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A Kinetic Study of the Oxidation of Mercaptans Catalyzed by Hydroquinone and its Homologs

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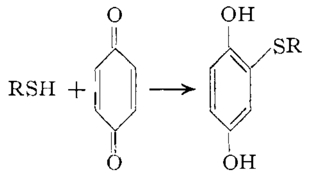
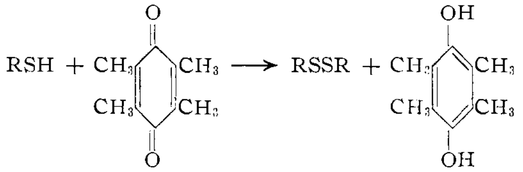
The kinetics of the hydroquinone-catalyzed oxidation of hexyl mercaptan in the presence of sodium hydroxide was studied at constant oxygen pressure. Maximum rates of oxygen absorption depend on the first powers of catalyst and base concentrations. At the steady state, the reaction is of pseudo-zero order. Substitution of methyl groups in the ring of hydroquinone decreases the activity of the catalyst. The reduction–oxidation reaction is preceded by addition of mercapto groups to the catalyst ring. A steady-state mechanism has been worked out.

The oxidation of mercaptans by air is strongly catalyzed by small amounts of hydroquinone in alkaline medium. Although this reaction has been widely used in the petroleum industry to remove mercaptans from petroleum fractions,[1] the reaction mechanism has not been studied. Most of the work done in the past has been concerned with (a) the products of the reaction of mercaptans with quinones, or (b) the effect of small amounts of mercaptan upon the rate of oxidation of hydroquinone.

When stoichiometric amounts of mercaptans and quinones react in the absence of oxygen, mercaptohydroquinones[2-4] are formed by 1,4-addition



In the presence of oxygen, di-, tri- and tetramercaptoquinones are formed through alternating successive oxidations and additions.[5-7] However, direct oxidation of mercaptan to disulfide occurs when a mercaptan is treated with duroquinone[8]



Here addition is impossible.

Weissberger and co-workers[5] found that small amounts of mercaptan will retard the rate of hydroquinone oxidation. They suggested that the mercaptan removed the quinone, the autoxidation catalyst, by the addition reaction. In later work,[9] the possibility of inhibition through reduction of the quinone was also considered and kinetic expressions were derived. As long as the quinone exceeds the mercaptan in concentration, inhibition seems to occur through addition, unless addition is impossible, as in duroquinone and hindered quinones. When the mercaptan concentration is in excess, reaction may proceed first through addition until the ring is completely substituted and then through direct reduction. In such a system, the mercaptans are continuously oxidized to disulfides and the hydroquinone acts as catalyst. The catalytic activity of various hydroquinones has been studied by Bond.[10]

To understand better the steps involved in the hydroquinone-catalyzed oxidation of mercaptans, the rates of oxygen absorption at various concentrations of catalyst and sodium hydroxide were studied.

Experimental

Four different catalysts were used: hydroquinone, m.p. 173–174°; toluhydroquinone, m.p. 128–129°; 2,5-dimethyl-*p*-quinone, m.p. 124–125°; and duroquinone, m.p. 112–112.5°. Duroquinone was prepared from durene by the method of Smith[11]; the other three were Eastman Kodak Company products recrystallized from ethyl alcohol. The large amount of mercaptan in the solution converted the quinones to the corresponding hydroquinones before the start of the reaction. *n*-Hexanethiol from Matheson Chemical Company was distilled under reduced pressure, and a middle fraction boiling within 0.5° was collected and stored under nitrogen. Reagent-grade acetone, methanol and sodium hydroxide were used without further purification. Solutions of hexanethiol in acetone–methanol or methanol and catalysts in methanol were prepared with minimum exposure to air and were not stored longer than 3 days.

Rates of oxygen absorption were measured at atmospheric pressure in a constant pressure apparatus.[12] The 50-ml. round-bottomed reaction flask was thoroughly flushed with pure oxygen, and 15 ml. of the mercaptan solution and 1.0 ml. of the sodium hydroxide solution were pipetted into it. The flask was stoppered, immersed in a bath held at 30.20 ± 0.02°, and attached to the arm of a wrist-action shaker. After thermal equilibration, 1.0 ml. of the catalyst solution was added. The flask was immediately connected to the oxygen buret, the excess pressure was released, and the shaker was started to begin reaction. The volume of oxygen absorbed was recorded at appropriate intervals. Although the shaker could be operated up to 250 complete strokes per minute, shaking speeds above 200 did not alter the oxidation rate.

Results

In a typical run, the rate of absorption was at first slow, gradually rose to a maximum, then decreased almost to zero toward the end of the reaction. Changes in color during the reaction accom-

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(1) E. F. Pevere, U. S. 2,015,038 (Sept. 17, 1935).

(2) J. Traeger and A. Eggert, *J. prakt. Chem.*, [2] **53**, 482 (1896).

(3) T. Posner, *Ann.*, **336**, 85 (1904).

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(5) T. H. James and A. Weissberger, THIS JOURNAL, **61**, 442 (1939).

(6) O. Dimroth, L. Kraft and K. Aichinger, *Ann.*, **545**, 124 (1940).

(7) M. Schubert, THIS JOURNAL, **69**, 712 (1947).

(8) J. M. Snell and A. Weissberger, *ibid.*, **61**, 452 (1939).

(9) J. E. LuValle and A. Weissberger, *ibid.*, **69**, 1821 (1947).

(10) D. C. Bond, *Oil Gas J.*, **44**, No. 31, 83 (1945).

(11) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, New York, 1943, p. 254.

(12) L. Bateman, G. Gee, A. L. Morris and W. F. Watson, *Disc. Faraday Soc.*, No. 10, 256 (1951).

panied the variations in rate; the initial colorless mixture changed to deep red at the maximum, then faded again as the rate slowed down.

The effect of sodium hydroxide concentration is shown in Fig. 1. In the absence of caustic, oxygen absorption due to mercaptan oxidation did not occur at any catalyst concentration. As the concentration of caustic was increased, the duration of the initial slow rate shortened and the maxmuim rate increased.

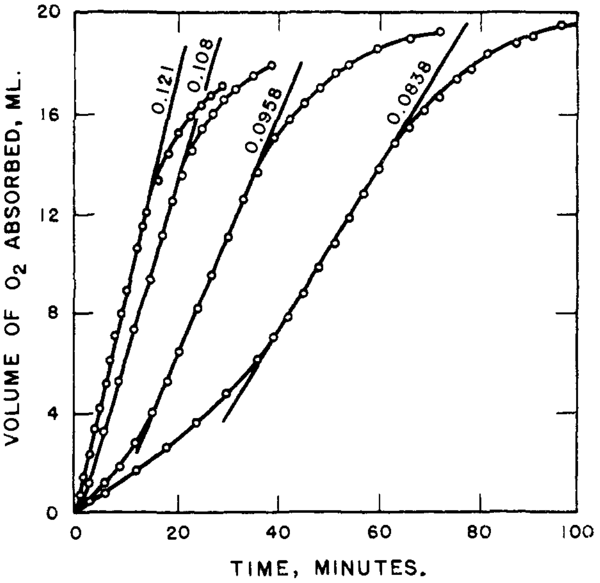

Fig. 1.—Oxygen absorption with 2.50 × 10^{-4} M hydroquinone. Curves identified by molarity of NaOH.

The effect of hydroquinone concentration is shown in Fig. 2. At the concentrations of sodium hydroxide used, the rate of uncatalyzed oxidation of the mercaptan was negligible. As the catalyst concentration was increased, the induction period again shortened and the maximum rate increased.

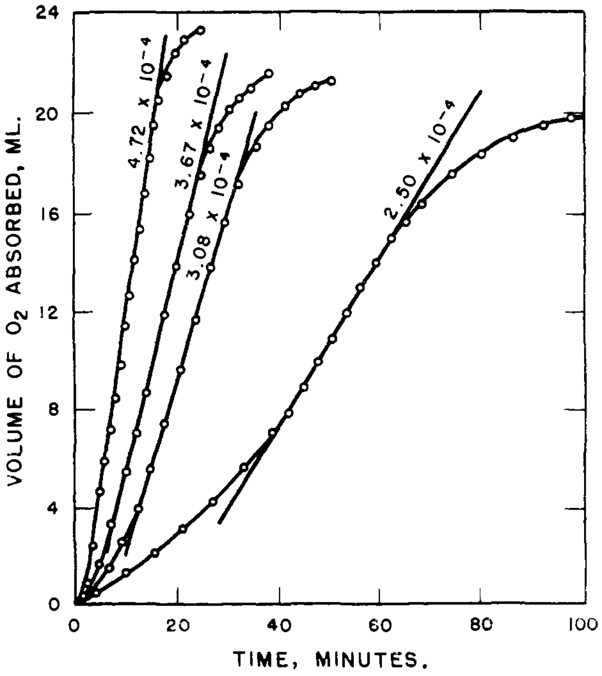

Fig. 2.—Oxygen absorption with 0.0838 M NaOH. Curves identified by molarity of hydroquinone.

The maximum rates of oxygen absorption for several series of runs at various caustic and hydroquinone concentrations are given in Table I. Figure 3 shows that these maximum rates depend on the first power of either concentration when the other is kept constant. This relationship can be expressed (a) for constant catalyst concentration

$$\text{Rate} = k_a\,[\text{QH}_2]_c\,[\text{NaOH}] - K' \qquad (1)$$

Table I

Maximum Rates of Oxidation of Hexanethiol

Catalyst, hydroquinone; solvent, 29.5% acetone, 64.5% methanol, 6% water; RSH concn. 0.212 M.

Catalyst, moles/l., × 10^4	NaOH, moles/l., × 10^2	Max. rate, moles/sec. × 10^7	Catalyst, moles/l., × 10^4	NaOH, moles/l., × 10^2	Max. rate, moles/sec. × 10^7
4.72	8.38	9.44	3.08	12.10	9.03
3.67	6.02	2.65	2.50	8.38	2.27
3.67	8.38	6.21	2.50	9.58	3.45
3.67	10.80	9.80	2.50	10.80	4.82
3.08	7.53	2.76	2.50	12.10	6.21
3.08	8.38	4.02	1.57	10.80	0.89
3.08	10.80	7.17			

(b) for constant caustic concentration

$$\text{Rate} = k_a[\text{NaOH}]_c[\text{QH}_2] - K' \qquad (2)$$

where k_a is apparent rate constant, and the subscript, c, shows that the concentration was held constant. The apparent rate constants were determined by the method of averages and are given in Table II. For any given run where neither hydroquinone nor caustic is consumed, the maximum rate is given by

$$\text{Rate} = k_a[\text{QH}_2]_t[\text{NaOH}]_t \qquad (3)$$

Table II

Apparent Rate Constants

Hydroquinone, moles/l., × 10^4	NaOH, moles/l., × 10^2	K_a × 10^2, l.,^{2}/mole sec.
3.67	[a]	4.1
3.08	[a]	4.5
2.50	[a]	4.3
[a]	12.10	4.0
[a]	10.80	4.0
[a]	8.38	4.0

[a] Varied.

The intercepts in Fig. 3 show that, for catalytic oxidation to occur, the concentrations of catalyst and caustic used must be larger than the limiting values $[\text{QH}_2]_0$ and $[\text{NaOH}]_0$. This requirement results from the acidic nature of mercaptans and hydroquinones. For a series of runs at constant initial mercaptan concentration, the limiting values, $[\text{QH}_2]_0$ and $[\text{NaOH}]_0$, should be inversely proportional to $[\text{NaOH}]_c$ and $[\text{QH}_2]_c$, respectively, according to equations 1 and 2. This relationship for $[\text{NaOH}]_0$ is shown in Fig. 4.

Rates obtained with all four hydroquinones are presented in Table III. Figure 5 is a plot of the data. The straight lines again show that the maximum rate depends upon the first power of caustic concentration. Values for k_a given in Table IV

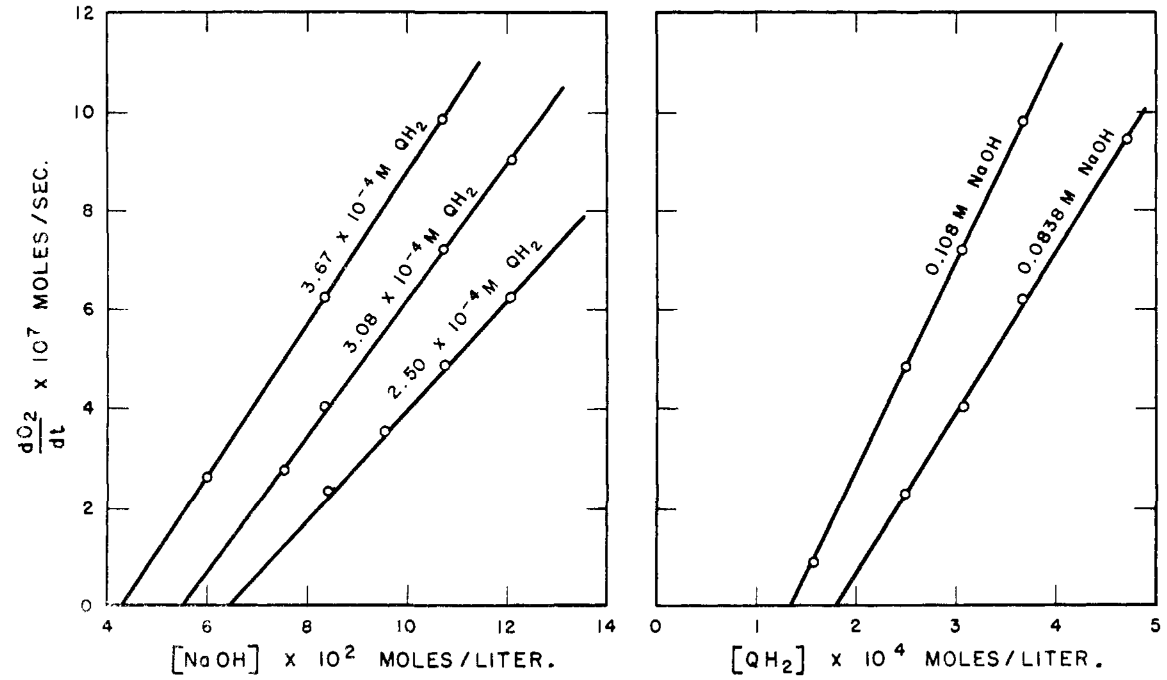

Fig. 3.—Dependence of maximum rates upon caustic and hydroquinone concentrations.

show that methyl substitution decreases catalytic activity.

TABLE III

MAXIMUM RATES OF OXIDATION OF HEXANETHIOL

Solvent 94% aq. MeOH; RSH concn. 0.212 *M*

NaOH, moles/l., × 10^2	Max. rate × 10^7, moles/sec.	NaOH, moles/l., × 10^2	Max. rate × 10^7, moles/sec.
Hydroquinone, 0.242 × 10^3 moles/l.		*p*-Xyloquinone, 1.67 × 10^3 moles/l.	
8.82	1.52	2.88	2.89
10.95	3.73	5.21	5.57
13.29	6.57	6.51	6.89
15.95	9.25	Duroquinone, 1.53 × 10^3 moles/l.	
Toluhydroquinone, 1.14 × 10^3 moles/l.		5.50	1.00
		8.46	1.51
4.12	4.34	13.60	2.41
5.54	7.94		
6.99	11.38		
8.47	15.20		

TABLE IV

APPARENT RATE CONSTANTS

Catalyst	k_a × 10^2	Relative activity	Relative rate of oxidation[13]
Hydroquinone	4.5	1.00	1.00
Tolhydroquinone	2.2	0.48	3.9
p-Xyloquinone	0.65	0.15	17.0
Duroquinone	0.11	0.025	1.00

In the absence of mercaptans, oxygen and caustic degrade the catalysts to products that show no activity. To suppress such side reactions, large amounts of mercaptan were needed. Nevertheless near the end of the reaction, the degradation reactions predominated and the catalyst was consumed; the color faded and the rate decreased almost to zero. Degradation was hastened by either raising the caustic concentration or lowering the catalyst concentration. This complication prevented a study of the effect on the reaction rate of large variations in initial mercaptan concentration. However, with duroquinone as catalyst, 0.212, 0.106 and 0.053 *M* hexanethiol gave the same maximum rate.

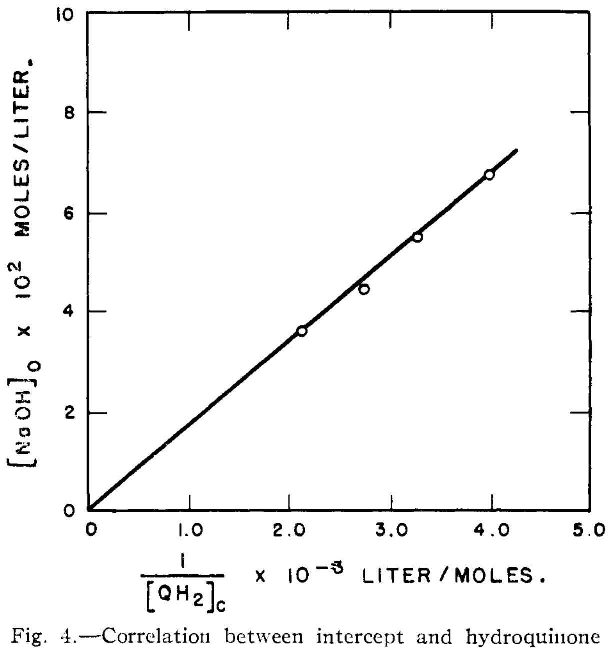

Fig. 4.—Correlation between intercept and hydroquinone concentration.

Discussion

A possible mechanism that agrees with the experimental data is

$$QH_2 + NaOH \underset{}{\overset{K_{eq.}}{\rightleftarrows}} QH^- + H_2O$$

$$QH^- + O_2 \xrightarrow{k_1} QH + O_2^-$$

$$QH + RSH \xrightarrow{k_2} QH_2 + RS\cdot$$
$$2RS\cdot \longrightarrow RSSR$$

where QH_2, QH^- and QH are, respectively, the reduced state, the monovalent ion and the semiquinone of the catalyst. Steady-state treatment gives the rate expression

$$-\frac{dO_2}{dt} = kK_{eq.}\frac{[QH_2][NaOH][O_2]}{[H_2O]} \qquad (4)$$

which is independent of the mercaptan concentration. At constant oxygen pressures, this expression leads to a pseudo-zero-order reaction, because neither quinone nor sodium hydroxide is consumed during the reaction and because the amount of water produced is negligible compared to the amount initially present. Furthermore, for any given run, $[QH_2]$ and [NaOH] of equation 4 are directly proportional to the total concentrations of catalysts $[QH_2]_t$ and caustic $[NaOH]_t$. The equation can then be rewritten

$$-\frac{dO_2}{dt} = k_a[QH_2]_t[NaOH]_t \qquad (5)$$

which is similar to the experimentally derived equation 3.

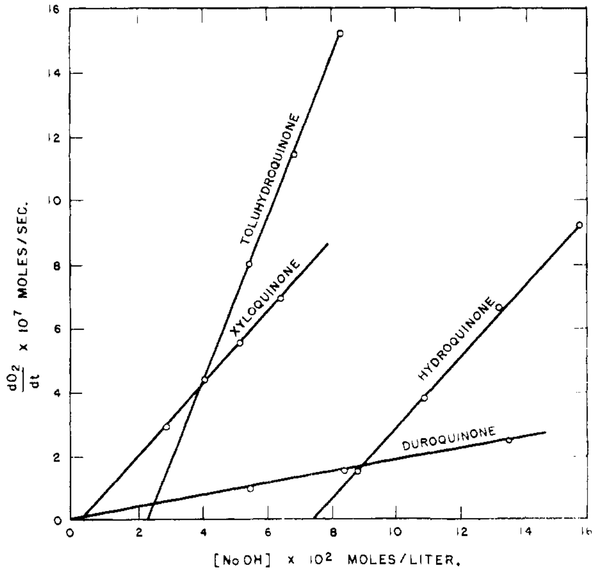

Fig. 5.—Dependence of maximum rate on [NaOH] for: hydroquinone, 0.24 × 10^{-3} *M;* toluhydroquinone, 1.14 × 10^{-3} *M;* xyloquinone, 1.67 × 10^{-3} *M;* duroquinone 1.53 × 10^{-3} *M.*

The oxidation of hydroquinone and its homologs has been studied by Weissburger and co-workers[13] in buffered aqueous solutions at about *p*H 8; the relative rates are compared in Table IV with the order of catalytic activity found in the present work. The orders are entirely different. This apparent contradiction could be due to the different conditions of the two sets of experiments. In the absence of mercaptans, the rates measured by Weissberger and co-workers were those of oxidation of the divalent hydroquinone ion catalyzed by the quinone. In the present work, in the presence of mercaptans, the monovalent ion is the active species. Substituents may not have the same effect upon the two active forms. On the other hand, if the quinone first undergoes substitution before it acts as catalyst, the order would then represent the activities of the mercapto derivatives rather than the quinones.

Confirmation for this explanation was obtained by measuring the total amounts of oxygen absorbed in a two-phase oxidation. Hydroquinone in an aqueous solution containing various amounts of caustic and methanol was oxidized in the presence of hexanethiol in isoöctane. The results, given in Table V, show that the volumes of oxygen absorbed for different runs are increments of 3.2 ml., the volume of oxygen necessary to oxidize all the hydroquinone present. Thus, by varying the methanol or caustic concentration, the reaction can be stopped after mono-, di-, tri- or tetra-substitution. When the conditions are favorable, oxidation–reduction takes place after tetra-substitution.

TABLE V

EFFECT OF CAUSTIC AND METHANOL CONCENTRATIONS UPON THE REACTION OF QUINONE WITH HEXANETHIOL

Hydroquinone, 1.325 × 10^4; hexanethiol, 3.59 × 10^3 moles

NaOH, moles/l. × 10^2	Methanol, %	Total ml. O_2 absorbed at 25°	Type of reaction
2.38	None	6.2	Mono-substitution
0.264	72	9.1	Di-substitution
0.411	56	12.3	Tri-substitution
0.528	72	16.0	Tetra-substitution
2.38	72	28.0	Tetra-substitution followed by catalyzed oxidation

The substitution of alkylmercapto groups in the ring of a hydroquinone will increase its acidity[14] and, hence, the equilibrium constant, K_{eq}, in equation 4. Therefore, the activity of a hydroquinone may be assumed to increase with the number of alkylmercapto groups in the ring. When $K_{eq.}$ is small, as in durohydroquinone, $[QH_2]$ in equation 4 will approximately equal $[QH_2]_t$ and the plots of rate *versus* either $[QH_2]_t$ or $[NaOH]_t$ will pass through the origin, as shown in Fig. 5.

The proposed mechanism thus accounts for (a) first-order dependence of the reaction rate upon the caustic and catalyst concentrations and (b) reduction of activity of hydroquinone by methyl substitution.

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[13] T. H. James, J. M. Snell and A. Weissberger, THIS JOURNAL, **60**, 2084 (1938).

[14] E. A. Fehnel and M. Carmack, *ibid.*, **71**, 2889 (1949).