Oxidation Processes. XIII.[1] The Inhibitory Action of Sulfite and other Compounds in the Autoxidation of Hydroquinone and its Homologs

By T. H. James and A. Weissberger

The preservative action of sulfite in a hydroquinone developer was first observed by Berkeley.[2] It was attributed by Luther[3] to the oxidation of the sulfite, which prevented oxidation of the organic matter by removing oxygen from the solution. This explanation, however, was not supported by further experiments, which showed that the rate of uptake of oxygen by a solution containing both hydroquinone and sulfite is much lower than that of sulfite alone.[4,5] Hydroquinone and sulfite mutually inhibit their autoxidation.[5,6]

The inhibitory action of hydroquinone and of other substances on the autoxidation of sulfite is due to their function as chain breakers.[7,8] The action of sulfite on hydroquinone, on the other hand, is not yet understood. Pinnow's[9] own assumption that the sulfite removes traces of copper which catalyze the autoxidation of the hydroquinone did not satisfy him, nor is it in agreement with the findings of the present authors. Reinders and Dingemans considered the possibility that sulfite acts as a chain breaker in the autoxidation of hydroquinone, but rejected the chain mechanism as improbable for the latter reaction.

In previous papers,[1,10] it has been shown that the autoxidation of durohydroquinone and of ψ-cumohydroquinone is catalyzed by quinones, and it has been suggested that small amounts of quinones are highly active catalysts also for the autoxidation of the xylohydroquinones, toluhydroquinone, and hydroquinone itself. On this basis, it appears possible that sulfite and other inhibitors retard the autoxidation of hydroquinone and its homologs because they remove the catalyzing quinone.

(1) Part XII, James, Snell and Weissberger, This Journal, 60, 2084 (1938).

(2) Berkeley, Photographic News, 26, 41 (1882).

(3) Luther, "Die chem. Vorgänge in den Photographie," W. Knapp, Halle, 1899.

(4) Schilow and Fedotoff, Z. Elektrochem., 18, 930 (1912).

(5) Reinders and Dingemans, Rec. trav. chim., 53, 231 (1934).

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

(7) Bäckström, This Journal, 49, 1460 (1927); H. N. Alyea and H. L. J. Bäckström, ibid., 51, 90 (1929).

(8) Jeu and Alyea, ibid., 55, 575 (1933).

(9) Pinnow, Z. wiss. Phot., 11, 289 (1913); 27, 344 (1930).

(10) Part XI, James and Weissberger, This Journal, 60, 98 (1938).

Experimental

Materials

Sodium Hydroquinone Monosulfonate.—A mixture of 390 ml. of concentrated sulfuric acid and 46 ml. of water was added to 550 g. of hydroquinone contained in a 2-liter distilling flask. The mixture was heated on a steam-bath with mechanical stirring until all the hydroquinone was dissolved (about three hours) and then kept under suction at 100° for ten hours. The reaction mixture was poured into 3900 ml. of cold saturated sodium sulfate solution, the filtered precipitate washed with 1 liter of ice-cold saturated sodium sulfate solution, and dried. It was pulverized and extracted seven times with boiling methanol, using 3 liters at a time; each extract was cooled, filtered, and the filtrate re-used: yield, 395 g. (37.3%). The material used in the autoxidation experiments was recrystallized from pure ethanol.

Potassium Hydroquinone Disulfonate.—One hundred and ten grams of hydroquinone was heated with 415 g. of 95% sulfuric acid for eight hours at 95° in the steam-bath. The mixture was poured into a cold solution of 260 g. of potassium chloride in 800 ml. of water. After cooling, the precipitated sludge was filtered off and recrystallized twice from hot water: yield, 88 g. (21%).

The other materials were of the qualities reported in the preceding papers of this series.

The apparatus and procedure were those described in preceding papers of the series.

Hydroquinone

Reaction Products.—When hydroquinone undergoes autoxidation in the presence of excess sodium sulfite, according to Pinnow,[9] Lehmann and Tausch,[11] in the early stages of the reaction, approximately two moles of sulfite are used up for every mole of hydroquinone oxidized, one mole of sulfate and one mole of free alkali are formed, and sodium hydroquinone monosulfonate can be isolated from the solution (see (1)).
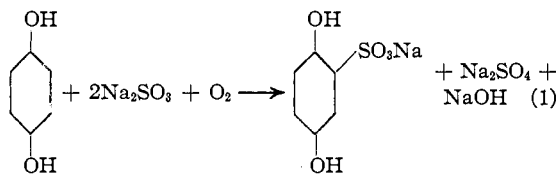

It has been suggested that the hydroquinone monosulfonate is formed from quinone and sulfite[12] (4), and on the evidence that in the absence of

(11) Lehmann and Tausch, Phot. Korr., 71, 17, 135 (1935).

(12) Storch, Ber., 27, Ref. 77 (1894); Kaufmann, ibid., 40, 4550 (1907); Pinnow, Z. wiss. Phot., 13, 44 (1914); Seyewetz and Szymson, Bull. soc. chim. France, [4] 53, 1260 (1933).

sulfite the first oxidation products of hydroquinone are quinone and hydrogen peroxide,[1] (1) appears to be composed of (2), (3), and (4).

$$(2)$$

$$H_2O_2 + Na_2SO_3 \longrightarrow Na_2SO_4 + H_2O \quad (3)$$

$$(4)$$
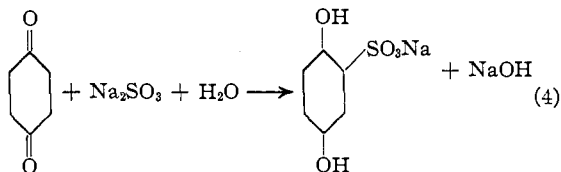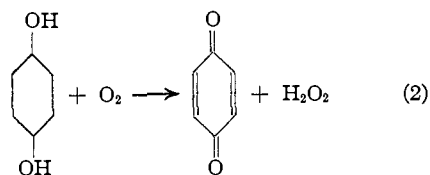
As the oxidation proceeds, sodium hydroquinone disulfonate is formed, presumably due to the oxidation of the monosulfonate, and to the reaction of the quinone with sulfite (5) and (6).

$$(5)$$

$$(6)$$
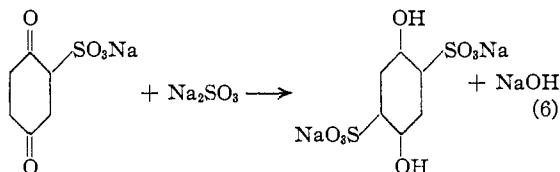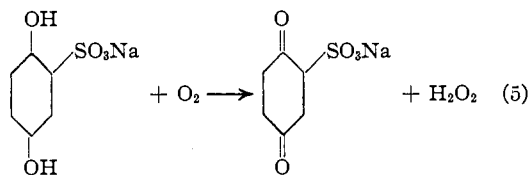
All compounds involved in equation (1), except the sodium hydroquinone monosulfonate, of which no satisfactory determination has been made, were formed or consumed in quantitative agreement with the formulation, when sufficient sulfite was present and when the solution was made alkaline by sodium carbonate. Hence, under the prevailing conditions, any direct autoxidation of sulfite is smaller than the limits of error of these determinations.

Kinetics.—Schilow and Fedotoff[4] showed that a hydroquinone–sulfite mixture autoxidizes at a lower rate, but eventually absorbs more oxygen than hydroquinone alone. Their curve for the reaction (ml. O_2 abs./time) has two distinct breaks. The data, however, are insufficient for a closer analysis. This is also the case with the data of Reinders and Dingemans who made an extensive study in the pH range 7.35–8.18, since, in these experiments the sulfite autoxidized to a

considerable extent, and the absorption of oxygen by the hydroquinone itself in the presence of sulfite cannot be isolated.

The present authors have, therefore, examined the kinetics of the sulfite-inhibited autoxidation of hydroquinone, taking care to *suppress the direct autoxidation of the sulfite* sufficiently below that of the hydroquinone, so that the former becomes insignificant.

Reinders and Vles[13] and other authors showed that the rate of autoxidation of sulfite depends on the pH of the solution with a maximum between pH 9 and 10.5. The addition of *inhibitors*, like glycerol, reduces the maximum and shifts it to about 6.5, and the oxidation becomes very slow at and beyond pH 9.5. Hydroquinone itself is an even more powerful inhibitor than glycerol,[14] and at pH 9.6 and above, the autoxidation of sulfite can be suppressed sufficiently by the hydroquinone itself and. by its oxidation products in concentrations at which these compounds are used in our autoxidation runs. The efficiency of these "inhibitors" is illustrated by Table I, giving initial oxidation rates of the sulfite at a pH at which the autoxidation of hydroquinone and its oxidation products can be ignored.

TABLE I

ACTION OF INHIBITORS ON THE AUTOXIDATION OF SULFITE

Buffer, phosphate; solvent, water; sulfite, 2 mmoles; temperature, 20.0 ± 0.02°; pH, 7.2; volume, 50 cc.

Inhibitor (0.1 mmole)	Initial oxidation rate, ml. O_2 abs./min.
0	9.6
Hydroquinone	0.026
Monosulfonate	.027
Disulfonate	.025
"Ultimate Product"[a]	.030

[a] A hydroquinone sulfite solution of pH about 10.6 was oxidized until 3.2 moles of oxygen had been absorbed, the pH was lowered to 7.2, and sulfite to make up to 2 m. moles was added.

With increasing pH, the autoxidation rate of the sulfite drops, whereas the autoxidation rates of the dihydroxybenzenes rise, and at pH 9.6 and above, the former can be neglected against the latter. This will become evident through the analysis of the autoxidation of hydroquinone.

The rate of autoxidation of hydroquinone at a pH of 9.6 is, however, very great, even in the presence of a large excess of sulfite. This impairs the accuracy of measurements in the beginning of the reaction, and limits the possibilities

(13) Reinders and Vles, *Rec. trav. chim.*, **44**, 249 (1925).
(14) Bäckström, THIS JOURNAL, **49**, 1460 (1927).

of variations so that measurements at lower pH values were desirable for the study of the reaction. In these, *ethanol* and *potassium cyanide* were further added as inhibitors. Their action is well known and the efficiency for our purpose is evident from Table II.

TABLE II

ACTION OF INHIBITORS ON THE AUTOXIDATION OF SULFITE

Temperature, 20.0 ± 0.02°; volume, 50 ml.; buffer, borate.

pH	Ethanol, %	Potassium cyanide, g.	Sodium sulfite, mmoles	Initial oxidation rate, ml. O₂ abs./min.
8.2	20	...	5	0.04
8.63	..	0.5	2.5	.025
8.90	..	.5	2.5	.002
9.00	..	.5	20	.030
9.0	15	...	2.5	.004

The very different chemical nature of ethanol and potassium cyanide serves as a control to offset the possibility that relations are obtained through some experimental artifact. ·The use of these inhibitors opened up the pH range 8.8–9.3 for investigation.
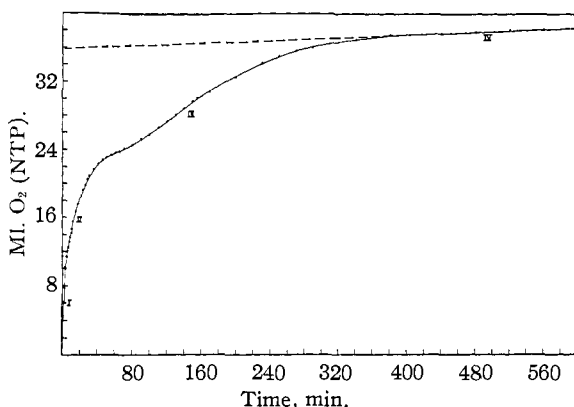

Fig. 1.—pH 9.90; 0.5 mmole hydroquinone + 6 mmoles Na₂SO₃.

, Figure 1 shows the curve of *the oxidation of a hydroquinonesulfite solution of pH 9.9, with a ratio of hydroquinone to sulfite of 1:12. The uptake of oxygen proceeds beyond one mole per mole of hydroquinone. The assumption that the greater absorption is due to the oxidation of hydroquinone monosulfonate, formed according to (4), was supported by values obtained for the oxidation of hydroquinone monosulfonate alone and by making sure that this oxidation is not influenced by hydroquinone itself or by its disulfonate. The oxidation of the *hydroquinone monosulfonate* follows a first-order equation as is shown by Table III, and its course is identical with that of Section II

of the curve in Fig. 1, *i. e.*, the part beyond the uptake of one mole of oxygen per mole of hydroquinone (Table IV).

TABLE III

AUTOXIDATION OF HYDROQUINONE MONOSULFONATE, 0.25 MMOLE

Temperature, 20.0 ± 0.02°; pH 9.87 at 25°; Na₂SO₃ 2.5 mmole; buffer, Na₂CO₃–KHCO₃.

Time, min.	Ml. O₂ absorbed	k^a
1.5	0.87	0.048
2	1.15	.044
2.5	1.40	.048
3.5	1.90	.042
4.5	2.30	.042
6	2.90	.042

^{a} First-order reaction constant, decadic logarithms.

TABLE IV

ANALYSIS OF DATA FOR OXIDATION OF 1/4 MMOLE HYDROQUINONE IN PRESENCE OF 3 MMOLE Na₂SO₃, CARBONATE BUFFER

Initial pH, 9.87; volumes at 20°; 745 mm.

Time, min.	Total O abs. by Hq.–Na₂SO₃	Vol. due to hydroquinone	Calcd. vol. due to monosulfonate	Exptl. vol. due to monosulfonate	Diff.
5	7.70	6.05	1.65	1.55	+0.10
7	8.50	6.15	2.35	2.45	− .10
10	9.45	6.15	3.30	3.40	− .10
15	10.60		4.45	4.60	− .15
20	11.45		5.30	5.45	− .15
30	12.50		6.35	6.40	− .05
60	14.55		8.40	8.35	+ .05
80	16.10		9.95	9.85	+ .10
90	16.80		10.65	10.55	+ .10
120	18.35		12.20	12.10	+ .10
137	18.95		12.80	12.75	+ .05

The further uptake of oxygen, Fig. 1, Section III, is due to the oxidation of the hydroquinone disulfonate. Separate experiments showed that hydroquinone disulfonate is autoxidized after an induction period, which also appears in Fig. 1, at a rate of about 0.02 of that of the oxidation of hydroquinone under comparable circumstances.[15] Section IV of Fig. 1 represents the oxidation of the sulfite.

A closer examination of the *initial rates of the autoxidation of hydroquinone in sulfite solutions under various conditions* reveals that this reaction does not follow a simple first-order law. These experiments were made at a lower pH value, namely, 8.9–9.3, to reduce the rate of oxygen absorption to values which can be accurately observed in the beginning of the reactions. At this low pH, it was necessary to inhibit the oxidation of sulfite by potassium cyanide or ethanol. Both inhibitors gave identical results.

(15) For the products see Pinnow, *Z. wiss. Phot.*, **37**, 76 (1938).

Figure 2 illustrates that the absorption of oxygen in the beginning of the reaction is very nearly a linear function of the time. Tables V to VIII give the uptake of oxygen (X) as a function of varying concentrations of the reactants. The volume of the reacting solutions was 50 ml.;

The hydroquinone concentration is expressed in millimoles per liter.

Table V shows that the initial rate is proportional to a higher power of the hydroquinone concentration than 1. The exponent increases, according to experiments 425 to 429, with the hydro-

TABLE V
AUTOXIDATION OF HYDROQUINONE. VARIATION OF CONCENTRATION OF HYDROQUINONE

No.	pH	Concn. of hydroq.	Na$_2$SO$_3$, g.	EtOH, ml.	KCN, g.	X_1	Oxygen absorbed, ml. X_2	X_3	X_4	X_5	t_1	Time (min.) t_2	t_3	t_4	t_5	Remarks
425	8.90	10	0.325	..	0.50	0.15	0.40	0.63	1.25	2.20	1/2	2/2	3/2	3	5	O$_2$:744 mm.
427	8.90	5	.325	..	.50	.10	.27	.43	0.70	0.82	1	2	3	5	6	O$_2$:746 mm.
428	8.90	2.5	.325	..	.50	.10	.12	.22	.37	.51	1/2	1	2	6	8	O$_2$:746 mm.
429	8.90	20	.325	..	.50	.60	1.00	1.30	2.50	4.90	2/4	3/4	4/4	2	4	O$_2$:746 mm.
430	10	10	2.00	..	...	1.20	1.80	2.30			3/6	4/6	5/6			O$_2$:751 mm.
431	10	2.5	2.00	..	...	0.60	0.80	1.35			2/6	3/6	6/6			O$_2$:751 mm.
432	10	5	2.00	..	...	.75	1.20	1.55			2/6	3/6	4/6			O$_2$:750 mm.
434	9.2	10	1.00	..	.50	.40	0.60	0.83	1.55	2.30	2/4	3/4	4/4	2	3	O$_2$:743 mm.
435	9.2	20	1.00	..	.50	.90	1.35	1.75	2.65	3.80	2/4	3/4	4/4	3/2	4/2	O$_2$:743 mm.
436	9.2	2.5	1.00	..	.50	.00	0.10	0.25	0.32	0.50	1/2	1	2	3	5	O$_2$:743 mm.
437	9.2	5	1.00	..	.50	.2	.3	.55	1.10	1.60	1/2	1	2	4	6	O$_2$:743 mm.
446	9.0	10	0.325	10	...	.05^2	.18	.29	0.50	1.00	1/2	2/2	3/2	3	6	O$_2$:746 mm.
447	9.0	20	.325	10	...	.20	.48	.75	1.02	2.20	1/2	2/2	3/2	2	4	O$_2$:746 mm.
448	9.0	5	.325	10	...	.05	.10	.15	0.29	0.40	1/2	1	2	4	6	O$_2$:746 mm.
449	9.1–9.3	10	.325	12	...	.30	.40	.50	.89	1.59	2/4	3/4	4/4	2	4	O$_2$:746 mm.
450	9.1–9.3	20	.325	12	...	.60	.95	1.30	2.65	4.03	2/4	3/4	4/4	2	3	O$_2$:745 mm.
451	9.1–9.3	2.5	.325	12	...	.05	.10	0.14	0.20	0.35	1	2	4	6	10	O$_2$:745 mm.
452	9.1–9.3	5	.325	12	...	.10	.23	.34	.65	.85	1	2	3	6	8	O$_2$:746 mm.
711	9.2	10	1.00	..	0.50	.04	.09	.15	.55	1.05	1	2	3	10	20	Air
713	9.2	20	1.00	..	.50	.00	.13	.35	.95	1.95	1	2	4	10	20	Air
714	9.2	40	1.00	..	.50	.00	.20	.42	1.60	3.28	1	2	3	9	18	Air
715	9.2	5	1.00	..	.50	.00	.02	.10	0.22	0.60	1	2	5	10	25	Air
438	9.2	10	1.00	..	.50	.00	.07	.17			1/2	1	2			Air
439	9.2	20	1.00	..	.50	.00	.13	.27			1/2	1	2			Air

TABLE VI
AUTOXIDATION OF HYDROQUINONE. VARIATION OF OXYGEN PRESSURES

No.	pH	Concn. of hydroq.	Na$_2$SO$_3$, g.	EtOH, ml.	KCN, g.	X_1	Oxygen absorbed, ml. X_2	X_3	X_4	X_5	t_1	Time (min.) t_2	t_3	t_4	t_5	Remarks
453	9.1–9.3	20	0.325	12	...	0.00	0.10	0.22	0.70	1.47	1/2	1	2	6	12	Air
514	9.3	5	.065	12	...	.05	.22	.35	.60	1.10	1	2	3	5	9	Air
515	9.3	5	.065	12	...	.30	.70	1.10	1.45	2.70	1/4	2/4	3/4	1	2	O$_2$:754 mm.

TABLE VII
INITIAL STAGES OF REACTION, VARIATION OF pH

No.	pH	Concn. of hydroq.	Na$_2$SO$_3$, g.	EtOH, ml.	KCN, g.	X_1	Oxygen absorbed, ml. X_2	X_3	X_4	X_5	t_1	Time (min.) t_2	t_3	t_4	t_5	Remarks
423	8.63	10	0.325	..	0.50	0.1	0.2	0.38	0.90	1.90	1	2	4	9	18	O$_2$:739 mm.
424	8.75	10	.325	..	.50	.25	.45	.80	1.75	3.60	1	2	4	8	16	O$_2$:744 mm.
425	8.90	10	.325	..	.50	.15	.40	.63	1.25	2.64	1/2	2/2	3/2	3	6	O$_2$:744 mm.
426	9.05	10	.325	..	.50	.4	.7	.95	1.95	3.92	2/4	3/4	4/4	2	4	O$_2$:745 mm.

TABLE VIII

AUTOXIDATION OF HYDROQUINONE. INITIAL STAGES OF REACTION, VARIATION OF SODIUM SULFITE

No.	pH	Concn. of hydroq.	Na₂SO₃, g.	EtOH, ml.	KCN, g.	X_1	Oxygen absorbed, ml. X_2	X_3	X_4	X_5	Time (min.) t_1	t_2	t_3	t_4	t_5	Remarks
338	9.0	10	0.130	..	0.50	1.20	1.70	2.15	2.60	3.80	2/6	4/6	5/6	1	3/2	O₂:743 mm.
339	9.0	10	.52	..	.50	0.30	0.50	0.65	1.27	2.48	2/4	3/4	4/4	2	4	O₂:743 mm.
340	9.0	10	1.05	..	.50	.20	.40	.55	1.00	2.05	1/2	2/2	3/2	3	6	O₂:744 mm.
341	9.0	10	2.10	..	.50	.2	.4	.55	1.25	2.20	1	2	3	7	12	O₂:744 mm.
515	9.1–9.3	5	0.0650	12	...	.30	.70	1.10	1.45	2.70	1/4	2/4	3/4	1	2	O₂:754 mm.
516	9.1–9.3	5	.1625	12	...	.20	.50	0.75	1.45	2.70	1/2	2/2	3/2	3	6	O₂:754 mm.
517	9.1–9.3	5	.4875	12	...	.10	.20	.30	0.60	1.20	1/2	2/2	3/2	3	6	O₂:754 mm.
518	9.1–9.3	5	.0810	12	...	.25	.50	.75	1.05	2.10	1/4	2/4	3/4	1	2	O₂:754 mm.
519	9.1–9.3	5	.325	12	...	.15	.28	.52	1.02	1.90	1/2	1	2	4	8	O₂:754 mm.
510	9.1–9.3	10	.1625	12	...	.75	1.10	1.40	2.75	4.00	2/4	3/4	4/4	2	3	O₂:754 mm.
511	9.1–9.3	10	.4875	12	...	,50	0.80	1.05	1.80	2.80	1/2	2/2	3/2	3	5	O₂:754 mm.
512	9.1–9.3	10	.1625	12	...	.08	.17	0.30	1.05	2.09	1/2	4	2	9	18	Air:754 mm.
513	9.1–9.3	10	.4875	12	...	.20	.25	.40	0.82	1.30	1	2	5	18	25	Air:754 mm.

quinone concentrations from 1.07 to 1.69. Similar results were found in all the other experiments, where oxygen of atmospheric pressure was used. If, however, air was used, thus reducing the oxygen pressure to one-fifth, the initial reaction rate varied very nearly with the first power of the hydroquinone concentration (Experiments 711–715 and 438–439). The influence of the oxygen concentration on the reaction rate itself was found to lie between the first and second power. This is illustrated by comparing No. 514 with No. 515 in Table VI, and No. 453 from Table VI with No. 450 from Table V. The influence of pH on the initial reaction rate can be seen from Table VII:

Fig. 2.—Autoxidation of hydroquinone in presence of sulfite: hydroquinone, 0.5 mmole; Na₂SO₃, 1.00 g. KCN, 0.5 g.; pH, 9.2.

$\Delta X/\Delta t$ varies with a power higher than the second (between 2.5 and 2.7) of the hydroxy-ion concentration.

There is a linear relation, however, between reaction velocity and concentration of sodium sulfite. As can be seen from Table VIII, the initial reaction velocity is inversely proportional to the concentration of the sulfite. The two straight lines in Fig. 3 illustrate the validity of this law over a wide range with the accuracy to be expected under the experimental conditions.
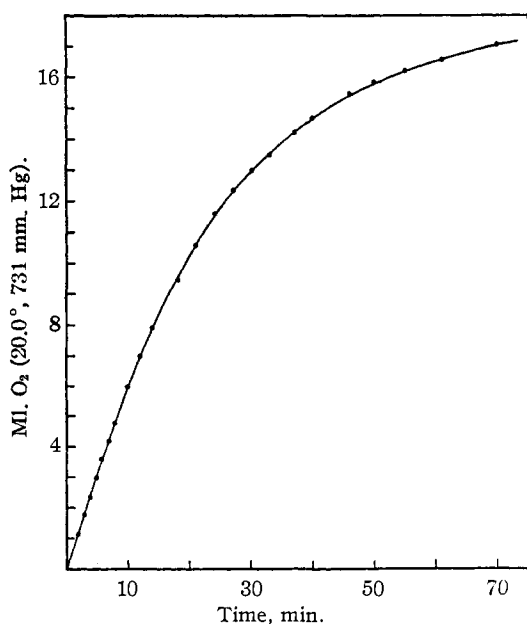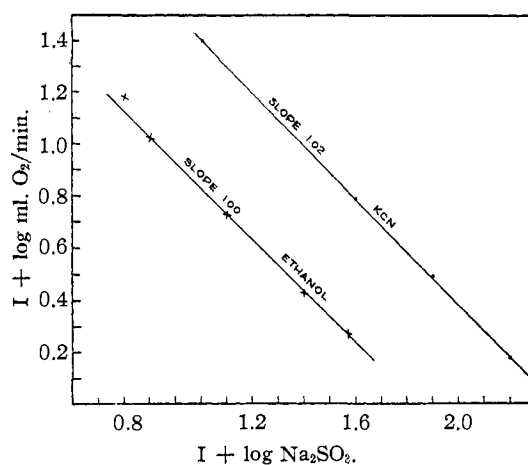

Fig. 3.—Variation of rate with [Na₂SO₃].

Hydroquinone Homologs

The oxidation of the hydroquinone homologs was examined at a pH of about 11, in solution with 12 moles of sulfite per mole of hydroquinone and 10% ethanol, which served both to increase the solubility of the hydroquinone homologs and to decrease the rate of oxidation of the sulfite. The reactions were followed until the rate of the oxygen uptake equaled that of sulfite alone in the

absence of hydroquinone. It is likely that under these circumstances some oxygen was still absorbed by the organic material, because of the inhibitory action of the hydroquinone oxidation products on the sulfite oxidation.

If we disregard the tail ends of the curves which are due to the oxidation of the sulfite, so that hydroquinone shows three sections in Fig. 1, we also obtain three sections for toluhydroquinone, two for m-xylohydroquinone, and for ψ-cumohydroquinone and only one for durohydroquinone. We may deduce from these results that toluhydroquinone, the xylohydroquinones, and ψ-cumohydroquinone form monosulfonates and that these oxidize with uptake of 1 mole of oxygen. Toluhydroquinone, furthermore, forms a disulfonate.

The case of ψ-cumohydroquinone was investigated somewhat more in detail. The curve for 1/4 mmole ψ-cumohydroquinone in the presence of 3 mmoles of sulfite, at pH 11, showed a sharp break at 6.1 ml. of oxygen, corresponding to an uptake of one mole of oxygen. Then, the reaction proceeded at a slower rate which, however, was still higher than that of the sulfite oxidation alone. In a second experiment, the mixture of 1/2 mmole of ψ-cumoquinone and 3 mmoles of sulfite was stored in an atmosphere of nitrogen at a pH of 11 for seventy-five minutes in the apparatus previously described.[10] The color of the solution changed from faint yellow to amber. Then, the autoxidation rate was measured. A sharp break occurred at 1.7 ml. and a total of 4.5 ml. of oxygen was absorbed. In a third experiment, 1/4 mmole of ψ-cumoquinone and 1/4 mmole of sodium sulfite were mixed at a pH of 7.46. The mixture was completely colorless after twenty seconds, and showed no absorption of oxygen at this pH in one hour's time. Hence, the quinone has not been reduced to the hydroquinone by the sulfite because ψ-cumohydroquinone would, under these circumstances, absorb oxygen at an appreciable rate. The reaction indicated by the disappearance of the yellow color is obviously the formation of the ψ-cumohydroquinone monosulfonate. This is further substantiated by the fact that when the pH of the solution was raised to 11, oxygen absorption occurred at a measurable rate. These experiments show that at low pH values, ψ-cumohydroquinone sulfonate is formed rapidly. At the high pH values, other reactions become noticeable, in which some of the quinone is transformed into a rapidly oxidizable material, perhaps by dismutations and condensations.

Table IX illustrates the extent to which sulfite inhibits the autoxidation of hydroquinone and its homologs
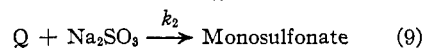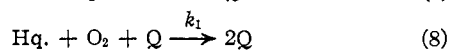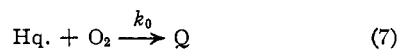
Discussion of Results

If the suggestion that the inhibitory action of sulfite is due to the removal of the quinone catalyst is correct, then the concentration of quinone in an oxidizing hydroquinone–sulfite mixture at

Table IX

Volume, 50 ml.; temperature, $20.0 \pm 0.02°$

Oxidand	Amount in mmole	Sulfite in mmole	k_{10}
Hydroquinone	1/2	0	0.0216
		1/2	.0036
o-Xylohydroquinone	1/4	0	.024
		1/4	.0038
m-Xylohydroquinone	1/2	0	.045
		1/2	.014
		1/4	.0172
p-Xylohydroquinone	1/4	0	.042
		1/4	.0117
			Ml. O_2 abs./min.
ψ-Cumohydroquinone	1/4	0	0.90 (max.)
		1/4	0.125

any given stage will be controlled by the relative rates of two opposing reactions: that of the oxygen with hydroquinone, forming quinone and that of the quinone with the sulfite, removing quinone. A complete quantitative treatment is not possible at present. However, with the aid of some plausible assumptions, certain simplified limiting cases may be studied.

By analogy with the experimental findings for the durohydroquinone and ψ-cumohydroquinone autoxidation, it may be assumed that at very low quinone concentrations the quinone catalysis is proportional to the quinone concentration. We then have as the rate-defining reactions

$$\text{Hq.} + O_2 \xrightarrow{k_0} Q \qquad (7)$$

$$\text{Hq.} + O_2 + Q \xrightarrow{k_1} 2Q \qquad (8)$$

$$Q + \text{Na}_2\text{SO}_3 \xrightarrow{k_2} \text{Monosulfonate} \qquad (9)$$

Equation (8) is valid in a region where the rate of oxidation of the semiquinone is of a lower order of magnitude than the rate of its destruction by competitive reactions.[16] The rate of change of the quinone concentration is accordingly given by the expression

$$k_0(\text{Hq.})(O_2) + k_1(\text{Hq.})(O_2)(Q) - k_2(\text{Na}_2\text{SO}_3)(Q)$$

If (9) is fast enough, the quinone will be consumed as quickly as it is produced; for this particular steady state the expression just given will equal zero and the "steady" concentration of quinone will be

$$(Q) = \frac{k_0(\text{Hq.})(O_2)}{k_2(\text{Na}_2\text{SO}_3) - k_1(\text{Hq.})(O_2)}$$

The measured rate of oxygen uptake, which will be the sum of the uptake by reactions (7) and (8), will then be

(16) Kornfeld and Weissberger, This Journal, 61, 360 (1939).

$$\frac{dO_2}{dt} = k(\text{Hq.})(O_2)\left\{1 + \frac{k_1(\text{Hq.})(O_2)}{k_2(\text{Na}_2\text{SO}_3) - k_1(\text{Hq.})(O_2)}\right\}$$ (10)

Equation (10), as can easily be seen, demands a dependence of the reaction rate on the concentration of hydroquinone and of oxygen, which for both these reactants lies between the first and second powers. This result agrees with the reported experimental findings. The simple inverse proportionality, however, between initial reaction rate and sulfite concentration throughout the whole range of the experiments cannot be deduced from equation (10), and the suggested mechanism cannot be considered as completely satisfactory until this dependence is understood. It should be borne in mind that the mechanism discussed in the present paper does not yet consider the ways in which the semiquinone or the hydroquinone ions react with the oxygen, and that the latter reaction will become more important, the more the quinone-catalyzed reaction is suppressed by the removal of the quinone.

As a mechanism for the elimination of the quinone, one might consider, besides the addition of sulfite resulting in formation of the sulfonate, the reduction to the hydroquinone producing oxidation of the sulfite to sulfate. This latter reaction, however, is improbable in alkaline solutions,[17] and it would not provide for the rise in alkalinity which is observed in the autoxidation of hydroquinone in sulfite solution. The analysis of Curve I excludes this reaction further, and so do the experiments with ψ-cumoquinone, and the fact that sulfite inhibits the autoxidation only of those homologs of hydroquinone which have at least one replaceable nuclear hydrogen. The autoxidation of hydroquinone and of its homologs containing nuclear hydrogen in the presence of much sulfite is well represented by equations (2) to (6). From the results given in the preceding papers of this series, it further can be expected that (11) will be in competition with (3) and (4),
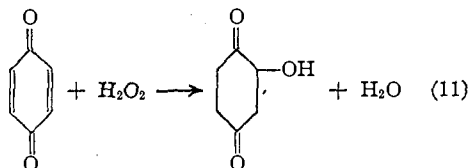
and, perhaps, the analogous reaction of the quinone monosulfonate in competition with (3) and (6). If, therefore, the sulfite is not in suffi-

(17) Dodgson, *J. Chem. Soc.*, **105**, 2435 (1914).

cient excess, reaction (11) will become marked, and the ratio of oxidized hydroquinone to consumed sulfite become larger than 0.5, whereas the ratio of consumed sulfite to formed sulfate should remain 2, provided that the hydroxyquinone does not react with the sulfite. With a large excess of sulfite the relationship between oxidized hydroquinone, sulfite consumed and sulfate formed is, according to Pinnow[9,12,15] and Lehmann and Tausch,[11] precisely 1:2:1. Pinnow and Lehmann and Tausch have found, however, in several instances that the ratio of consumed sulfite to formed sulfate was somewhat greater than 2, but it was always much closer to this figure than the accompanying ratio of hydroquinone:sulfite was to 0.5. These results, while unexplainable on the basis of the mechanism used by Lehmann and Tausch and Pinnow, follow from the mechanism given above. The slightly larger than 2:1 ratio found for the consumed sulfite:formed sulfate follows if some of the hydroxyquinone formed reacts with sulfite before it has a chance to polymerize, or if the polymer adds some sulfite.

Inhibitors Other than Sulfite

On the basis of the theory under consideration in this paper, it can be expected that compounds other than sodium sulfite also inhibit the autoxidation of hydroquinone and its homologs, if they remove the catalyzing quinone at a sufficient rate. This was found to be the case with cysteine, thioglycolic acid, thioglycolic anilide, and p-thiocresol (Table X).

TABLE X
INHIBITORY ACTION OF –SH COMPOUNDS

Borate buffer, pH 8.2; hydroquinone, 1/2 mmole; inhibitor, 1/20 mmole.

Inhibitor	Initial velocity (Vi) ml./min.
0	1.0
Cysteine	0.017
Thioglycolic acid	.016
Thioglycolic anilide	.015
p-Thiocresol[a]	.036

[a] Much of the p-thiocresol remained undissolved.

The inhibitory action of cysteine and of thioglycolic acid was investigated in some detail. There is no principal difference in their action. The oxidation curves in Fig. 4 are typical. After a period of slow, almost constant oxygen uptake, the curves break sharply and the rate becomes that of the uninhibited hydroquinone autoxidation. Figure 4 shows that the initial rate of

oxygen uptake is higher than that of the inhibitor alone. The reaction products of quinone with cysteine and with thioglycolic acid, namely, hydroquinone cysteine I, quinone, hydroquinone thioglycolic acid II, and quinone thioglycolic acid[18] in alkaline solution absorb oxygen at high rates (Table XI).
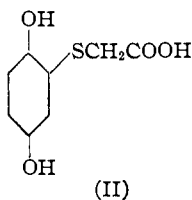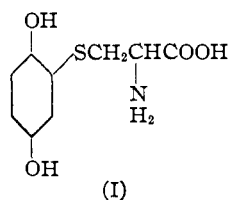
(I)   (II)

TABLE XI

Volume, 50 ml.; temperature, 20.0 ± 0.02°; pH 8.0.

Material	Amount, mole	Velocity (ml. O_2/min.)	
Hydroquinone	0.25	0.19	(initial)
Quinone	.25	.019	(maximum)
Hydroquinone thioglycolic acid	.25	.20	(maximum)
		.10	(initial)
Quinone thioglycolic acid	.25	.04	(initial)
Quinone + thioglycolic acid	.25	.90	(maximum)
	.60	.12	(initial)
Hydroquinone + thioglycolic acid	.25	.003	(initial)
	.025	.19	(maximum)
Thioglycolic acid	.25	.0025	(initial)

The quinoid derivatives autoxidize about as fast as hydroquinone alone under the same conditions, the hydroquinone derivatives even at considerably higher rates. It appears, therefore, that the initial part of the curves in Fig. 4 consists of the autoxidation of the inhibitor, of the autoxidation of the hydroquinone, which is slow, owing to the removal of the catalyzing quinone, and of the autoxidation of the reaction products of the quinone with the inhibitor. If, by these processes, the inhibitor has been removed, the rate jumps up to that of the uninhibited hydroquinone autoxidation.

It is noteworthy that the rate of the initial reaction is very much slower than that obtained with sulfite as inhibitor at the same concentrations. The rate of oxidation of hydroquinone is almost independent of the cysteine or thioglycolic acid concentrations over the range covered in these experiments.

Both cysteine and thioglycolic acid strongly inhibit the autoxidation of toluhydroquinone. A definite, although weaker, inhibition appears in the autoxidation of the xylohydroquinones.

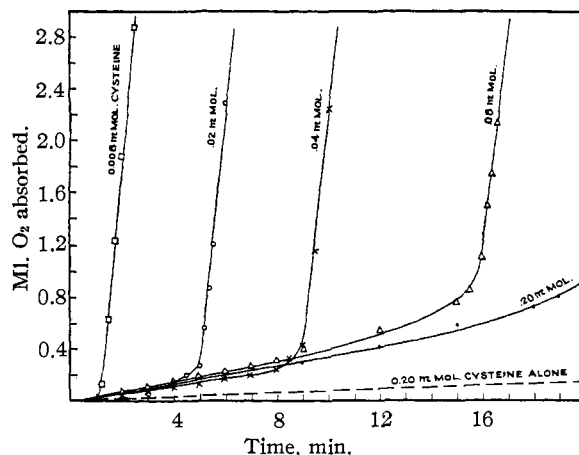(18) Snell and Weissberger, THIS JOURNAL, **61**, 450 (1939),

Fig. 4.—Inhibitory action of cysteine, 1 mmole hydroquinone, pH 8.2.

Neither ψ-cumohydroquinone nor durohydroquinone was inhibited under the conditions of these experiments.

Cysteine and thioglycolic acid increase the rate of autoxidation of quinone (Table XI). This is probably due to the fact that the reaction products of quinone with cysteine and with thioglycolic acid form quickly and autoxidize at higher rates than quinone itself. When the quinone is in excess, a small and very rapid initial uptake of oxygen occurs, followed by a region in which the rate is roughly independent of the quinone concentration and still much greater than that of the oxidation of quinone alone.

Summary

1. Conditions have been found under which the autoxidation of hydroquinone and its homologs can be measured in the presence of excess sulfite.

2. This was made possible, (a) by adjustment of pH, (b) by use of the fact that the oxidands and their oxidation products are inhibitors of the autoxidation of sulfite but do not affect each other, and (c) by the addition of specific inhibitors which do not affect the oxidation of the organic material but hinder that of the sulfite. The influence of these factors was studied closely.

3. The nature and relative amounts of the reaction products, and the kinetics of the sulfite-inhibited autoxidation of hydroquinone and its

homologs agree well with the suggestion that these compounds react with molecular oxygen to form quinones and hydrogen peroxide.

4. Hydrogen peroxide oxidizes the sulfite to sulfate.

5. If the quinone formed has at least one nuclear hydrogen, it reacts with the sulfite with formation of the corresponding hydroquinone monosulfonate.

6. The hydroquinone monosulfonate is autoxidized and the oxidation products undergo the reactions mentioned under (4), and, if the conditions are fulfilled, (5); thus, hydroquinone monosulfonate and toluhydroquinone monosulfonate form the disulfonates.

7. The oxidation of hydroquinone in sulfite solution does not follow a simple first-order law. The dependence of the reaction rate on the con-

centrations of oxidand and oxygen, and on the pH are in good agreement with a mathematical expression found on the assumption that the inhibitory action of sulfite is due to the removal of quinone which acts as a catalyst for the autoxidation.

8. The linear dependence on the sulfite concentration which has been observed throughout the whole range of the experiments does not follow from this expression.

9. The inhibitory action of thiol compounds (cysteine, thioglycolic acid, thiocresol, etc.) also agrees with the assumption that their action is caused by the removal of the catalyzing quinone.

10. The autoxidation of various reaction products of quinones with thiol compounds has been measured.


The Reaction of Thiol Compounds with Quinones

BY J. M. SNELL AND A. WEISSBERGER

In connection with work on the inhibitory action of thiol compounds in the autoxidation of hydroquinones,[1,2] some experiments were made on the reaction of thiol compounds with benzoquinone and substituted benzoquinones. Two types of reaction may be expected: (A), oxidation of the thiol to a disulfide with reduction of the quinone to the hydroquinone; (B), addition of the thiol to the quinone according to (1)


$$\text{(1)}$$
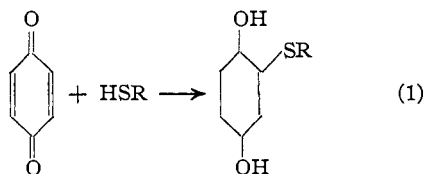
They are analogous to the reactions of quinones with sulfite.[3] Both types have been recorded in the literature. Bongartz[4] observed that quinone and thioglycolic acid in the absence of a solvent form hydroquinone. Tarboureich[5] caused quinone and ethyl mercaptan to react under widely varying conditions and, in all cases, even at 140° in a bomb, isolated only hydroquinone or quin-

hydrone. Addition products were isolated by Troeger and Eggert[6] and by Posner,[7] who added various thiols to quinone in ligroin solution and treated the resulting molecular compounds with alcohol. Working with a four-fold excess of quinone, only disubstituted quinones of the type I were obtained.[7] Sharvin and Lukin[8] added thiosalicylic acid to quinone in xylene and also
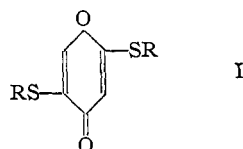
obtained a disubstituted quinone, quinonedithiosalicylic acid. Our own experiments which are described below suggest that these reactions proceed according to (1), that the substituted hydroquinone is in equilibrium with the quinone (2),

$$\text{(2)}$$
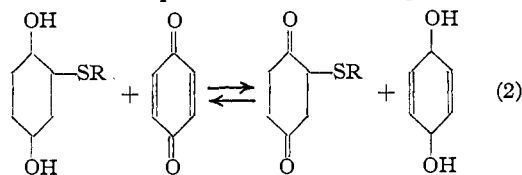
(1) James, Snell and Weissberger, THIS JOURNAL, 60, 2084 (1938).

(2) James and Weissberger, ibid., 61, 442 (1939).

(3) Dodgson, J. Chem. Soc., 105, 2435 (1914).

(4) Bongartz, Ber., 21, 483 (1888).

(5) Tarboureich, Bull. soc. chim., [3] 25, 313 (1901).

(6) Troeger and Eggert, J. prakt. Chem., [2] 53, 482 (1896).

(7) Posner, Ann., 336, 85–167 (1904).

(8) Sharvin and Lukin, J. Russ. Phys. Chem. Soc., 59, 217–20 (1927); C. A., 22, 1583 (1928).