

trogen fraction, and not one-half as would be expected if every CH_2Br radical reacted with silica (the remainder of the fraction being methane), CH_2Br radicals must also clean up in some additional way. West and Schlessinger found rather more than one third of the methyl iodide decomposed appearing as methylene diiodide. It is possible that methylene dibromide is formed in this case but relatively less than with the iodide, and hence its identification was not possible. Alternatively, reaction of CH_2Br with a methyl radical might produce ethyl bromide, which was also looked for without success. In the absence of more experimental evidence, it is of no advantage to speculate further on the fate of the remaining CH_2Br radicals.

The authors wish to thank Dr. M. Burton for his help in this work.

Summary

1. The photolysis of methyl bromide chiefly by light of wave length 2537 Å. gives a quantum yield based on bromine produced of 4×10^{-3} . The principal products other than bromine are methane and carbon monoxide.

2. In the presence of nitric oxide, the quantum yield based on nitrosyl bromide produced is about unity. The presence of free nitrogen, other oxides

of nitrogen, and carbon monoxide show the reaction to be complex. It is, however, necessary to conclude that the low yield in pure methyl bromide photolysis is due to the back reaction.

3. In presence of silver, the quantum yield based on methane production is again about unity. Methane and carbon monoxide are the sole products.

4. The absence of ethane, denying the possibility of recombination of methyl radicals, is accounted for on the basis of about 6 kcal. difference in the energy of activation of ethane and methane production. It is shown that if ethane results from reaction of a methyl radical with methyl halide, approximately equivalent amounts of methane and ethane are to be expected from methyl iodide as found, but no ethane from methyl bromide.

5. Increase of temperature up to 250° does not change the above findings qualitatively. From the data at room temperature and at 100° , the energy of activation of methane production under the prevailing experimental conditions is found to be 6.6 kcal.

6. The presence of carbon monoxide is shown probably to be due to reaction of CH_2Br radicals with silica.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Influence of Hydroxyl Ion Concentration on the Autoxidation of Hydroquinone

BY JOHN R. GREEN AND GERALD E. K. BRANCH

Confusion exists in the literature regarding the exact kinetic expression for the rate of oxidation of hydroquinone by oxygen in alkaline solutions. LaMer and Rideal¹ measured the rate of absorption of oxygen in borate buffer solutions. Their experiments indicated that the rate was proportional to the first power of the hydroquinone concentration, to the first power of the oxygen pressure, and to the three-halves power of the hydroxyl ion concentration. Later, Reinders and Dingemans² repeated the investigation with both phosphate and borate buffers. Their results differed from those of LaMer and Rideal in that their experimentally deduced rate law contained the sec-

(1) Victor K. LaMer and Eric K. Rideal, *THIS JOURNAL*, **46**, 223 (1924).

(2) W. Reinders and P. Dingemans, *Rec. trav. chim.*, **53**, 209 (1934).

ond power of the hydroxyl ion concentration, instead of the three-halves power. It was with the object of deciding which of the laws is correct or whether either is correct that the present investigation was undertaken.

Experimental

The apparatus consisted of a gas buret and a water-jacketed reaction vessel attached to a shaker. These parts were connected by a pair of ground glass joints and a set of spiralled tubes. The latter permitted our shaking the reaction vessel to keep the contents in a froth without disturbing the buret. The temperature in the reaction vessel was kept constant by a flow of water from a thermostat through the jacket.

The buffer solution was poured into the reaction vessel. A tube with a flattened bottom containing the hydroquinone and a little water was placed upright in the reaction vessel. The buret was attached and the whole system evacuated and then filled with oxygen at the desired pressure. When the shaker was started, the reagents were mixed automatically and the absorption of oxygen began.

The buret was fitted to a device that permitted mercury to enter. This flow of mercury was regulated so that during a run the pressure in the system was constant. The constancy of pressure was shown on a water manometer between the buret and the large source of oxygen from which the system was originally filled.

The quantity of oxygen absorbed during any run was equivalent to only a small fraction of the hydroquinone. The rate of absorption was essentially constant during any run, and all variations in the rate were obtained by altering the initial conditions.

The apparatus described above gave reproducible results over a limited range of absorption rates. The accuracy was estimated as better than 5% for rates between 0.3 and 3.0 cc. per minute.

The hydroquinone used was Eastman Kodak Co. product, a pure white crystalline material melting at 170°. No further purification was made.

The buffers were prepared from mono-potas-

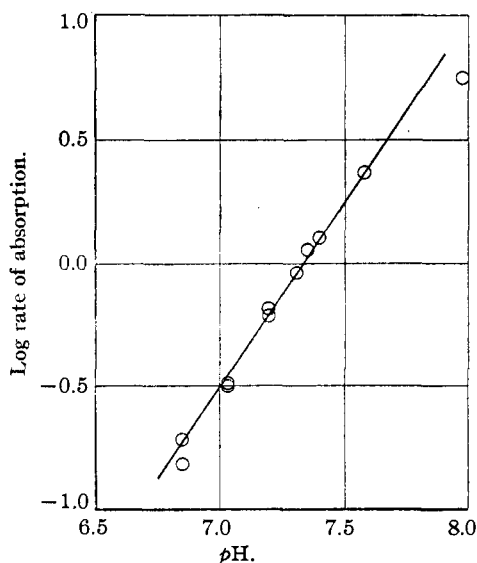


Fig. 1.—Logarithm of the rate of absorption of oxygen plotted against pH .

sium phosphate and di-potassium phosphate, the total phosphate being 1 *M*. Their ionic strengths were made 3 with sodium chloride. Their pH 's were measured with a standard hydrogen electrode before the addition of hydroquinone, and were such that they could not be appreciably changed by the proportions of hydroquinone added. The pH range was such that no appreciable change in the concentration of undissociated hydroquinone was produced by reaction with the buffer.

The Rate Law

Both previous investigations agree that the reaction is first order with respect to oxygen and hydroquinone. We therefore did not vary the oxygen pressure and the hydroquinone concentration except in a couple of preliminary runs. These showed the rate to be first order with respect to oxygen pressure and almost but not quite first order with respect to hydroquinone.

Our measurements on the variation of rate with pH are given in Table I. These results obtained with the same buffer and over the same range of pH used by Reinders and Dingemans agree with the three-halves order found by LaMer and Rideal at a higher pH range (7–8.56). This is shown in

TABLE I
RATE OF ABSORPTION OF OXYGEN
650 mm. O_2 total pressure; 0.1 *M* hydroquinone; 1.0 *M* phosphate buffer with ionic strength of 3

pH	Cc. O_2 /min.	pH	Cc. O_2 /min.
6.85	0.153	7.31	0.913
6.85	.191	7.35	1.148
7.03	.316	7.35	1.142
7.03	.324	7.39	1.280
7.19	.610	7.58	2.330
7.19	.649	7.97	5.625

the figure in which the logarithm of the rate of absorption is plotted against the pH , and a line with the theoretical slope (1.5) of a three-halves order reaction is drawn. Except for the slowest and the fastest reaction, the points fall fairly well on this line, but they would not agree with a line having a slope of 2.0.

It must be noted that unless the present results are taken in conjunction with those of LaMer and Rideal, they do not extend over a sufficient range of pH to show that the reaction is readily three-halves order with respect to hydroxide ion. The authors' results would also fit, though not very well, simultaneous first and second order reactions. The rate law

$$-dO_2/dt = k_1(O_2)(C_6H_6O_2)(OH^-) + \frac{K_2(O_2)(C_6H_6O_2)(OH^-)^2}{K_2(O_2)(C_6H_6O_2)(OH^-)^2}$$

can become approximately three-halves order with respect to OH^- over a limited pH range.

An approximate three-halves order reaction over a limited range of pH in the neighborhood of pH 7 can also be obtained on the assumption that at the concentration of buffer used, the main reaction is one between oxygen and the first ion and hydroquinone catalyzed by the second ion of phosphoric acid. The rate law would be

$$-\frac{1}{(O_2)(C_6H_6O_2)} \frac{d(O_2)}{dt} = \frac{k_1 T(OH^-)}{1 + K(OH^-)} + \frac{k_3 T(OH^-)^2}{1 + K(OH^-)} + k_8(OH^-)^2$$

where T is the total phosphate concentration, K the second dissociation constant of phosphoric acid divided by K_w , with the first and third terms on the right-hand side of the equation negligible with respect to the middle term.

However, if we can assume that our results can be taken in conjunction with those of LaMer and Rideal, the three-halves order persists over so long a pH range (7-8.56) that it must be taken as genuine.

Mechanism.—A mechanism for a reaction cannot be formulated on the rate law alone. Such factors as applicability to the mechanisms of closely related reactions, and the plausibility of the steps composing the mechanism should be taken into account. Thus one would expect the mechanism for the autoxidation of hydroquinone to be similar to that for the autoxidation of catechol, at least as far as the oxygen and the phenol are concerned. The latter is a chain reaction whose rate law is $-d(O_2)/dt = k(O_2)(C_6H_6O_2)(OH^-)$ in the range of pH where the phenol is only slightly ionized.³ If similar mechanisms are assumed for both reactions, the difference in the rate laws for the two phenols, with respect to hydroxide ion concentration, can be attributed to differences in the states of ionization of the phenols in corresponding reactions.

The simplest type of chain mechanism that would give a rate law first order with respect to oxygen and the phenol, but which could contain the three-halves or first power of the hydroxide ion, is one in which the chain-continuing process is first order with respect to oxygen and the phenol, while the chain terminating step is the same order

with respect to oxygen and the phenol as the initial step, and second order with respect to the intermediate whose alternate removal and reformation are the steps of the chain-continuing process. The rate law for this type of mechanism is $-d(O_2)/dt = k(O_2)(C_6H_6O_2)(OH^-)^{1/2m + n - 1/2p}$ where m , n and p are the states of ionization of the phenol in the initial, chain-continuing and chain terminating reactions, respectively. With the proper choices of m , n and p this rate law agrees with those found experimentally for the autoxidations of polyhydric phenols. The suggested type of mechanism can be taken as a working hypothesis, provided a plausible set of constituent reactions can be found.

The frequency of chain mechanisms in autoxidations of organic substances suggests that the reactions of oxygen and substrate can form a class of substances capable, in general, of acting as catalysts for autoxidations. Peroxy radicals of the general formula ROO would fit these requirements. In these radicals the shift of the odd electron from one oxygen atom to the other leads to resonance and a consequent stabilization. This type of resonance exists to a still greater extent in oxygen, which has two odd electrons. Hence the removal of these radicals by their combination with themselves or with oxygen is not effective. The radicals would however oxidize the substrate, either by preliminary reversible addition to oxygen followed by action on a substrate molecule, or by a three-center reaction with the substrate followed by addition of the resulting radical to oxygen. In either case the final products include a peroxy radical, and a chain mechanism results.

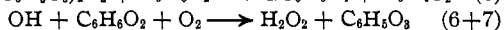
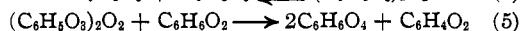
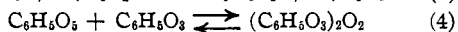
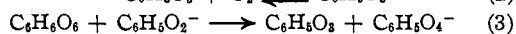
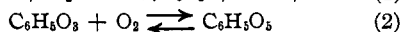
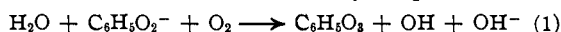
In the particular case of the autoxidation of the polyhydric phenols the rate laws show that if the peroxy radical theory is true, the substrate or both oxygen and substrate are involved in a follow reaction with two radicals. Since the reactants have an even number of electrons, radicals can be removed in this process. A likely mechanism for this chain terminating reaction is the reversible combination of oxygen and two molecules of the radical followed by reduction of the resulting peroxide by the substrate.

Oxygen acting as a substituting radical in a three-center reaction with the substrate is a plausible mechanism for the formation of peroxy radicals in the absence of light or extraneous catalysts. The initiation of autoxidation chains by light or

(3) M. A. Joslyn and G. E. K. Branch, *THIS JOURNAL*, **57**, 1779 (1935).

one-unit oxidizing agents can be readily explained on the peroxy-radical theory.

To make the above theory more concrete we append the following hypothetical series of reactions for the autoxidation of hydroquinone:



Assuming equilibrium to be nearly reached in those steps given as reversible, the rate law for this series of reactions is $-d(\text{O}_2)/dt = k(\text{CO}_2)(\text{C}_6\text{H}_5\text{O}_2)(\text{OH}^-)^{3/2}$. By using the first ion $\text{C}_6\text{H}_5\text{O}_2^-$ in reaction 5 the mechanism is applicable to the autoxidation of catechol.

The product of the reaction $\text{C}_6\text{H}_5\text{O}_4$ or its ion

can be taken as either a definite substance (Reinders and Dingemans) or as an equivalent mixture of quinone and hydrogen peroxide (LaMer and Rideal). In either case complex condensation products or quinhydrone, depending on the pH of the solution, will be formed by reactions with hydroquinone.

Summary

The expression $(-d(\text{O}_2)/dt = k(\text{O}_2)(\text{C}_6\text{H}_5\text{O}_2)(\text{OH}^-)^{3/2})$ obtained by LaMer and Rideal for the rate law of the autoxidation of hydroquinone has been confirmed.

A chain mechanism has been proposed for the reaction. By a change of the state of ionization of the phenol in one of the steps, this mechanism is applicable to the autoxidation of catechol.

BERKELEY, CALIF.

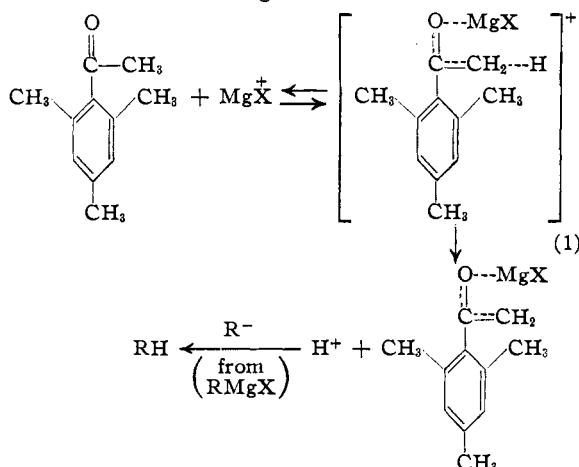
RECEIVED JUNE 11, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Resonance and the Hindered Carbonyl-Grignard Reaction. I

BY RICHARD T. ARNOLD, HAROLD BANK AND R. WINSTON LIGGETT¹

It is well known that many sterically hindered ketones (such as acetomesitylene) react with the Grignard reagent to form enolates and hydrocarbons.^{2,3,4} This reaction is not necessarily preceded by simple enolization of the ketone. In fact, a more probable mechanism involves the coordination of a solvated halomagnesium cation (MgX^+) with the carbonyl oxygen atom followed by the direct ionization of a proton from the α -carbon atom according to the scheme below.³



(1) Du Pont Post-doctorate Fellow, 1941-1942.

(2) Smith and Guss, *THIS JOURNAL*, **59**, 804 (1937).

(3) Gilman and Jones, *ibid.*, **63**, 1162 (1941).

(4) Fuson, Fugate and Fisher, *ibid.*, **61**, 2362 (1939).

The thermodynamic stability of such resonating ions as allyl, crotyl, benzyl, etc., should allow them to act qualitatively like the proton in the above type of reaction.

To test this hypothesis we have, for convenience, studied the reaction between allylic esters with sterically hindered carbonyl groups and the Grignard reagent. It was predicted that the reaction between phenylmagnesium bromide and allyl β -isodurylate should take the course shown by equation (2).

Actually allylbenzene was isolated in 67-70% yield and the magnesium halocarboxylate almost quantitatively. *o*-Tolylmagnesium bromide gave *o*-allyltoluene in comparable yield.

This type of cleavage is important only when normal addition to the carbonyl group is exceedingly slow or impossible. Allyl benzoate reacts with phenylmagnesium bromide to give triphenylcarbinol (86%) and small amounts of allylbenzene.⁵

We have now shown that one *o*-methyl group does not greatly interfere with normal addition. Thus allyl *o*-toluate with the Grignard reagent gives the carbinol (68%) and an unresolvable mixture.

In the aliphatic series the reaction of allyl tri-

(5) Gilman and Robinson, *Bull. soc. chim.*, **45**, 636-641 (1929).