The Mechanism of the Periodate Oxidation of Aromatic Systems. I. A Kinetic Study of the Periodate Oxidation of Hydroquinone and p-Methoxyphenol in Acidic Solution[1]

BY E. T. KAISER AND S. W. WEIDMAN[2]

The kinetics of the oxidation at pH 1 of hydroquinone and its monomethyl ether by periodate to form p-benzoquinone have been thoroughly examined by spectrophotometric means. The oxidation reactions show a first-order dependence on the substrate concentration and a first-order dependence on the total periodate concentration. No evidence for the formation of appreciable concentrations of intermediates was found even with stopped-flow methods.

Introduction

The oxidative cleavage of glycols by periodic acid was reported by Malaprade[3] in 1928 (reaction 1).

$$R_2-\underset{\underset{OH}{|}}{C}---\underset{\underset{OH}{|}}{C}-R_2' + HIO_4 \longrightarrow$$

$$R_2CO + R_2'CO + HIO_3 + H_2O \quad (1)$$
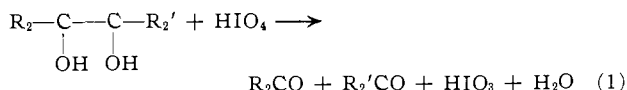
Pennington and Ritter[4] found that periodic acid also oxidizes *ortho*- and *para*-aromatic diols and their monoethers to the corresponding quinones (reactions 2 and 3).

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$$(3)$$
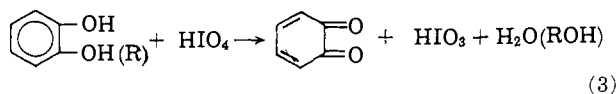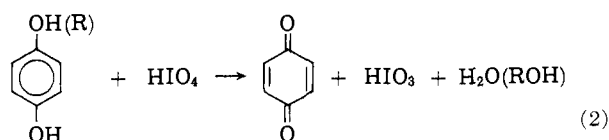
The kinetics of periodate oxidation of 1,2-glycols have been studied extensively.[5-12] Kinetic and spectrophotometric evidence[11] has suggested that (for most simple glycols) a glycol–periodate complex is first formed in a rapid and reversible step. The step is then followed by a rate-determining decomposition to products (reaction 4).

$$glycol + periodate \underset{}{\overset{K}{\rightleftarrows}} complex \overset{k}{\underset{slow}{\longrightarrow}} products \quad (4)$$
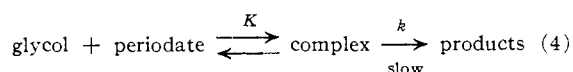
Using this assumption, the equilibrium constant for complex formation and the rate constant for its decomposition could be calculated from the kinetic data. From the effect of pH on the equilibrium constant, K, and on the rate constant, k, it was concluded that the complex was I or a hydrated form, II.[10,11]
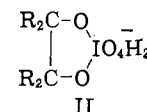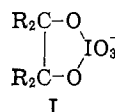
An oxygen-18 tracer study[13] of the oxidation of pinacol showed that the oxygen atoms of the acetone produced were those of the original glycol. This evidence suggested that the intermediate is formed by electrophilic attack of the periodate on the glycol oxygens.

The periodate oxidations of aromatic diols and their monoethers have heretofore not been subjected to thorough kinetic investigation. The only reported studies of a mechanistic nature are those in which the reactions were carried out in unbuffered H_2O^{18}.[14]

The work described in the present paper was undertaken in order to determine the mechanism of periodate oxidation of aromatic diols and its relationship to that postulated for the 1,2-glycols. It is reasonable to suppose that an intermediate diester similar to I or II above might be formed during the reaction of periodate with catechol and a monoester in the cases of hydroquinone and o- and p-methoxyphenol. Alternatively, other mechanisms (such as free radical pathways) less related to the glycol oxidation process might operate.

Experimental

Materials.—Hydroquinone was obtained from Matheson Coleman and Bell and was recrystallized from toluene; m.p. 172–173° (lit.[15] 172.3°). p-Methoxyphenol was obtained from Matheson Coleman and Bell and was recrystallized from Skelly F; m.p. 54.8–56.9° (lit.[15] 53°). Sodium metaperiodate was obtained from Fisher Scientific Co. (Fischer Certified Reagent) and was used without further purification. Stock solutions of periodate were analyzed by the usual method.[16] The solutions of periodate used in the kinetic studies were made from diluted aliquots of these stock solutions and were checked by their ultraviolet spectra.[17,18] All solutions were protected from light. Perchloric acid solutions of pH 1.0 were diluted from concentrated perchloric acid (Baker and Adamson, reagent grade). Sodium perchlorate (hydrated) was obtained from the G. F. Smith Chemical Co. and was dried before use at 140°. The water used was twice distilled, the last time from alkaline permanganate. A Beckman Model G pH meter was used for pH measurements.

Kinetic Measurements.—The periodate oxidations were followed spectrophotometrically directly in a Cary 14 recording spectrophotometer. The wave length chosen for the kinetic studies was that at which the difference of molar absorptivities

(1) The initial phases of the work reported here were performed in the Department of Chemistry, Washington University, St. Louis, Mo. This research was supported in part by a Du Pont Summer Research Grant and by the Block Fund of the University of Chicago.

(2) Predoctoral Fellow of the National Aeronautics and Space Administration.

(3) L. Malaprade, Compt. rend., **186**, 382 (1928).

(4) D. E. Pennington and D. M. Ritter, J. Am. Chem. Soc., **68**, 1391 (1946); **69**, 187 (1947).

(5) C. C. Price and H. Kroll, ibid., **60**, 2726 (1938).

(6) C. C. Price and M. Knell, ibid., **64**, 552 (1942).

(7) F. R. Duke, ibid., **69**, 3054 (1947).

(8) J. E. Taylor, ibid., **75**, 3912 (1953); **77**, 2656 (1955).

(9) F. R. Duke and V. C. Bulgrin, ibid., **76**, 3803 (1954).

(10) G. J. Buist and C. A. Bunton, J. Chem. Soc., 1406 (1954); 4580 (1957).

(11) G. J. Buist, C. A. Bunton, and J. H. Miles, ibid., 4567, 4575 (1957); 743 (1959).

(12) V. C. Bulgrin and G. Dahlgren, Jr., J. Am. Chem. Soc., **80**, 3883 (1958).

(13) C. A. Bunton and V. J. Shiner, Jr., J. Chem. Soc., 1593 (1960).

(14) E. Adler, I. Falkehag, and B. Smith, Acta Chem. Scand., **16**, 529 (1962).

(15) "Handbook of Chemistry," N. A. Lange, Handbook Publishers, Inc., Sandusky, Ohio, 1952.

(16) E. L. Jackson, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

(17) C. E. Crouthamel, H. V. Meek, D. S. Martin, and C. V. Bank, J. Am. Chem. Soc., **71**, 3031 (1949).

(18) C. E. Crouthamel, A. M. Hayes, and D. S. Martin, ibid., **73**, 82 (1951).

between the reactants and products caused the maximum change in absorbance during the kinetic runs. This occurred at 246.5 mμ, the wave length of maximum absorption of p-benzoquinone (ϵ 2.16 $\times$ 10^4 M^{-1} cm.$^{-1}$). The absorbances at infinite time were in good agreement with those calculated from the concentrations and molar absorptivities of reactants and products (determined beforehand). The reactions were initiated by the addition with a micropipet of one reactant to the aqueous solution of the other reactant which had previously been thermostated in a quartz cuvette (1-cm. path length) in the cell compartment of the Cary 14. Most kinetic runs were made with the substrate held at 10^{-5} M while the periodate concentration was varied from 1–20 $\times$ 10^{-4} M. Typical first-order plots of the kinetic data are shown in Fig. 1.

Kinetic studies at higher periodate concentrations required the use of a stopped-flow apparatus since the rates of reaction became too fast to measure accurately with the Cary. An apparatus very similar to that described by Dulz and Sutin[19] was used. In these runs hydroquinone or its monomethyl ether were held at 5 $\times$ 10^{-3} M while the periodate concentration was varied from 5–15 $\times$ 10^{-2} M. Since the apparatus was equipped with a visible light source the reactions were followed by observing the p-benzoquinone formation at 425 mμ with a Beckman Model DU spectrophotometer.

Analysis for Methanol Produced in the Oxidation of p-Methoxyphenol.—In order to determine the yield of methanol produced in the oxidation of p-methoxyphenol at pH 1, analysis of a reaction mixture was carried out by gas chromatography. p-Methoxyphenol (0.1 M) was allowed to react with $NaIO_4$ (0.3 M) at pH 1, and the resultant solution was analyzed on a 20% diethylene glycol succinate column in an Aerograph A-600-B vapor phase chromatograph. The peak area was compared to that obtained for a standard methanol–water solution. The yield of methanol measured in several determinations was essentially quantitative.

Results and Discussion

At periodate concentrations which are high with respect to the substrate the sequence outlined in reaction 4 above leads to the following expression for the rate of reaction[7] where (P) is the concentration of un-

$$\text{rate} = \frac{kK(P)}{K(P) + 1}(S) \qquad (5)$$

coordinated periodate, (S) is the total substrate concentration, k is the rate constant for the breakdown of the complex to products, and K is the equilibrium constant for complex formation. If, instead, the substrate concentration is in considerable excess over the periodate, a related expression is obtained with (P) and (S) reversed (P now represents total P, and S represents uncoordinated S concentration).

Thus, with (P) in excess, first-order kinetics are obeyed at a given (P) concentration where k_1 is the first-order rate constant.

$$k_1 = \frac{kK(P)}{K(P) + 1} \qquad (6)$$

Equation 6 may be rewritten

$$1/k_1 = 1/k + 1/kK(P)$$

Then if a plot of $[1/k_1]$ on the ordinate against $[1/(P)]$ on the abscissa is made, a straight line is obtained with a positive intercept of $[1/k]$ on the ordinate and a slope of $[1/kK]$.

Kinetic Results.—The kinetic data for the periodate (in excess) oxidations at pH 1.0 are summarized in Table I. In Fig. 2 and 3 the reciprocals of the first-
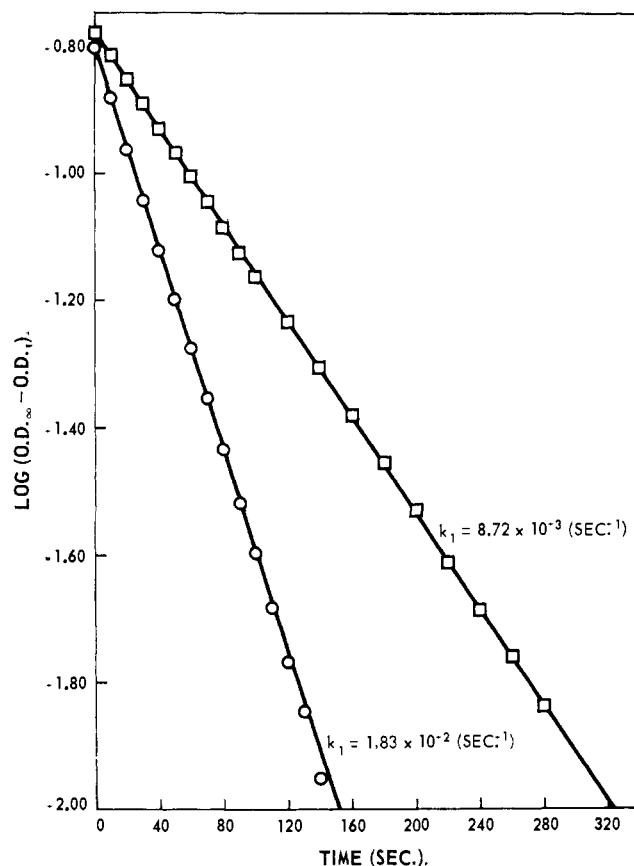
(19) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963). We wish to thank Professor J. Halpern for permission to use his stopped-flow apparatus and Dr. J. Candlin for helping us make our measurements.

Fig. 1.—First-order plots for the reaction of periodate with hydroquinone and p-methoxyphenol at 25.0°: O, 3 $\times$ 10^{-4} M $NaIO_4$, 10^{-5} M hydroquinone; $\square$, 4 $\times$ 10^{-4} M $NaIO_4$, 10^{-5} M p-methoxyphenol.

order rate constants (the values used are the average of 3–6 determinations at each concentration) are plotted against the reciprocals of the periodate concentration at half reaction. All of the straight lines in the figures pass through the origin. The absence of a measurable positive intercept on the $1/k_1$ axis can be interpreted as an indication that the oxidation reactions follow second-order kinetics or, alternatively, that the rate constant for the breakdown of an intermediate complex is very large and the equilibrium constant for its formation is small.

TABLE I

KINETIC DATA FOR THE PERIODATE OXIDATION OF HYDROQUINONE AND p-METHOXYPHENOL AT pH 1.0

| $NaIO_4$, | Hydroquinone,[a,c] | | p-Methoxyphenol,[b,c] | |
| | $10^3 k_1$, sec.$^{-1}$ | | $10^3 k_1$, sec.$^{-1}$ | |
10^4 M	15.1°	25.0°	15.1°	25.0°
0.951	3.08	5.88	...	...
1.15	3.80	7.38	...	...
1.35	4.20	8.42	...	...
1.55	5.12	9.90	...	...
1.95	6.46	12.2	2.19	4.21
2.35	7.86	14.7	...	5.06
2.95	9.82	18.4	3.42	6.50
3.95	13.0	24.7	4.50	8.72
4.95	16.5	...	5.69	10.8
6.96	22.4	43.6	8.22	15.3
9.96	33.8	...	11.8	22.2
20.0	...	...	24.3	...

[a] [Hydroquinone] = 9.96 $\times$ 10^{-6} M. [b] [p-Methoxyphenol] = 9.99 $\times$ 10^{-6} M. [c] The values of k_1 given at each periodate concentration are generally the average of 3–6 determinations.
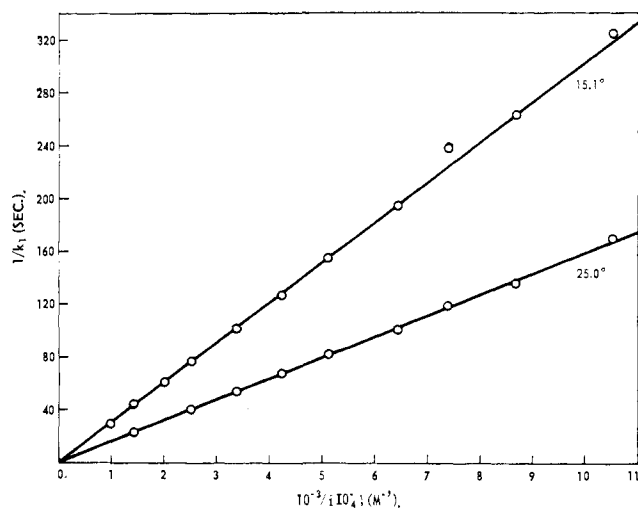
Fig. 2.—Dependence of reciprocal of first-order rate constant on reciprocal of periodate concentration; substrate, hydroquinone (9.96×10^{-6} M).
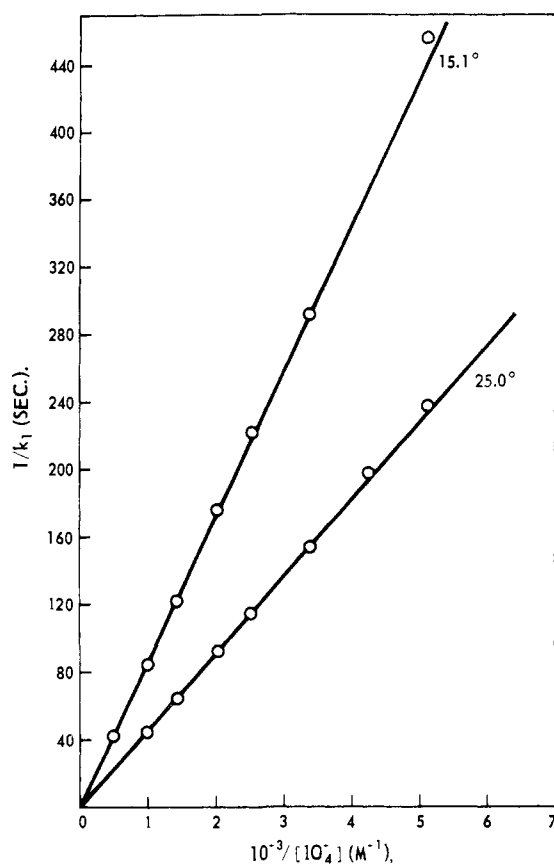

Fig. 3.—Dependence of reciprocal of first-order rate constant on reciprocal of periodate concentration; substrate, p-methoxyphenol (9.99×10^{-6} M).

In the study of the periodate oxidation of 1,2-glycols, apparent second-order kinetics are observed if the reactants are sufficiently low in concentration for the term $K(P)$ in eq. 6 to become negligible compared to unity. Then $k_2 = kK$ where k_2 is the observed second-order rate constant.

It seemed possible to us that at reactant concentrations of 10^{-5} to 10^{-4} M we observed no positive intercepts on the ordinates of Fig. 2 and 3 because we might be operating under limiting second-order reaction conditions. Therefore, it was conceivable that when we increased the reactant concentrations, kinetic evidence
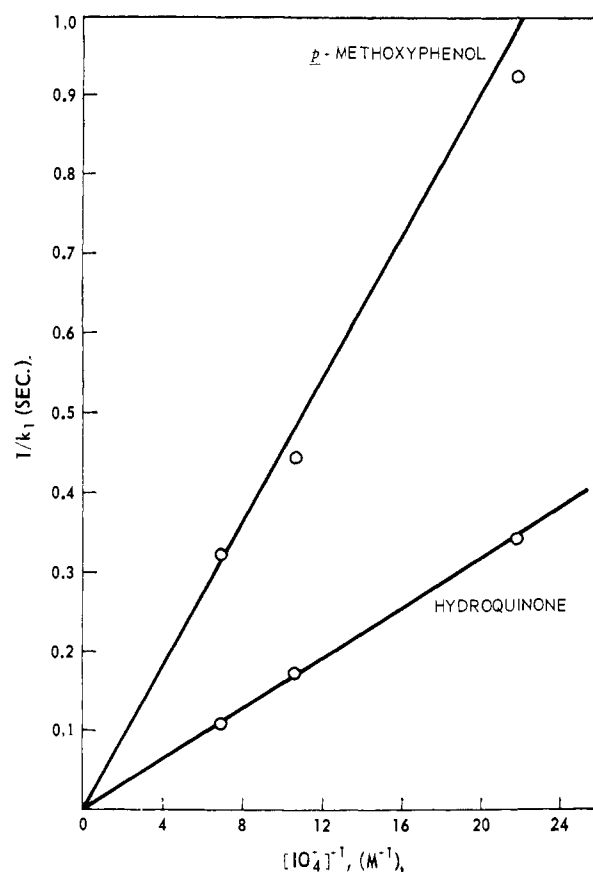

Fig. 4.—Dependence of reciprocal of first-order rate constant on reciprocal of periodate concentration at 25.0°; [substrate] = 5×10^{-3} M.

for a detectable intermediate complex could be obtained. In order to test this possibility we studied the kinetics of oxidation at 5×10^{-3} M substrate and 5-15 $\times 10^{-2}$ M periodate at pH 1 and at a temperature of 25.0° with a stopped-flow apparatus. We had previously established that the addition of salt in concentrations up to 3 M at pH 1 had a negligible effect on the rates of oxidation of both hydroquinone and p-methoxyphenol. Hence, no complications due to a salt effect were anticipated at the high periodate concentrations.

The results of the stopped-flow measurements are given in Table II. In Fig. 4 [$1/k_1$] values are plotted

TABLE II

KINETIC DATA FROM STOPPED-FLOW RUNS AT pH 1 AND 25.0°

NaIO₄,	—Hydroquinone[a,b]—		—p-Methoxyphenol[a,b]—	
10^2 M	k_1, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$	k_1, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
4.62	2.91	63.1	1.08	23.4
9.46	5.78	61.1	2.25	23.8
14.6	9.14	62.8	3.10	21.3

[a] [Hydroquinone] = [p-methoxyphenol] = 5×10^{-3} M. [b] The values of the rate constants given at each periodate concentration are the average of 4–6 determinations.

against [$1/(P)$]. The lines drawn in Fig. 4 are extrapolated from those of the low reactant experiments illustrated in Fig. 2 and 3. The points at the high reactant concentrations fall reasonably close to these lines, indicating good agreement between kinetic measurements determined over very wide concentration ranges (1×10^{-5} to 5×10^{-3} M for hydroquinone, 1×10^{-4} to 1.5×10^{-1} M range for periodate).

TABLE III

SUMMARY OF KINETIC DATA

Substrate	Temp., °C.	k_2, M^{-1} sec.$^{-1}$	E_a. kcal./mole	ΔH^*, kcal./mole	ΔS^*, e.u.	ΔF^*, kcal./mole
Hydroquinone	15.1	32.9 ± 0.2				
	25.0	62.8 ± .2	11.2 ± 0.2	10.6 ± 0.2	−14.7 ± 0.7	14.9 ± 0.4
p-Methoxyphenol	15.1	11.6 ± .1				
	25.0	21.9 ± .1	11.0 ± 0.2	10.4 ± 0.2	−17.5 ± 0.7	15.6 ± 0.4

If the interpretation of the reaction kinetics observed at high periodate concentrations as being second order is valid, then similar rate behavior should be found when the oxidations are run with substrate concentrations in excess over periodate. Under these conditions, however, the competing oxidation of the hydroquinone by the iodate which is formed during the course of the reaction becomes a significant complication. The second-order rate constant for this oxidation reaction determined at 10^{-5} NaIO$_3$ and 1–5 × 10^{-4} M hydroquinone is 8.6 M^{-1} sec.$^{-1}$.
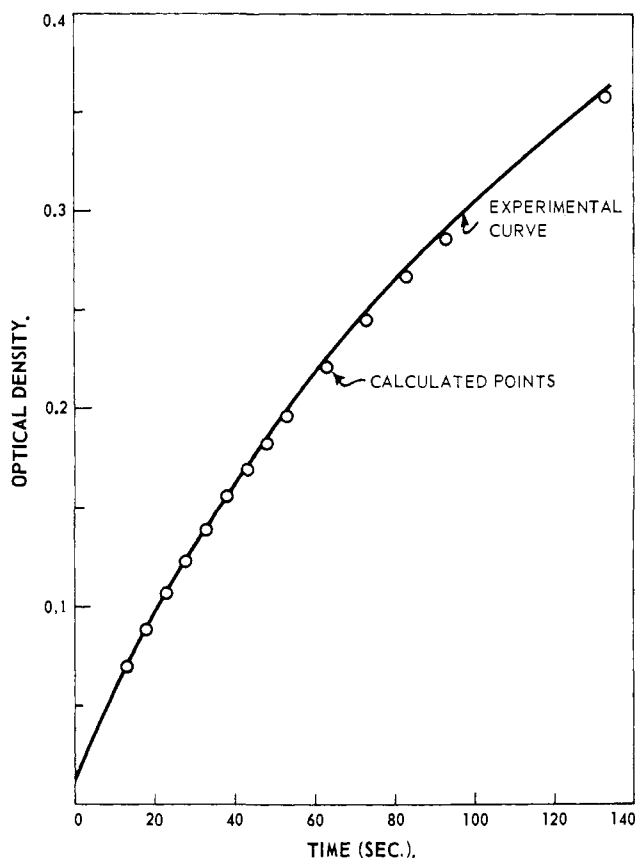

Fig. 5.—Change in optical density with time at 246.5 mμ for the reaction of 4 × 10^{-4} M hydroquinone with 10^{-5} M sodium periodate.

Using the previously found rate constants for periodate and iodate oxidation of hydroquinone together with the known extinction coefficients of the reactants and products, the change in optical density with time could be predicted for the runs at low periodate concentration.[20] These predicted values agreed well with the experimentally obtained curve as illustrated in Fig. 5. Thus, the kinetic parameters obtained with periodate in excess also hold when hydroquinone is in excess as required by the second-order rate law.

The reaction of iodate with p-methoxyphenol is much slower than with hydroquinone. Hence, kinetic

(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 166–171.

runs with p-methoxyphenol in excess over periodate were usually unaffected by competing iodate oxidation for a substantial part of the reaction, and they obeyed first-order kinetics. Second-order rate constants calculated from these data agreed with the value determined from the experiments with periodate in excess to within 10%.

Kinetic measurements made with equivalent concentrations of reactants were also complicated by iodate oxidation. However, satisfactory second-order rate constants for the oxidation of both substrates could be calculated from the initial phase of the reactions.

pH Effects in Acidic Solution and Mechanistic Considerations.—In order to understand the process by which periodate oxidizes hydroquinone and its monomethyl ether at pH 1, it is necessary to know what species of periodate are active in these reactions. Therefore, the pH–rate profiles for the oxidation of these substrates have been determined in the pH range 0–4. The second-order rate constants, k_2, which were observed were analyzed in terms of the kinetic contributions made by the un-ionized and monoionized forms of periodate.[21] At pH 1 periodate exists 81% as the un-ionized species and 19% as the monoionized form, and at pH 4 it is 0.4% un-ionized and 99.6% monoionized. When the values of k_2 found in the oxidation reactions at pH 1 and pH 4, together with the percentages of the un-ionized and monoionized species, were substituted into the equation below, values of k_a and k_b could be calculated.[22]

$$k_2(\text{total NaIO}_4) = k_a(\text{H}_5\text{IO}_6) + k_b[(\text{IO}_4^-) + (\text{H}_4\text{IO}_6^-)] \quad (7)$$

At 25.0°, k_a is 71.7 M^{-1} sec.$^{-1}$ and k_b is 24.2 M^{-1} sec.$^{-1}$ for hydroquinone while k_a is 25.5 M^{-1} sec.$^{-1}$ and k_b is 6.65 M^{-1} sec.$^{-1}$ for p-methoxyphenol. The validity of eq. 7 was tested by calculating predicted values of k_2 in the pH range 0–4 and comparing them to those observed. As can be seen from Tables IV and V,

TABLE IV

VARIATION OF THE SECOND-ORDER RATE CONSTANT FOR THE OXIDATION OF HYDROQUINONE WITH pH AT 25.0°

pH	Obsd. k_2,[a] M^{-1} sec.$^{-1}$	Calcd. k_2,[b] M^{-1} sec.$^{-1}$
0.105	75.3	70.4
0.78	65.6	66.0
1.00	62.8	62.8
2.01	39.5	38.4
2.97	24.6	26.3
4.05	24.5	24.4

[a] Except for the pH 1 data, all observed k_2 values are the result of 3 runs at each pH. [b] k_2 is calculated from eq. 9 with k_a = 71.7 M^{-1} sec.$^{-1}$ and k_b = 24.2 M^{-1} sec.$^{-1}$ for hydroquinone.

(21) V. J. Shiner, Jr., and C. R. Wasmuth, J. Am. Chem. Soc., 81, 27 (1959).

(22) These calculations made use of data obtained at pH 1 since more runs were carried out there than at any other pH and of results found at pH 4 because at this pH periodate is largely in the monoionized form.
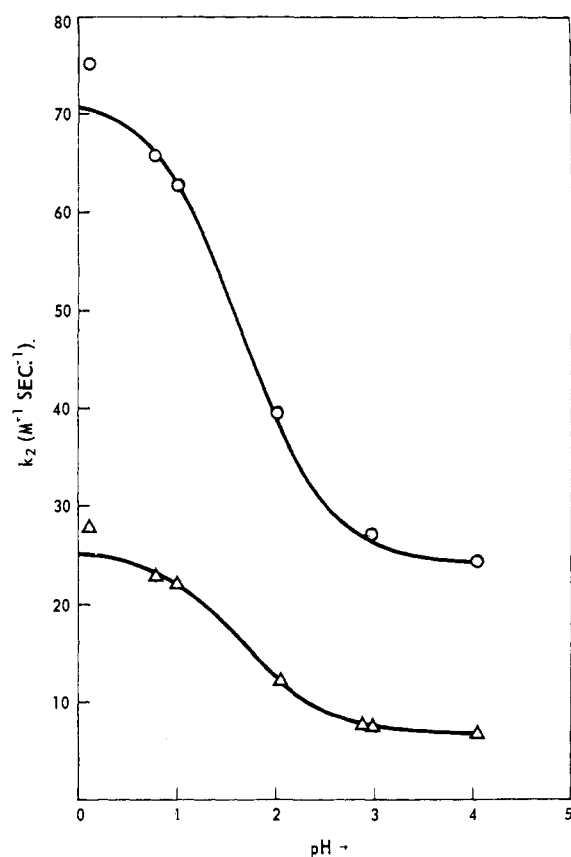
Fig. 6.—Dependence of second-order rate constant on pH at 25.0: O, experimental points for hydroquinone; △, experimental points for p-methoxyphenol.

the agreement between calculated and observed values is good. Our results are depicted graphically in Fig. 6, and they lead to the conclusion that both the un-ionized and monoionized forms of periodate are active in oxidizing hydroquinone and p-methoxyphenol.

TABLE V

VARIATION OF THE SECOND-ORDER RATE CONSTANT FOR THE OXIDATION OF p-METHOXYPHENOL WITH pH AT 25.0°

pH	Obsd. k_2,[a] M^{-1} sec.$^{-1}$	Calcd. k_2,[b] M^{-1} sec.$^{-1}$
0.105	27.9	25.0
0.78	22.9	23.2
1.00	21.9	22.0
2.04	12.9	12.0
2.89	7.83	7.67
2.97	7.65	7.48
4.05	6.76	6.72

[a] Except for the pH 1 data, all observed k_2 values are the result of 3 runs at each pH. [b] k_2 is calculated from eq. 9 with $k_a = 25.5\ M^{-1}$ sec.$^{-1}$ and $k_b = 6.65\ M^{-1}$ sec.$^{-1}$ for p-methoxyphenol.

The kinetic results obtained for the oxidation of hydroquinone and p-methoxyphenol contrast markedly with those previously reported for aliphatic glycols. We have found no evidence for the formation of a kinetically detectable intermediate in the oxidation of hydroquinone and its monomethyl ether at pH 1 even with stopped-flow methods. Our results are best interpreted in terms of second-order kinetics. However, this does not rule out the possibility that substrate–periodate complexes are intermediates in oxidation at pH 1 if their formation rather than their decomposition to products is rate controlling.
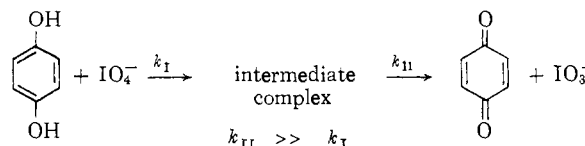
Further evidence concerning the mechanism of the periodate oxidation of aromatic diols and their mono ethers is being actively sought in our laboratory.

The Reduction of Multiple Bonds by Low-Valent Transition Metal Ions. The Homogeneous Reduction of Acetylenes by Chromous Sulfate

BY C. E. CASTRO AND R. D. STEPHENS

The homogeneous reduction of acetylenes by chromous sulfate in water or aqueous dimethylformamide at room temperature yields trans-olefins in high yields. The stoichiometry, stereospecificity, kinetics, and reactivities of the acetylenes toward Cr^{+2} are in accord with a mechanism which involves a rate-determining attack of Cr^{+2} upon a 1:1 acetylene–Cr^{+2} complex.

Introduction

Low-valent transition metal species are present in Ziegler–Natta polymerization catalysts[1] and active sites in these systems have been located at a transition metal center.[2] Moreover, transition metal complexes are well known to play a key role in many enzymatic transformations in which a valence change of the metal species occurs.[3] Yet, much is to be learned about the nature of the interaction of low valent ions with organic structures in less complicated environments.

As part of a study of the homogeneous reduction of organic molecules by transition metal ions we have found the acetylenic bond to be one of the most effective multiply bonded structures to accomplish the oxidation of Cr(II) to Cr(III).[4]

The reduction of acetylene to ethylene by an am-

(1) M. L. Cooper and J. B. Rose, J. Chem. Soc., 795 (1959); C. Beerman and H. Bestian, Angew. Chem., 71, 618 (1959).

(2) W. L. Carrick, F. J. Karol, G. J. Karapinka, and J. J. Smith, J. Am. Chem. Soc., 82, 1502 (1960); W. L. Carrick, et al., ibid., 82, 5319 (1960), et seq.

(3) J. S. Fruton and S. Simonds, "General Biochemistry," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 11, 12, and 13.

(4) This work has been reported in part: C. E. Castro and R. D. Stephens, 143nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, Abstracts, p. 23Q.