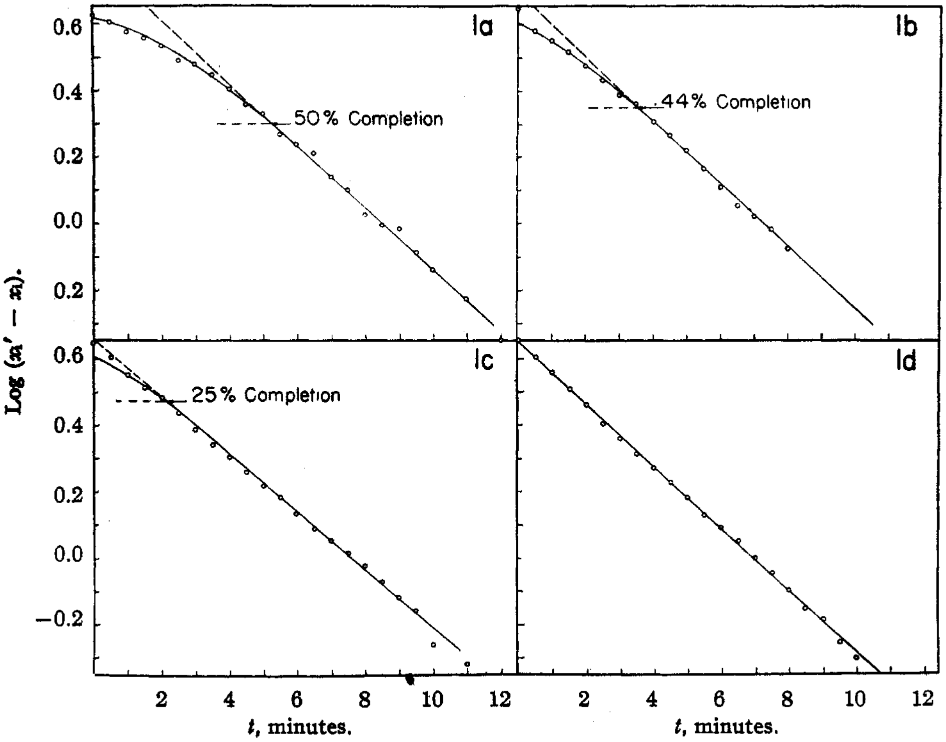

Fig. 1.—Guggenheim curves for pseudo-cumohydroquinone (3.33×10^{-3} M) in oxygen; $\overline{pH}$ 8.33 ± 0.02; ψ-cumoquinone added: (a) 0.00; (b) 0.416×10^{-3} M; (c) 1.67×10^{-3} M; (d) 3.33×10^{-3} M. The point at which $R = T$ is indicated by →, except in cases where $R_0 = T_0$.

the total substrate and x the reacted portion. Guggenheim's curve is analogous to the customary $\log (a - x)$ *vs.* time plot, and deviations from first-order reactions affect the shape of both curves in the same way.

The fraction of the reaction completed is calculated as x/a, where a is the initial number of moles of R and x is the number of moles of oxygen absorbed.

The fraction of the reaction completed for the time at which R = T

$$(x/a)_{R=T} = (a - T_0)/2a \qquad (3)$$

where T_0 is the initial amount of T present in the reaction mixture. This equation is valid as long as the semiquinone formation constant is small.

Results

Pseudo-cumohydroquinone.—The measurements were made in 20% ethanol, for reasons of solubility. The rate data are summarized in Table I.

Columns 1 and 2 give the initial and the final pH, respectively. The oxygen pressure of the experiments is listed in column 3. The initial concentration of pseudo-cumohydroquinone, the amount of pseudo-cumoquinone added, and the ratio of both compounds at the beginning of the reaction are given in columns 4, 5 and 6, respectively. Column 7 lists the value of x/a for the time at which R = T, and column 8 gives the value of x/a for the time at which k, *i.e.*, the slope of the Guggenheim curve, becomes constant (Fig. 1). The values of k are given in column 9.

The Guggenheim curves for several initial values of T are given in Figs. 1 and 2. The experiments of Fig. 1 were made under oxygen, those of Fig. 2 were carried out under air. The data of Table VI of James, Snell and Weissberger[2] are given in Fig. 3.

The data show that under oxygen the saturation of the quinone catalysis occurs in every case when R = T, irrespective of pH and of the initial values of (R) and (T). Within the experimental error, the rate constant at saturation, *i.e.*, the maximum and constant value of k, is independent of the initial concentrations of the quinone and the hydroquinone. The constant rate is first-order with respect to the initial concentration of pseudo-cumohydroquinone, and very closely first-order with respect to the concentration of oxygen throughout the reaction. Under air (Fig. 3), the value of k becomes constant at 15, 15 and 19% completion of the reaction at pH 7.40, 7.64 and 7.84, respectively, *i.e.*, the *steady state* is established *earlier in air* than in oxygen.

2,5-Xylohydroquinone.—James, Snell and Weissberger[2] noted a slight induction period in several experiments with xylohydroquinones without establishing it beyond doubt. The new rate data for one of the xylohydroquinones, 2,5-dimethylhydroquinone, were obtained in 33%

TABLE I

ψ-CUMOHYDROQUINONE IN 20% ETHANOL, POTASSIUM PYROPHOSPHATE BUFFER

1 *p*H initial	2 *p*H final	3 P_{O_2}, mm.	4 *R*, moles/liter × 10^3	5 *T*, moles/liter × 10^3	6 *T/R* initially	7 (*x/a*) R = T Calcd.	8 (*x/a*) *k* = const. Obsd.	9 *k* min.$^{-1}$
8.30	8.33	733.7	3.33	..	0.0	0.50	0.5	0.206
8.23	8.27	726.6	3.33	3.33	1.0	.00	.0	.175
8.15	8.20	741.9	3.33	..	0.0	.50	.5	.109
8.15	8.18	742.5	3.33	3.33	1.0	.00	.0	.122
7.95	8.00	740.7	3.33	..	0.0	.50	.5	.0598
8.00	7.93	737.1	3.33	3.33	1.0	.00	.0	.0562
8.37	8.37	737.4	3.33	..	0.0	.50	.5	.212
8.36	8.36	736.8	3.33	1.67	.5	.25	.25	.200
8.32	8.32	734.0	3.33	..	.0	.50	.5	.194
8.31	8.30	725.8	3.33	3.33	1.0	.00	.0	.215
8.32	8.32	735.7	3.33	5.00	1.5	.00	.0	.233
8.31	8.30	728.1	1.67	..	0.0	.50	.5	.156
8.31	8.32	727.3	1.67	3.33	2.0	.00	.0	.216
8.30	8.32	154.0	3.33	..	0.0	.50	.17	.0518
8.32	8.32	154.0	3.33	3.33	1.00	.00	.00	.0506
8.33	8.37	736.5	3.33	1.67	0.50	.25	.25	.218
8.32	8.32	726.6	3.33	0.416	.125	.44	.41	.217
8.26	8.28	742.2	1.67	1.67	.0	.00	.0	.208
8.27	8.31	743.0	1.67	0.833	.50	.25	.2	.195
8.25	8.29	743.3	1.67	3.42	2.05	.00	.0	.244
8.22	8.23	736.5	1.67	3.33	2.00	.00	.0	.256
7.68	7.76	732.5	3.33	3.33	1.0	.00	.0	.0346
7.70	7.72	734.3	3.33	6.67	2.0	.00	.0	.0322
7.72	7.73	732.5	3.33	1.67	0.5	.25	.3	.0352
7.70	7.72	729.9	3.33	0.832	.25	.375	.4	.0324
7.70	7.73	748.0	3.33	..	.0	.50	.5	.0302

TABLE II

2,5-XYLOHYDROQUINONE IN 33% ETHANOL

1 Initial	2 Final	3 Buffer	4 P_{O_2}, mm.	5 *R*, moles/liter × 10^3	6 *T*, moles/liter × 10^3	7 *T/R* initially	8 (*x/a*) *k* = const.	9 *k* min.$^{-1}$
9.33	9.39	Na-*p*-phenol sulfonate	152.2	3.33	...	0.0	0.00	0.265
9.30	9.39	Na-*p*-phenol sulfonate	155.0	3.33	...	.0	.00	.276
9.30	9.37	Na-*p*-phenol sulfonate	154.5	3.33	0.416	.13	.00	.274
9.31	9.36	Na-*p*-phenol sulfonate	152.0	3.33	.416	.13	.00	.286
9.32	9.32	Na-*p*-phenol sulfonate	151.0	3.33	.834	.25	.0	.274
9.33	9.34	Na-*p*-phenol sulfonate	156.0	3.33	.834	.25	.0	.285
9.34	9.34	Na-*p*-phenol sulfonate	154.2	3.33	1.67	.50	.0	.272
8.89	8.88	Na-*p*-phenol sulfonate	153.0	3.33	...	.00	.0	.0425
8.88	8.90	Na-*p*-phenol sulfonate	152.8	3.33	0.416	.12	.0	.0425
8.92	8.94	Na-*p*-phenol sulfonate	156.4	3.33	.834	.25	.0	.0425
7.95	7.98	K_2HPO_4	737.0	3.33	...	.0	19	.0059
8.39	8.39	$K_4P_2O_7$	733.0	3.33	...	.0	22	.042
8.46	8.50	$K_4P_2O_7$	733.0	3.33	...	1.0	0.0	.037
8.68	8.60	Na-*p*-phenol sulfonate	730.2	3.33	...	0.0	17	.111
8.75	8.77	Na-*p*-phenol sulfonate	731.1	3.33	3.33	1.0	0.0	.115

ethanol solution. They are summarized in Table II, which corresponds to Table I.

In air, no autocatalysis was detected. The Guggenheim curves for three runs, in which the xyloquinone concentration was varied are given in Fig. 4a. For the start and the larger part of the reactions, the data are fitted by a straight line. For the last 25% of the reactions, the rate drops below that expected for a first-order process. This drop is much more pronounced than for pseudo-cumohydroquinone.

Experiments under *oxygen* revealed autocatalytic periods extending through 15 to 20% of the reaction. When quinone is added to make $R_0 = T_0$, the reactions are first-order from the start. Guggenheim curves are given for several values of *p*H in Figs. 4b, 4c and 4d. In the latter part of these reactions, a departure from first-order

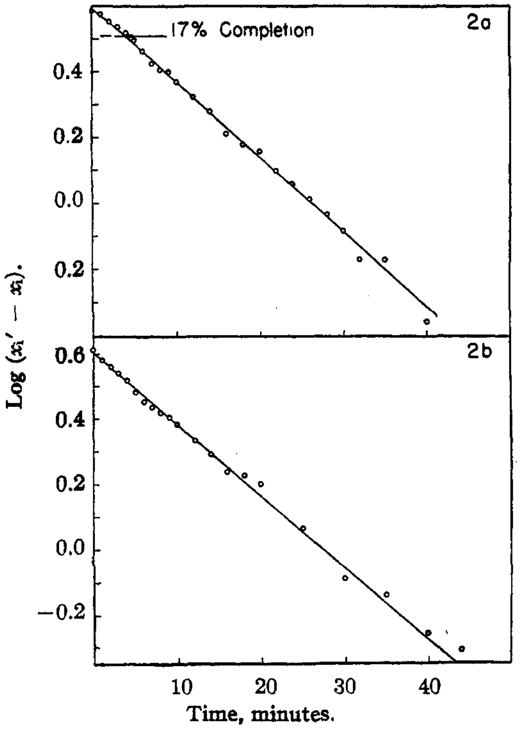

Fig. 2.—Guggenheim curves for pseudo-cumohydroquinone (3.33×10^{-3} *M*) in air; *p*H 8.33 ± 0.02; ψ-cumoquinone added: (a) 0.00; (b) 3.33×10^{-3} *M*. → indicates point at which T/R = 0.2.

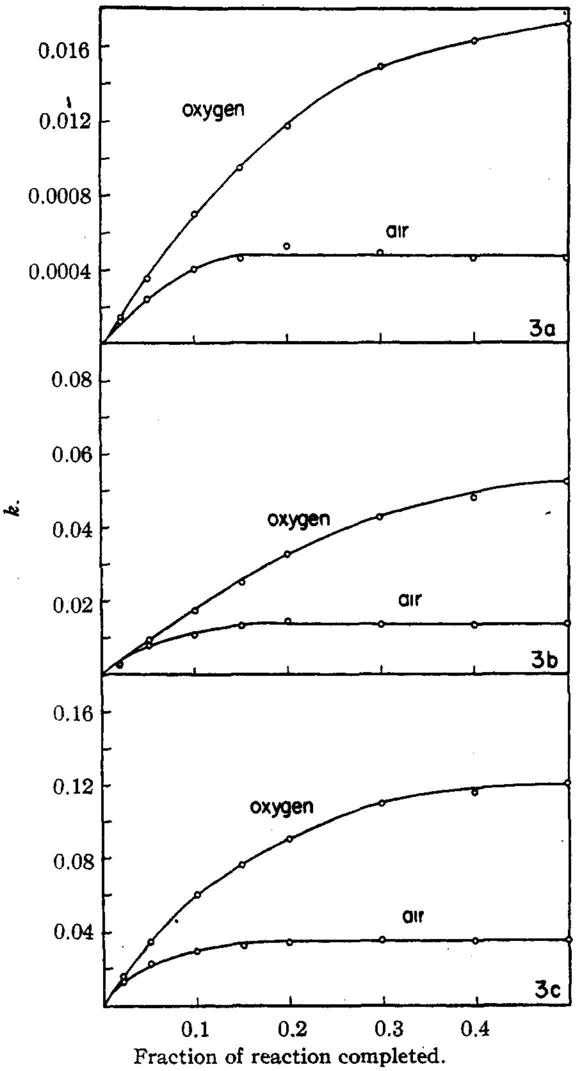

Fig. 3.—*k* values against fraction of reaction completed for ψ-cumohydroquinone: (a) *p*H 7.40; (b) *p*H 7.64; (c) *p*H 7.84.

takes place, which increases with increase in *p*H (Figs. 4c and 4d).

The departure from first-order in the latter portion of the reaction is accompanied by an increase in the total oxygen absorbed beyond the theoretical uptake. It is probably caused by the removal of T by reaction with oxygen, hydrogen peroxide, or solvent, followed by autoxidation of the products of these reactions.[1] The removal of T decreases the rate of autoxidation, and autoxidation of the product increases the total uptake. Reactions of R or S with hydrogen peroxide may also be involved, although these reactions, as such, would lower the oxygen uptake.

Experiments on toluhydroquinone and hydroquinone confirmed the data of James, Snell and Weissberger,[2] in that they did not reveal any trace of autocatalysis. The reactions follow a first-order law for about 60% of the reaction for toluhydroquinone or 45% for hydroquinones as shown by Fig. 5. After that, the rate drops off. The total uptake of oxygen is greater than that calculated from (1). Both deviations are greater than with 2,5-xylohydroquinone.

Dimer Formation of Semiquinones and Irreversible Destruction of Quinones.—Equimolar solutions of hydroquinone and quinone, and of toluhydroquinone and toluquinone when mixed become instantaneously amber; 2,5-xylohydroquinone and 2,5-xyloquinone form an amber color somewhat slower than the monomethyl compounds, and pseudo-cumohydroquinone and pseudo-cumoquinone form an amber color still rapidly but much slower than the dimethyl compounds. Durohydroquinone and duroquinone show no color change upon mixing. When solutions of varying molar ratio of the respective quinones and hydroquinones are mixed, and the total concentration is kept constant, the most intense color is obtained when the ratio is unity. If the volume of the solutions is increased, the intensity of the color decreases more rapidly than would follow from Beer's law, indicating that the color arises from a dimer rather than from a monomeric radical.[9]

According to Michaelis,[10] durohydroquinone and duroquinone do not form a dimer but readily

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[9] Michaelis and Schubert, *Chem. Rev.*, **22**, 437 (1938).

[10] Michaelis, Schubert, Raber, Kuck and Granick, THIS JOURNAL, **60**, 1678 (1938).

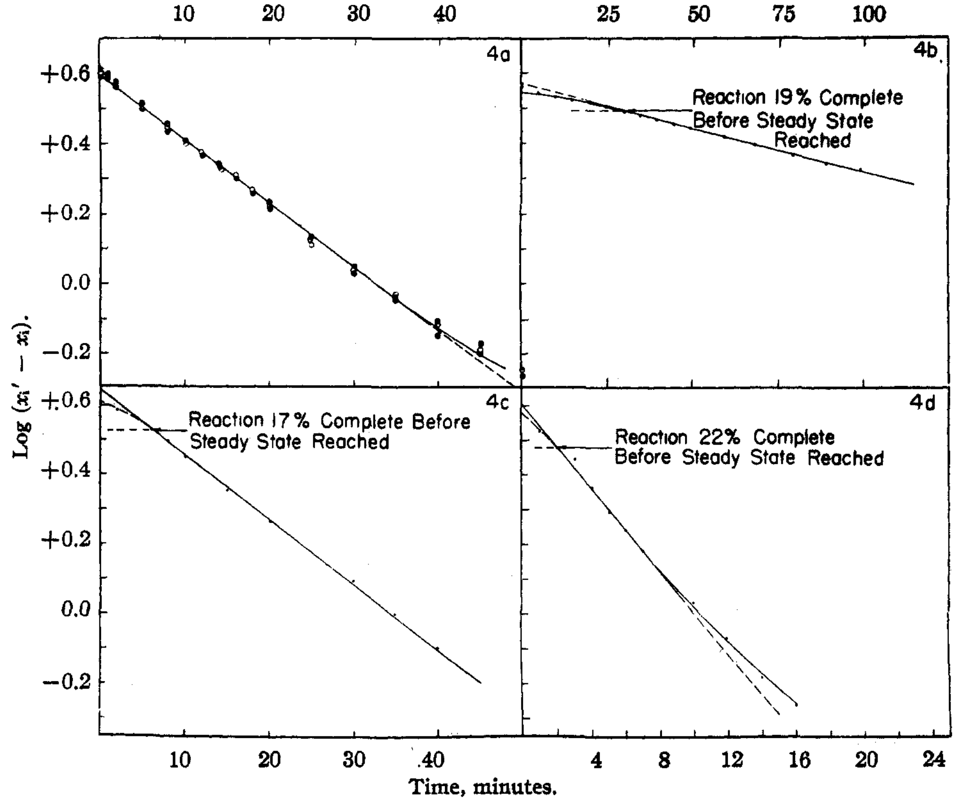

Fig. 4.—Guggenheim curves for 2,5-dimethylhydroquinone (3.33×10^{-3} *M*): (a) in air; *p*H 8.90 ± 0.02: -O-O-, 2,5-methylquinone = 0.00; -●-●-, 3,5′-dimethylquinone = 0.416×10^{-3} *M*; -⊗-⊗-, 2,5-dimethylquinone = 0.832×10^{-3} *M*. In oxygen: (b) *p*H 7.95; (c) *p*H 8.39; (d) *p*H 8.64.

form the semiquinone. The available evidence indicates that dimer formation is hindered by methylation of the aromatic nucleus and increases in the series, durohydroquinone, pseudo-cumohydroquinone, xylohydroquinones, toluhydroquinone and hydroquinone.

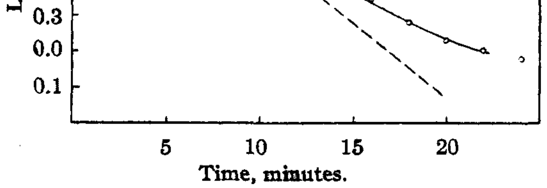

Fig. 5.—Guggenheim curve for hydroquinone at *p*H 8.41.

Some spectrophotometric experiments near the neutral point showed that the instantaneous darkening of the solutions of hydroquinone–quinone and toluhydroquinone–toluquinone is followed by a gradual increase in density. A spectrophotometric investigation of these systems therefore requires very rapid measurements or a kinetic study which permits extrapolation of the results to the time of mixing.[11]

The gradual change appears to be connected with the reactivity of quinone. This substance is unstable in hydroxyl-containing solvents in the dark,[12] and even more so in the light. The instability is particularly great in alkaline solution. Quinone reacts rapidly with hydrogen peroxide to form hydroxyquinone.[13]

Substitution with methyl in the ring has a great stabilizing effect on quinone. Duroquinone is stable even in strongly alkaline solutions,[2,9] and durohydroquinone was therefore chosen for the initial investigations of the autoxidation of hydroquinones.[2] The catalytic activity of pseudo-cumoquinone is not seriously impaired by standing at *p*H 7 to 8.5 for the length of time required for the autoxidation of the hydroquinone. Solutions of pseudo-cumohydroquinone which have undergone autoxidation below *p*H 8.5 remain light yellow for some time after

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[11] A flow machine of the type described by Chance [*J. Franklin Inst.*, **229**, 455 (1940)] which should be suitable for these measurements is under construction in these Laboratories.

[12] Braude, *J. Chem. Soc.*, 490 (1945).

[13] Reinders and Dingemans, *Rec. trav. chim.*, **53**, 209 (1934).

completion of the experiment. Most of the hydrogen peroxide formed is present at the end of the autoxidation, and the total oxygen uptake is nearly the theoretical.[3] Thus, pseudo-cumoquinone is relatively stable. The stability of **dimethylquinone, monomethylquinone** and **quinone** decreases. With decreasing number of methyl groups, the solutions discolor increasingly during the autoxidation, less hydrogen peroxide is present at the end of the reactions, and the observed uptake of oxygen increases beyond the theoretical value.

Discussion

If steric hindrance retards or prevents dimer formation, it can be presumed that it also retards or prevents formation of the complex, T·S. The autoxidation of durohydroquinone[2] proceeds by the mechanism of Class I-A-3 of Part XVIII.[1] This mechanism is the limiting case of Class I-E for a stable quinone with no tendency to form a dimer or a complex with the semiquinone.

Pseudo-cumoquinone is fairly stable under the conditions of the experiment, but forms a quinhydrone with pseudo-cumohydroquinone. In the beginning of the autocatalytic period, the rate of autoxidation of pseudo-cumohydroquinone is independent of the oxygen concentration. The rate in the region of saturation of the quinone catalysis is somewhat less than first-order with respect to oxygen. The end of the autocatalytic period is determined by the ratio of (T)/(R). The length of the autocatalytic period in air is about one-third as long as in oxygen. These properties place pseudo-cumohydroquinone in Class I-E[1] with k_7 (T) $\sim k_2(O_2)$. The Guggenheim curves of Fig. 1 are of the type of the log $(a - x)$ curves of Fig. 2 of the preceding paper.[1] Equations (18) and (24a) of the preceding paper explain why the steady-state rate and the length of the autocatalytic period are not strictly proportional to the oxygen pressure.

Homologs of hydroquinone which are less protected by methyl groups than pseudo-cumohydroquinone have a greater tendency to form quinhydrone, and the respective quinones are less stable than pseudo-cumoquinone. An irreversible loss of T takes place during the autoxidation of xylohydroquinone, toluhydroquinone and hydroquinone; and the reactions proceed according to Class I-E of the preceding paper[1] [$k_7(T) \gtrsim k_2(O_2)$].

2,5-Dimethylhydroquinone shows in oxygen an unmistakable autocatalytic period extending over approximately 20% of the total reaction. In air, no autocatalysis could be observed. This behavior can be expected, in view of the greater reactivity of the xyloquinone as compared with the trimethylquinone. It parallels the dependency of the autocatalytic period on the oxygen pressure, which was discussed above. Xylohydroquinone is in its behavior intermediate between the trimethyl compound and toluhydroquinone [$k_7(T) \gtrsim k_7(O_2)$].

Toluhydroquinone and **hydroquinone** do not permit the direct observation of autocatalysis under any conditions so far investigated [$k_7(T) > k_2(O_2)$]. This is exactly what should be expected in view of the trend of the length of the autocatalytic period with diminishing methylation of the ring and is to be expected from the first-order dependency with respect to oxygen. This extrapolation is supported by an estimate of the extent of the autocatalytic periods of the various hydroquinones on the basis of the steady-state autoxidation rates. It has been shown that the steady-state rate is proportional to the semiquinone concentration. Inasmuch as (S) is proportional to the product, (T) (R^-),[1,2,3,4b] and (S) at the end of the autocatalytic period is proportional to the length of the latter, k in the steady state is proportional to the length of the autocatalytic period, provided (R^-) is the same for all of the hydroquinones, *i.e.*, the *pK*'s are identical. The *pK*'s for the several hydroquinones have not been measured. The acidity of phenol decreases somewhat with increasing methylation, but the change from phenol to pseudo-cumenol is less than one order of magnitude in *pK*.[14]

The *pK*'s of hydroquinone and the various methylhydroquinones are probably also of the same order of magnitude. From the values of James, Snell and Weissberger[3] and the extent of the autocatalytic period for pseudo-cumohydroquinone (50% completion of the reaction), we calculate the autocatalytic periods in Table III.

TABLE III

EXTENT OF THE AUTOCATALYTIC PERIOD UNDER OXYGEN

Compound	Relative rates[a]	Extent of autocatalytic period (calcd.) %
Hydroquinone	1.00	1.6
Toluhydroquinone	3.9	6
2,3-Xylohydroquinone	10.5	16
2,6-Xylohydroquinone	18.2	29
2,5-Xylohydroquinone	17.0	27
Ψ-Cumohydroquinone	31.0	50

[a] Data of James, Snell and Weissberger.[3]

The assumption that (R^-) is the same for all of the hydroquinones will tend to make the values somewhat low.

However, the estimated value for the length of the autocatalytic period of 2,5-dimethylhydroquinone is about 40% higher than the experimental value. This indicates that factors are of importance, which are neglected in the assumption that (T) at the end of the autocatalytic period is proportional to k. The existence of such factors is obvious if it is realized that the assumed proportionality presupposes that the energies of activation and the entropies of dimer formation,

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[14] (a) Bader, *Z. physik. Chem.*, **6**, 290 (1890); (b) Hantzsch and Farmer, *Ber.*, **32**, 3066, 3089, 3101 (1899); (c) Kuhn and Wasserman, *Helv. Chim. Acta*, **11**, 33 (1928); (d) Swarzenback and Egli, *ibid.*, **17** 1176 (1934); (e) Summerbell, *J. Chem. Soc.*, 996 (1934).

semiquinone formation and semiquinone autoxidation are identical for hydroquinone and for the various methyl hydroquinones. In analogy with the findings for 2,5-dimethylhydroquinone, the extrapolated values for the length of the autocatalytic period for toluhydroquinone and for hydroquinone may therefore be too high.

Summary

1. The autoxidation of pseudo-cumohydroquinone, 2,5-dimethylhydroquinone, toluhydroquinone and hydroquinone is investigated further.
2. The saturation of the quinone catalysis in the autoxidation of pseudo-cumohydroquinone is explained.
3. The suggestion is corroborated that the apparent indifference of the autoxidation of hydroquinone and its lower homologs to the presence of the respective quinones is caused by the fact that the quinone catalysis reaches saturation at rather low concentrations of the quinones.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Direct and Sensitized Photochemically Induced Reaction of Chlorine and Oxalic Acid. Comparison with the Chemically Induced Reaction

BY ILSE L. HOCHHAUSER AND HENRY TAUBE

Previous studies of the reaction

$$H_2C_2O_4 + Cl_2 \longrightarrow 2H^+ + 2Cl^- + 2CO_2$$

have shown that the spontaneous reaction[1] proceeds slowly in 2*M* hydrochloric acid and that ferrous ion[2] acts as an inducing agent by the intiation of a chain reaction. While the extensive data on the ferrous ion induced reaction have been completely interpreted by a mechanism involving atomic chlorine and an oxalate free radical, it has appeared to us desirable to seek a more definite conclusion as to the identity of the active intermediates. In the work reported here, this has been attempted by studying the kinetics of the reaction above induced by light, and comparing for the chemically and photo induced reactions such properties of the reaction paths as specific rate, energy of activation and the effect of inhibitors. It has thus been established with reasonable certainty that the same intermediates operate in both systems; from a consideration of the methods of production and of the properties of the intermediaries, it likewise seems certain that they are, indeed, mainly atomic chlorine[3] and the oxalate free radical.[4]

A principal goal in these investigations is to establish absolute values for the various specific reaction rate ratios of the intermediate substances (*e. g.*, $k_2/k_5^{1/2}$, $k_6/k_5^{1/2}$, see Discussion) not only because the values themselves possess interest, but also because they may be regarded as properties of the intermediates useful in identifying them in other systems. It will be evident that to calculate the absolute values of such ratios from the experimental data, the actual rate of intermediate production must be known. This rate may be considered as the product of two factors: the rate at which the inducing agent, light quanta or chemical substance, is introduced, and the efficiency of the primary intermediate production process. The first factor can easily be measured, the second can in special cases be inferred. If, for example, the effects produced by widely differing means for intermediate production, such as light and a reducing agent, agree quantitatively (*i. e.*, one quantum being equivalent in its effect to two ferrous ions) it would seem fairly safe to conclude that the efficiency is unity for each type of process. While the possibility of accidental agreement on a value of the efficiency less than unity exists, it seems remote, and can be eliminated almost completely if a third method of intermediate production gives quantitative agreement. These arguments have been applied in reaching some tentative conclusions about the efficiency of the three primary processes which have been compared.

Experimental

Apparatus.—As light source for most experiments, a C-H-1 Mazda a. c. mercury vapor lamp was used; for a few runs, a Hanovia 550W d. c. lamp was employed. The energy input was checked with a voltmeter and, in some series, the constancy of radiant output was checked by means of photronic cells. The variation in voltage never exceeded 3% during a continuous series of experiments. A lens and a round-bottom flask served to concentrate the beam on the reaction cell. Directly in front of the cell were placed light filters and a shutter. To obtain substantially monochromatic light, filters were used: 3650 Å. Corning Glass filter no. 584; 4047 Å., Wratten filter no. 36; 4360 Å., Corning Glass filters no. 585 and no. 038. The reaction cell was cylindrical in shape and was painted black, except for the front and back windows, which were made of

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(1) Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 518 (1932).

(2) Taube, THIS JOURNAL, **68**, 611 (1946).

(3) *Cf.* ref. 2, footnote 2.

(4) The oxalate free radical will be represented as $C_2O_4^-$ rather than HC_2O_4. The assumption that HC_2O_4 is a strong acid seems reasonable from a consideration of its electronic configuration.