

Two new arsine oxides were also formed.

3. Two styrene polymers were obtained which retained the properties of the arsono and arseno groups.

4. Several intermediates were prepared for the first time; other intermediates were obtained by new methods in good yields.

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RECEIVED NOVEMBER 25, 1938

[COMMUNICATION NO. 702 FROM THE KODAK RESEARCH LABORATORIES]

## The Mechanism of the Autoxidation of $\psi$ -Cumohydroquinone

BY G. KORNFIELD AND A. WEISSBERGER

James, Snell and Weissberger<sup>1</sup> reported that the rate of absorption of oxygen by solutions of hydroquinone and its homologs is proportional to the square of the hydroxyl-ion concentration, and, with hydroquinone, methylhydroquinone, and the dimethylhydroquinones, to the concentration of these compounds. Accordingly, it was assumed that the reaction proceeds over the doubly charged hydroquinone ions. With tetramethyl hydroquinone (durohydroquinone), besides this dependency, a linear dependency on the concentration of the oxidation product, duroquinone, was observed,<sup>2</sup> and it was assumed that the doubly charged ion of durohydroquinone reacted with one molecule of duroquinone to form two singly charged ions of a semiquinone. The production of their semiquinone ions was further assumed to be the rate-controlling process of the quinone-catalyzed reaction, which was automatically followed by their oxidation to quinone, since the reaction rate of the auto-catalyzed reaction was found to be independent of the oxygen pressure. The same independence of the oxygen pressure as well as the linear dependence on the quinone concentration was found for the oxidation rate of trimethylhydroquinone ( $\psi$ -cumohydroquinone), but only as long as the  $\psi$ -cumoquinone concentrations were kept sufficiently low. With increasing concentration of  $\psi$ -cumoquinone, the reaction rate became increasingly independent of it, and, at the same time, the influence of the oxygen pressure on the reaction rate increased. Since the autoxidation rates of hydroquinone and its mono- and dimethyl homologs depend linearly on the oxygen pressure and were found to be independent of their quinone concentrations, the oxidation of  $\psi$ -cumohydroquinone represents a transition be-

tween the oxidation of the fully substituted durohydroquinone and the oxidation of hydroquinone and its mono- and dimethyl homologs. Therefore, it seems the more necessary to gain an insight into the mechanism which prevents the catalytic action of higher concentrations of  $\psi$ -cumoquinone, in the autoxidation of  $\psi$ -cumohydroquinone.

To compare quantitatively the results of theoretical considerations with the observed data, we went back to the original experiments. We wish to thank Dr. T. H. James of these Laboratories for permission to use them.

The reaction rate,  $\Delta x / \Delta t$ , was calculated from point to point for each experimental run. The decrease of  $\psi$ -cumohydroquinone was determined by the uptake of oxygen. At the same time it indicated the increase of  $\psi$ -cumoquinone from the start of the reaction. The initial rate was found to be very accurately proportional to the initial concentrations of  $\psi$ -cumohydroquinone. Accordingly, the reaction rate for each time interval was divided by the average  $\psi$ -cumohydroquinone concentration during this interval, and this expression (indicated by crosses in Fig. 1) was plotted against the average  $\psi$ -cumoquinone concentration. Curve I in Fig. 1 gives an example of the dependence of this reduced reaction rate on the  $\psi$ -cumoquinone concentration during the course of an experimental run. The concentrations are expressed in millimoles per liter, and the time is expressed in minutes. For this particular experiment, the initial concentration of  $\psi$ -cumohydroquinone was 5 millimoles per liter, and the pH 7.46. Other experiments (13 in number) in which the  $\psi$ -cumohydroquinone concentration, pH, and oxygen pressure varied, but in which, just as in the run represented in Fig. 1, no  $\psi$ -cumohydroquinone was added at the start, gave the same type of curve, except that most of them

(1) James, Snell and Weissberger, *THIS JOURNAL*, **60**, 2084 (1938).

(2) *Ibid.*, **60**, 98 (1938).

showed wider scattering of the points in the second half. All these experiments, therefore, seem to point to an optimum concentration of  $\psi$ -cumoquinone, at which the reaction rate reaches its highest value and beyond which it drops off. Before arriving at this conclusion, however, one ought to consider that the expression plotted on the ordinate, with decreasing  $\psi$ -cumohydroquinone concentration, becomes increasingly sensitive toward changes in that concentration.

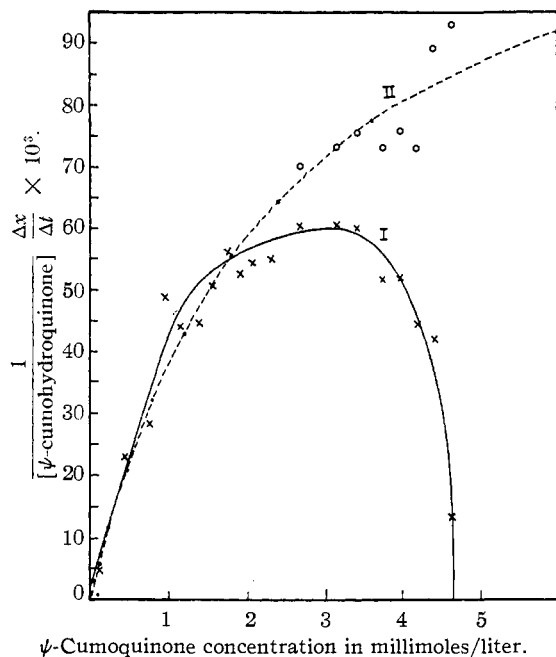


Fig. 1.—Dependence of reduced reaction rate on  $\psi$ -cumoquinone concentration during one run. Initial concentration of  $\psi$ -cumohydroquinone 5 millimoles per liter;  $pH$ , 7.46.

Now, the absorption of oxygen stops after absorption of about 90% of the theoretical amount. This may be due to a loss of  $\psi$ -cumohydroquinone by a reaction with the hydrogen peroxide which is formed in the oxidation,<sup>1,2</sup> to a decomposition of the latter, or to other causes.

To account roughly for this loss, the tentative assumption was made that, after the first half of the reaction had taken place, an additional 6% of the  $\psi$ -cumohydroquinone was lacking. In this way the circles in Fig. 1 were obtained which, indeed, give a strongly changed curve. This uncertainty in the later stages of the reaction makes it desirable to derive the dependence on the  $\psi$ -cumoquinone concentration from reaction rates measured in the earlier stages of the experiments, where varying concentrations of  $\psi$ -cumo-

quinone had been added from the start. The reaction rates taken for the initial time intervals of seven experimental runs where those additions had been made were divided by their respective  $\psi$ -cumohydroquinone concentrations and plotted against their  $\psi$ -cumoquinone concentrations. The experimental points are again marked by crosses and give the fully drawn curve in Fig. 2. This begins as a straight line, indicating proportionality between reaction rate and quinone concentration, but, with increasing quinone concentration, the line curves more and more toward the abscissa, indicating an asymptotical approach of the reaction rate toward complete independence of the quinone concentration.

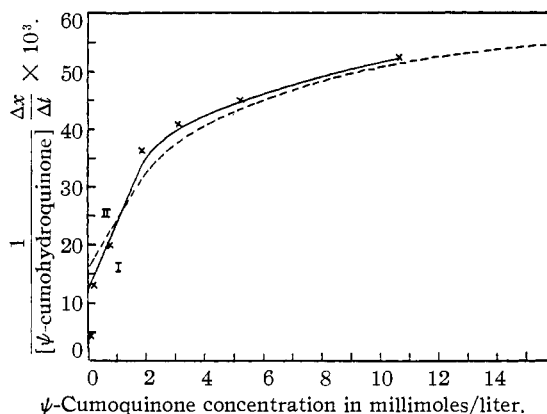


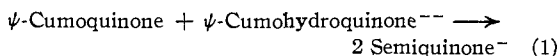
Fig. 2.—Dependence of reduced reaction rate on added  $\psi$ -cumoquinone concentrations in the initial stages. Initial concentration of  $\psi$ -cumohydroquinone 5 millimoles per liter;  $pH$ , 7.40.

To explain these experimental facts, it must be assumed that only for very low concentrations of  $\psi$ -cumoquinone is the formation of the semiquinone automatically followed by its oxidation, whereas, with increasing concentrations of  $\psi$ -cumoquinone, the semiquinone can react also in another way. This cannot be the polymerization of the semiquinone, since it would be favored not only by higher concentrations of  $\psi$ -cumoquinone, but also of  $\psi$ -cumohydroquinone and alkali. Hence, the simple relationship found experimentally between the reaction rate and these concentrations contradicts such an assumption.

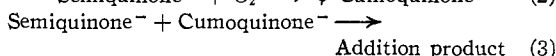
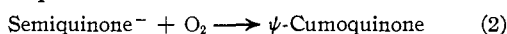
It was tentatively assumed, therefore, that the semiquinone reacts with the quinone to form an addition product, which does not enter into the reaction, but which, in some way, disintegrates into the original components,  $\psi$ -cumohydroquinone and  $\psi$ -cumoquinone. The latter assump-

tion is necessary to account for the fact that the total absorption of oxygen is independent of added  $\psi$ -cumoquinone.

The first step in this mechanism is the formation of the semiquinone ion from  $\psi$ -cumoquinone and the doubly charged ion of  $\psi$ -cumohydroquinone as follows



The semiquinone reacts either with oxygen to form quinone or with quinone to form the addition product



The rate of oxidation is then

$$dx/dt = k_2[\text{Semiquinone}^-][\text{O}_2]$$

The stationary concentration of the semiquinone ion can be found when its disappearance by (2) and (3) is put equal to its formation by (1) as follows

$$[\text{Semiquinone}^-] = \frac{k/2 [\text{Cumoquinone}] [\text{Cumohydroquinone}^{--}]}{k_2[\text{O}_2] + k_3[\text{Cumoquinone}]}$$

This gives for the reaction rate

$$dx/dt = \frac{k_1}{2} [\text{Cumohydroquinone}^{--}] \frac{k_2[\text{O}_2] [\text{Cumoquinone}]}{k_2[\text{O}_2] + k_3[\text{Cumoquinone}]} \quad (4)$$

It is shown qualitatively by (4) that for low concentrations of  $\psi$ -cumoquinone and high concentrations of oxygen the reaction rate will be proportional to the  $\psi$ -cumoquinone concentration, since by ignoring  $k_3[\text{Cumoquinone}]$  against  $k_2[\text{O}_2]$ , equation (4) becomes

$$\frac{dx}{dt} = \frac{k_1}{2} [\text{Cumohydroquinone}^{--}] [\text{Cumoquinone}] \quad (5)$$

For high concentrations of  $\psi$ -cumoquinone and low concentrations of oxygen, on the other hand, we get proportionality with the concentration of oxygen, according to the equation

$$\frac{dx}{dt} = \frac{k_1}{2} [\text{Cumohydroquinone}^{--}] \frac{k_2}{k_3} [\text{O}_2] \quad (6)$$

The good agreement of the results with the experiments encourages a more quantitative treatment.

Figures 1 and 2 give the variation of concentration for constant alkalinity and oxygen pressure. If the mechanism assumed is true, an expression of the form

$$\frac{a[\text{Cumoquinone}]}{b + k_3[\text{Cumoquinone}]}$$

where  $b$  represents  $k_2[\text{O}_2]$ , should show the same dependence on the  $\psi$ -cumoquinone concentration. This expression was therefore plotted (indicated by Curve II in Fig. 1) against the  $\psi$ -cumoquinone concentration (with the additional assumption that, for a  $\psi$ -cumoquinone concentration of 2.4 millimoles per liter,  $b = k_3[\text{Cumoquinone}]$ , and with a suitably chosen value of  $a$ ). The two curves coincide well in the first part of the reaction; in the second half, no agreement with Curve I could be expected, in view of the experimental complications just discussed, whereas the roughly corrected points (indicated by circles) lie well in the path of the theoretical curve.

In Fig. 2, the experimental general curve (I) is compared with the theoretical curve (II) in a similar way. The agreement is excellent, particularly if the first experimental point is ignored.

To compare the observed dependence on the oxygen pressure of the reduced reaction rate (*i. e.*, the reaction rate divided by the  $\psi$ -cumohydroquinone concentration) with the theoretical expectation, we transform equation (4) into the expression

$$\frac{1}{[\text{Cumohydroquinone}]} \frac{dx}{dt} = a' \frac{k_2[\text{O}_2]}{k_2[\text{O}_2] + c}$$

which is valid for constant  $\psi$ -cumoquinone concentrations.

If we choose 2.4 millimoles per liter as the  $\psi$ -cumoquinone concentration, then  $k_2[\text{O}_2] = c$ , and

$$a' \frac{k_2[\text{O}_2]}{k_2[\text{O}_2] + c} = \frac{a'}{2}$$

If, now, we take air instead of oxygen at atmospheric pressure, the expression given above will become

$$a'/5/(1/5 + 1) = a'/6$$

This means that the reduced reaction rate will vary from 3 to 1. The experimental result for this variation was 3.3 to 1 in one case, and 3.6 to 1 in another, in satisfactory agreement with the theory.

The formation of a complex between one semiquinone and one quinone molecule is not an entirely new conception, since verdoflavin, which Kuhn and Ströbele<sup>3</sup> isolated, is a compound of this type. Potentiometrically, Michaelis and Schwarzenbach<sup>4</sup> did not find this intermediate in the oxidation of lactoflavin in dilute solutions. This would not, however, preclude its existence in extremely low concentrations: for the kinetics

(3) Kuhn and Ströbele, *Ber.*, **70**, 753 (1938).

(4) Michaelis and Schwarzenbach, *J. Biol. Chem.*, **123**, 527 (1938).

of the oxidation only the formation is essential, which might well be followed by a decomposition whenever two molecules of the intermediate collide. With hydroquinone itself and its homologs, no compound of the type in question has been described. The suggestion that the semiquinone-quinone complex does not exist with the tetramethyl compound and is formed more easily the fewer methyl groups there are present in the molecule fits in well, however, with observations<sup>5</sup> on the existence of dimeric quinhydrones.

### Summary

An explanation is offered for the complicated non-linear dependence of the autoxidation rate of  $\psi$ -cumohydroquinone on the concentrations of  $\psi$ -cumoquinone and of oxygen which was found by James, Snell, and Weissberger.

(5) Michaelis, Schubert, Reber, Kuck and Granick, *THIS JOURNAL*, **60**, 1678 (1938).

A linear dependence in the region of low  $\psi$ -cumoquinone concentrations and a deviation from this dependence in the region of higher  $\psi$ -cumoquinone concentrations follows if the semiquinone intermediate reacts not only with oxygen but also with  $\psi$ -cumoquinone, and forms a product with the latter which disintegrates into  $\psi$ -cumohydroquinone and  $\psi$ -cumoquinone.

A quantitative formulation of this assumption gives the functional dependence of the reaction rate on the  $\psi$ -cumoquinone concentration and on the oxygen pressure, which is in excellent agreement with the experimental results.

The supposed complex is analogous to verdo-flavin. The presence of methyl groups in the molecule appears to have an influence on the formation of the complex which is similar to that on the stability of dimeric quinhydrones.

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RECEIVED DECEMBER 5, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 70]

## Studies in Organo-silicon Synthesis. II. Reactions of Aryl Grignard Reagents with Silicon Halides

BY WALTER C. SCHUMB AND CHARLES M. SAFFER, JR.

In a preceding paper<sup>1</sup> it was demonstrated that hexaaryldisilanes are not formed from hexachlorodisilane by the Wurtz reaction. In view of this result it was thought to be of value to determine whether or not the Grignard reagent might be used successfully for this synthesis. When hexachlorodisilane was added to excess phenylmagnesium bromide in anhydrous ether and refluxed for two days, although a reaction occurred, no hexaphenyldisilane could be isolated, the final product being a brown tar, which probably resulted from the hydrolysis of the partially phenylated hexachlorodisilane.

A modification of this method was first used in 1933 by Cusa and Kipping<sup>2</sup> in the preparation of tetraphenyldisilane from silicon tetrachloride and phenylmagnesium bromide. It consisted of removing the ether by distillation after the reagents were well mixed, and heating the remaining solids

(1) Schumb, Ackerman and Saffer, *THIS JOURNAL*, **60**, 2486 (1938).

(2) Cusa and Kipping, *J. Chem. Soc.*, 1040 (1933). Although the procedure used often has been applied to the preparation of metal-organo compounds where higher temperatures are desired, we believe this was the first time it was employed in the synthesis of organo-silicon compounds.

at 160–180° for three to four hours. So far as we are aware, this case constitutes the only reported synthesis of a tetraarylsilane by means of the Grignard reagent. When this method was applied to the reaction of hexachlorodisilane and phenylmagnesium bromide, a good yield of hexaphenyldisilane was obtained, with only a trace of tetraphenyldisilane.

These results seem to disprove the findings of Schwarz and Sexauer,<sup>3</sup> who reported that the reaction of phenylmagnesium bromide and hexachlorodisilane in the usual manner "formed no derivatives of disilane, instead the Si-Si bond was broken by the Grignard reagent, and a mixture of monosilane derivatives resulted." They reported also the isolation of diphenyldichlorosilane. If this substance had been formed in the first stage of our experiment, the heating process would have converted it into tetraphenyldisilane, of which we were unable to isolate more than a minute amount. In other experiments it was found possible to identify as little as 1% of tetraphenyldisilane in a mixture with hexaphenyldisilane. These facts,

(3) Schwarz and Sexauer, *Ber.*, **59B**, 333 (1926).