

genated to a mixture of 3-methylhexane and 3-ethylpentane. This mixture was analyzed on the di-*n*-decyl phthalate column. The olefin yields varied from 26 to 52%, being higher in the runs at 110 than at 100°. A control experiment in which an analyzed olefin sample was carried by nitrogen into a simulated reaction mixture (see above) resulted in a 70% recovery of material which, on hydrogenation, gave a saturated hydrocarbon mixture analyzing within 0.7% of that obtained by hydrogenating the original olefin mixture. The validity of the hydrogenation procedure was demonstrated by hydrogenating and analyzing a synthetic mixture of olefins. The analysis was within 1% of the calculated composition.

Isolation of acetate ester was attempted in the same manner as in the neo-hexyl brosylate acetolysis. In the residue from fractionation of the petroleum ether was detected 0.3% of material having the same retention time as 2-ethyl-2-methyl-1-butyl acetate, along with ca. 0.6% of rearranged acetates. A control experiment with 3-ethyl-3-pentyl acetate showed the method of isolation was capable of extracting less than 0.04 g (corresponding to 1% yield) of ester.

A run with 2,2-diethyl-1-butyl brosylate was worked up so as to obtain any acetate ester formed. A trace of 2,2-diethyl-1-butyl acetate was noted.

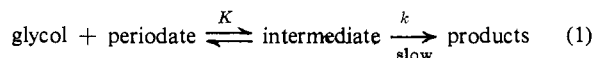
The Mechanism of the Periodate Oxidation of Aromatic Systems. III. A Kinetic Study of the Periodate Oxidation of Catechol

S. W. Weidman¹ and E. T. Kaiser²

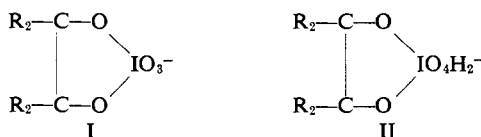
Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. Received July 22, 1966

Abstract: The kinetics of the periodate oxidation of catechol have been investigated over the pH range 0–10. An intermediate was directly observable on a stopped-flow apparatus over the pH range 0.45–7.26. The kinetics of intermediate formation were found to be second order (first order in each reactant concentration), and were adequately explained on the basis of differing reactivities of the various periodate and catechol species present in solution over the pH range 0–10. The intermediate was found to decompose to products in a first-order fashion which was independent of the catechol and periodate concentrations. The observed kinetics of intermediate decomposition were explained by the assumption of a combination of uncatalyzed, specific hydrogen ion and specific hydroxide ion catalyzed paths. Since the maximum half-life of the intermediate was only 2.9 sec, it was not possible to isolate and characterize it. While the assumption of a cyclic diester of periodic acid as the structure of the intermediate is logical in light of the proposed mechanism of periodate oxidation of α -glycols, this postulate does not appear to be supported by all of the experimental evidence now in hand.

The kinetics of the oxidative cleavage of α -glycols by periodic acid have been studied extensively.^{3,4} The observed kinetics were satisfactorily explained by assuming that an intermediate is first formed in a rapid and reversible step and that the rate-determining step is the breakdown of this intermediate to the products (reaction 1). Using this assumption, the equilibrium constant for intermediate formation, K , and the rate



constant for its breakdown to products, k , could be calculated from the kinetic data. From the effect of pH on these two quantities, it was concluded that the intermediate was a cyclic diester of periodic acid (I or a hydrated form, II). The formation of the intermediate



is, for most glycols, faster than the irreversible decomposition of the intermediate to products. Therefore, it was possible to follow the kinetics of intermediate

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

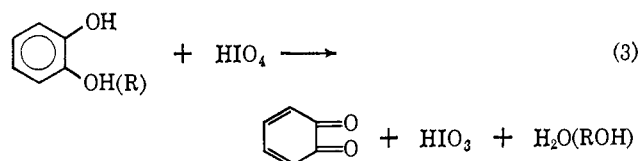
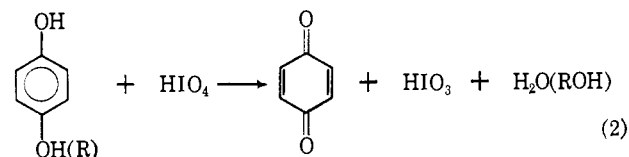
(2) To whom inquiries concerning this paper should be addressed.

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

(4) G. J. Buist, C. A. Bunton, and J. H. Miles, *ibid.*, 4567, 4575 (1957); 743 (1959); and references cited therein.

formation with negligible interference from the decomposition to products. In this manner checks were made on the equilibrium constants for intermediate formation obtained from the kinetic form of the over-all reaction.

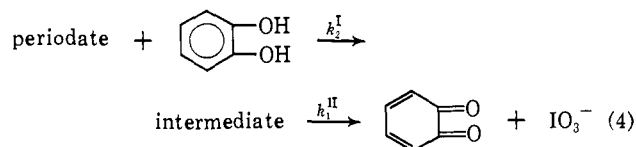
The periodate oxidations of aromatic diols and their monoethers (reactions 2 and 3) have not, until recently, been subjected to thorough kinetic investigation. In a previous paper we reported the results of a kinetic study of the periodate oxidation of hydroquinone and



p-methoxyphenol in acidic solution.⁵ The oxidation reactions showed 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.

(5) E. T. Kaiser and S. W. Weidman, *J. Am. Chem. Soc.*, **86**, 4354 (1964).

Later work on the periodate oxidation of catechol at pH 5, using the stopped-flow method, indicated that an intermediate is formed with this substrate in a second-order reaction and that this intermediate then decomposes to products in a first-order fashion⁶ (reaction 4).



We have now extended these investigations to cover the pH range 0–10, and we wish to report our results at this time.

Experimental Section

Materials. Catechol was obtained from Matheson Coleman and Bell and was recrystallized from benzene–carbon tetrachloride and then sublimed; mp 104.0–105.2° (lit.⁷ 105°). Paraperiodic acid and sodium periodate were obtained from the G. F. Smith Chemical Co. and J. T. Baker Co., respectively. Both were reagent grade and were used without further purification. Periodate solutions were prepared, analyzed, and stored as described previously.⁵ The following buffer solutions were used: pH 0–3.4, sodium periodate–perchloric acid; pH 3.6–5, sodium acetate–acetic acid; pH 6, phthalic or maleic acid–sodium hydroxide; pH 7–8, KH₂PO₄–K₂HPO₄ or NaH₂PO₄–Na₂HPO₄; and pH 9–10.3, NaHCO₃–Na₂CO₃. All these chemicals were reagent grade and were used without further purification. Phthalic and maleic anhydrides and phosphoric acid were employed as sources of phthalic and maleic acids and the sodium phosphates, respectively. The ionic strength of the solutions used in the kinetic runs was adjusted with anhydrous NaClO₄ obtained from G. F. Smith Chemical Co. This material was dried at 140° before use. The water used was twice distilled, the last time from alkaline permanganate, and pH measurements were made with a Radiometer Type 4C pH meter.

Determination of the Second Ionization Constant of Periodic Acid. A 5-ml portion of a 1.00 × 10⁻³ M NaIO₄ (also 0.186 M in NaClO₄) solution was titrated potentiometrically with 0.0195 M NaOH, using a Radiometer Type TTT1b titrator with a combined glass and calomel electrode. The temperature was controlled at 25.0 ± 0.1°. Before the titration, 30 μl of 0.05 M HClO₄ was added; the ionic strength was 0.17 at the end point. The average pK₂ from six determinations was 7.58 ± 0.09 (K₂ = 2.63 × 10⁻⁸ M). The pK₃ was also determined at an ionic strength of 2 × 10⁻³. The average of six determinations was 8.14 ± 0.03 (K₃ = 7.25 × 10⁻⁹ M).

Kinetic Measurements. The reaction of periodate with catechol proved to be too fast to be followed readily on the Cary 14 recording spectrophotometer, under most experimental conditions. The only kinetic runs where the Cary 14 was employed were those at 15.1° and pH 1. In these runs the catechol concentration was held constant at 10⁻⁵ M, while the periodate concentration was varied from 0.95 to 6.94 × 10⁻⁴ M. Spectral measurements at room temperature indicated that the wavelength of maximum difference between the absorptivities of the reactants and products was 220 mμ. This was an approximate value, since it was difficult to obtain an accurate spectrum of *o*-benzoquinone because of its rapid dimerization in aqueous solution. The maximum difference in absorbance appeared to be ~0.0274 (decrease) at room temperature for the reaction of 10⁻⁵ mole of catechol. It would be expected to be somewhat less than this at 15.1° due to a decrease in absorbance of the periodate.^{8,9} Experimentally, it was 0.027 at 15.1°. While this difference in absorption is extremely small, the reaction could be followed accurately with a 0.0–0.1 absorbance slide wire on the Cary. Since a true infinity absorbance could not be obtained (due to dimerization of *o*-benzoquinone), the Guggenheim¹⁰ method of obtaining the rate constant of a first-order reac-

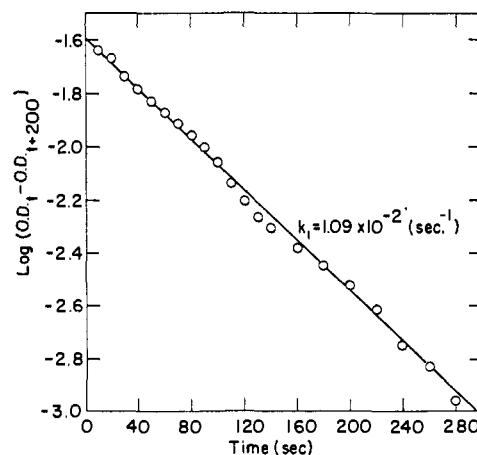


Figure 1. Typical first-order plot for the reaction of periodate with catechol at 15.1° (1.4 × 10⁻⁴ M NaIO₄, 10⁻⁵ M catechol).

tion was used. A typical first-order plot is shown in Figure 1. The experimental technique was the same as that described previously.⁵

The remainder of the work reported here for catechol was done with a stopped-flow apparatus.¹¹ The reactions were followed at 390 mμ, the wavelength of maximum absorbance of *o*-benzoquinone¹² (ε 1.8 × 10³ M⁻¹ cm⁻¹). At this wavelength none of the other reactants or products absorb. In these runs the catechol concentration was held constant over the range of 7–110 × 10⁻⁵ M, while the periodate concentration was varied over the range of 4–400 × 10⁻³ M. Solutions with pH above 6.8 were purged with nitrogen passed through acidic chromous chloride solutions before the catechol was introduced and were kept under an atmosphere of nitrogen during kinetic measurements. A typical oscilloscope photograph retraced by hand is shown in Figure 2 along with the resulting first-order plot.

Results and Discussion

When equal volumes of 0.1 M NaIO₄ and 10⁻³ M catechol (containing 0.1 M NaClO₄) solutions both at pH 5 are rapidly mixed in a stopped-flow apparatus and the flow is suddenly stopped, observation of the change in absorbance at 390 mμ shows the rapid formation of an intermediate which has a higher extinction coefficient at this wavelength than the final product, *o*-benzoquinone. This intermediate then decomposes to *o*-benzoquinone in a slower reaction (Figure 3). The initial reaction was studied using periodate concentrations which were high enough to ensure that the true infinity absorbance could be attained before the second reaction (decomposition) became significant. The decomposition of the intermediate to product was studied by employing a periodate concentration which was sufficient to assure that the intermediate would be formed rapidly in comparison to its decomposition. Also, the catechol concentration was raised in order to increase the difference in absorbance between the intermediate and products.

Intermediate Formation. The initial kinetic studies of the periodate oxidation of catechol were made at pH 1 and 15.1°, using a Cary 14 recording spectrophotometer. The periodate concentration was varied from 1 to 7 × 10⁻⁴ M, while holding the catechol concentration at 10⁻⁵ M. The data are tabulated in Table I.

(11) We wish to thank Professors J. Halpern and E. B. Fleischer for permission to use their stopped-flow apparatus and Mr. H. B. Tinker for his generous help and advice.

(12) H. S. Mason, *J. Biol. Chem.*, **181**, 803 (1949).

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

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

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

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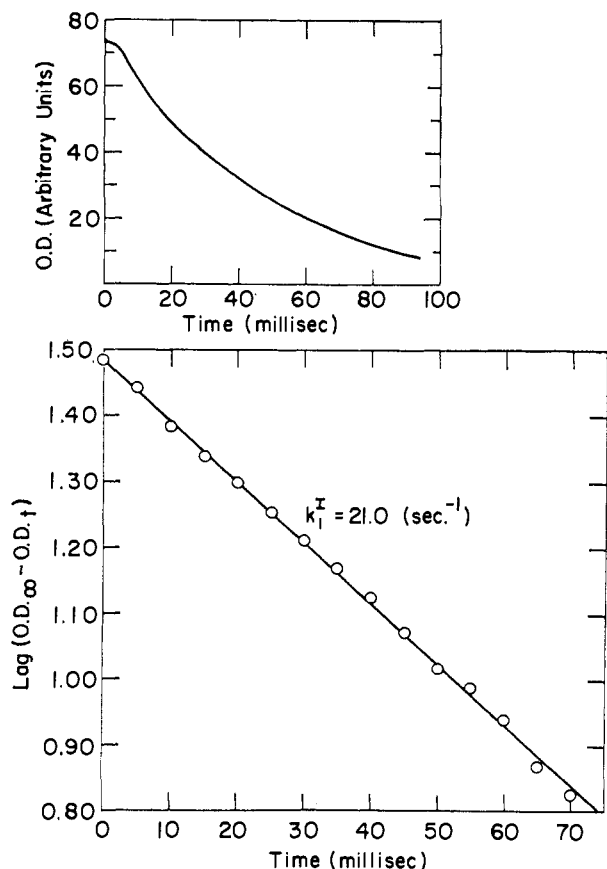


Figure 2. (Top) Typical oscilloscope photograph retraced by hand ($0.0125 M \text{ NaIO}_4$, $10^{-6} M$ catechol). (Bottom) First-order plot of the data of the top figure.

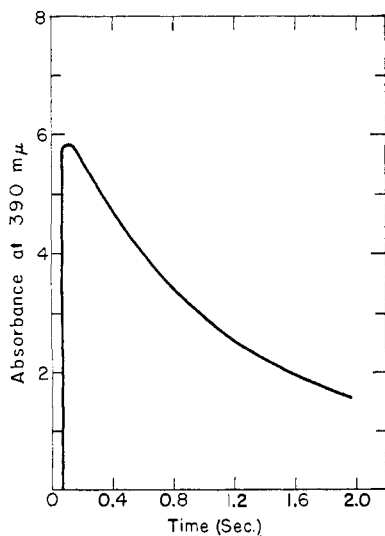


Figure 3. Oscilloscope trace showing rapid formation and slower decomposition of an intermediate during periodate oxidation of catechol at pH 5 ($0.0499 M \text{ NaIO}_4$, $5.75 \times 10^{-4} M$ catechol).

Figure 4 shows the results of a plot of the reciprocals of the observed first-order rate constants (the values used are the average of three to four determinations at each periodate concentration) against the reciprocals of the periodate concentrations at half-reaction. Such a plot should yield a straight line intersecting the ordinate at a positive value if a reaction scheme similar to reaction 1 is operating. However, due to the scatter of the

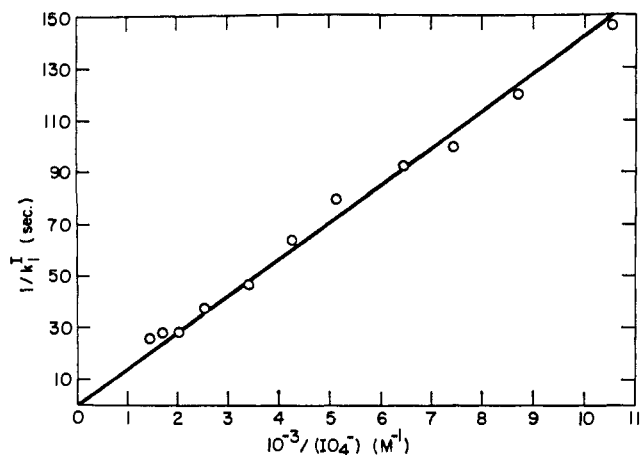


Figure 4. Dependence of reciprocal of first-order rate constant on reciprocal of periodate concentration at 15.1° ($9.95 \times 10^{-6} M$ catechol).

data, it was not obvious whether the line should be drawn through the origin or with a slight positive intercept on the ordinate. In light of later work we now know that this line in Figure 4 should be drawn through the origin, since the formation of an intermediate is the rate-determining step under these conditions. Thus, second-order kinetics are indicated (first order in each reactant concentration) with a second-order rate constant of $70.2 M^{-1} \text{ sec}^{-1}$.

Table I. Kinetic Data for the Periodate Oxidation of Catechol at pH 1.0 and 15.1°

NaIO_4 , ^a $10^4 M$	$\text{Av } 10^3 k_1$, sec^{-1}	Calcd k_2 , ^b $M^{-1} \text{ sec}^{-1}$
0.949	6.85	72.2
1.15	8.33	72.5
1.34	9.98	74.4
1.55	10.8	69.7
1.95	12.5	64.2
2.35	15.7	66.9
2.93	21.3	72.7
3.94	26.7	67.7
4.94	35.5	71.8
5.94	35.7	60.1
6.94	38.8	55.9

^a $10^{-5} M$ catechol. ^b Average $k_2 = 70.2 M^{-1} \text{ sec}^{-1}$, runs at 5.94 and $6.94 \times 10^{-4} M \text{ NaIO}_4$ excluded.

The data from the stopped-flow study of intermediate formation at pH 1 and 25.0° (all stopped-flow work was done at 25.0°) are shown in Table II. The periodate concentration was varied from 0.10 to $0.25 M$, while the catechol concentration was held at $7.22 \times 10^{-5} M$. A plot of the observed first-order rate constant, k_1^I , against the periodate concentration (Figure 5) yields a straight line through the origin. A first-order dependence on the catechol and periodate concentrations is again indicated. The average second-order rate constant is $163 M^{-1} \text{ sec}^{-1}$ at an ionic strength of 0.50. The results of kinetic runs at an ionic strength equal to that for the runs at 15.1° on the Cary are also shown in Table II. These runs indicated a second-order rate constant of $129 M^{-1} \text{ sec}^{-1}$ at an ionic strength of 0.10. Using this value along with the rate constant at 15.1° , ΔH^* , ΔS^* , and ΔF^* for the periodate oxidation

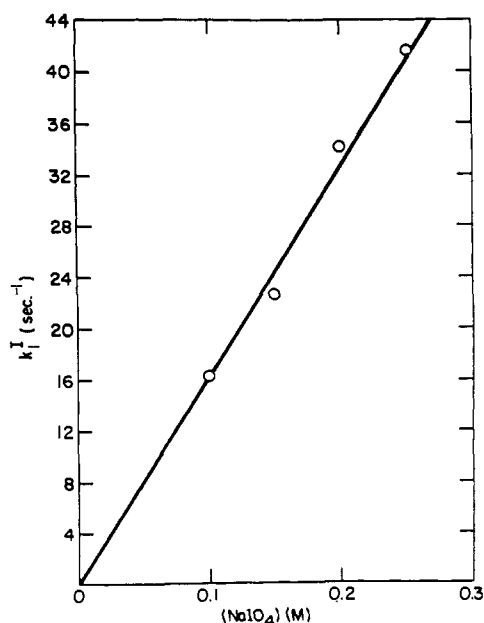


Figure 5. Dependence of first-order rate constant on periodate concentration ($7.22 \times 10^{-5} M$ catechol).

of catechol were calculated to be 9.9 kcal/mole, -15.6 eu, and 14.6 kcal/mole, respectively. These activation parameters are similar to those found for hydroquinone and *p*-methoxyphenol,⁵ for which no intermediate could be detected with the stopped-flow method.

Table II. Stopped-Flow Data for Intermediate Formation at pH 1.04

NaIO ₄ , ^a M	No. of runs	Range of k_1^I , sec ⁻¹	Av k_1^I , sec ⁻¹	Calcd k_2^I , ^b M ⁻¹ sec ⁻¹
0.0989	6	14.9–18.3	16.3	164.0
0.149	7	19.7–24.0	22.7	152.0
0.200	8	32.4–35.6	34.2	171.0
0.251	7	37.9–47.6	41.6	166.0
8.56×10^{-4} ^c	8	0.105–0.118	0.110	129.0

^a $7.22 \times 10^{-5} M$ catechol, $\mu = 0.50$. ^b Average $k_2^I = 163 \pm 7 M^{-1} \text{sec}^{-1}$ for runs at $\mu = 0.50$. ^c 7.5×10^{-5} catechol, $\mu = 0.10$.

The intermediate formation reaction was investigated further over the pH range 0–10. In the pH range 1–6.59 and at pH 9.98 at least two concentrations of periodate (always in excess over catechol) were used. Second-order kinetics were indicated at all these pH's. At pH 0 and pH 6.86–10.17, just one periodate concentration was used to evaluate the second-order rate constant. The pH rate profile is summarized in Table III and shown graphically in Figure 6. There are two values given in Table III for k_2^I at pH 3.95 and 4.98. The larger values correspond to the average second-order rate constants in acetate buffer. When an attempt was made to fit the data at these two points by the method to be discussed below, it was found that the calculated values were low compared to these experimental values. Acetate catalysis was suspected and was proved as indicated in Table IV. Here the acetate concentration was varied while holding the ionic strength constant. The smaller values of k_2^I given in Table III at pH 3.95 and 4.98 correspond to the values given in Table IV at zero acetate concentration. These

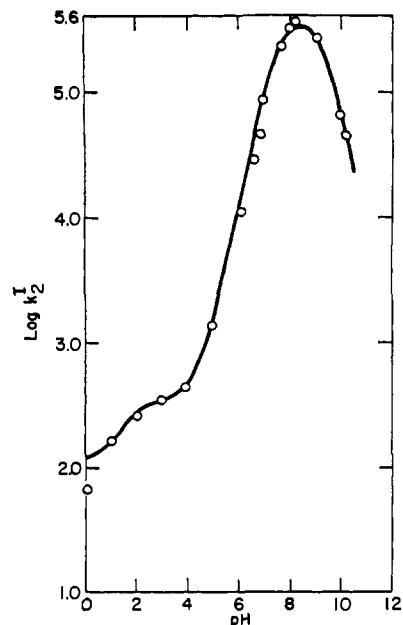


Figure 6. Dependence of second-order rate constant for intermediate formation on pH; \circ = experimental points.

values agree much better with the calculated k_2^I at these pH's and are the values plotted in Figure 6. The discovery of acetate catalysis here is not particularly

Table III. Summary of Kinetic Data for Intermediate Formation

pH	μ	Av k_2^I , M ⁻¹ sec ⁻¹	Calcd k_2^I , ^a M ⁻¹ sec ⁻¹
0.06	1.15	68.1 ± 0.4	122
1.04	0.50	163 ± 7	163
2.02	0.30	260 ± 11	283
2.97	0.17	352 ± 2	352
3.95	0.17	676 ± 20	452
		450.0^b	
4.98	0.17	$1.7 \pm 0.1 \times 10^3$	1.43×10^3
		1.37×10^{3b}	
6.12	0.17	1.14×10^4	1.48×10^4
6.59	0.17	$2.93 \pm 0.17 \times 10^4$	4.04×10^4
6.87	0.17	$4.67 \pm 0.20 \times 10^4$	7.06×10^4
6.94	0.17	$8.67 \pm 0.36 \times 10^4$	8.05×10^4
7.66	0.17	$2.3 \pm 0.3 \times 10^5$	2.3×10^5
8.00	0.17	$3.2 \pm 0.4 \times 10^5$	3.0×10^5
8.23	0.17	$3.58 \pm 0.45 \times 10^5$	3.25×10^5
9.06	0.17	$2.7 \pm 0.3 \times 10^5$	2.6×10^5
9.98	0.17	$5.8 \pm 0.7 \times 10^4$	7.2×10^4
10.17	0.17	$4.5 \pm 0.4 \times 10^4$	4.9×10^4

^a Calculated from eq 5 using the parameters given in text. ^b Zero acetate concentration.

Table IV. Effect of Acetate Concentration on Intermediate Formation at pH 4 and 5

pH	NaOAc, ^a M	$k_2^I \times 10^{-2}$, ^b M ⁻¹ sec ⁻¹
3.93	0.0	4.50
	0.009	5.93
	0.018	6.76 ^c
4.97	0.036	7.50
	0.0	13.7
	0.035	16.8
	0.070	17.0 ^d
	0.140	20.8

^a $7.5 \times 10^{-5} M$ catechol, $\mu = 0.17$. ^b Each value is the average of 6–11 runs. ^c Average of 34 runs. ^d Average of 30 runs.

surprising, since Shiner and Wasmuth¹³ found similar behavior by acetate in their study of the periodate oxidation of diacetyl.

As is indicated in Figure 6, the rate constant for intermediate formation is very pH sensitive, particularly in the pH range 4–10. In this pH range two ionizations are occurring, that of the periodate monoanion to the dianion and of un-ionized catechol to the catechol monoanion. The fact that the rate constant achieves a maximum value around pH 8.5 is indicative that the rate of reaction depends on the product of the periodate dianion concentration with the un-ionized catechol concentration and/or the product of the periodate monoanion and catechol monoanion concentrations. Therefore, the following expression was used to fit the experimentally observed rate constants

$$k_2^I(\text{total periodate})(\text{total catechol}) = k_{10}^I(\text{H}_5\text{IO}_6) \times (\text{Cat}^0) + k_{-10}^I[(\text{IO}_4^-) + (\text{H}_4\text{IO}_6^-)](\text{Cat}^0) + k_{-20}^I(\text{H}_3\text{IO}_6^{2-})(\text{Cat}^0) + k_{-1-1}^I[(\text{IO}_4^-) + (\text{H}_4\text{IO}_6^-)](\text{Cat}^{-1}) \quad (5)$$

where Cat.⁰ and Cat.⁻¹ stand for un-ionized and monoionized catechol, respectively. It was found that the data could not be fitted well in the pH range 4–10, using a pK_2 of 8.33 for periodic acid¹⁴ and a pK of 9.28 for catechol.¹⁵ The pK_1 for catechol was determined by Fuller at the same ionic strength (0.17) as was used in this work in the pH range 4–10; so this value was accepted. This then led us to suspect that the value for K_2 for periodic acid as given in the literature¹⁴ was not suitable for the treatment of our results. Therefore, we determined the pK_2 for periodic acid at an ionic strength of 0.17 and 25°. The value obtained (7.58) differed considerably from the literature value, probably because of the effect of ionic strength on the activity coefficients of periodate mono- and dianions. Indeed, we found that at a low ionic strength (2×10^{-3}) the pK_2 rose to 8.14. The value of 7.58 for the pK_2 which we determined at an ionic strength of 0.17 enabled us to fit the experimental pH-rate profile to a theoretical curve to within an average of 13% over the pH range 0–10 (excluding the point at pH 0.06). The calculated pH-rate profile is shown with the experimental points in Figure 6.

It was not possible to fit the data in the pH range 4–10 by assuming positive values for both k_{-20}^I and k_{-1-1}^I . We had to assume that one or the other was zero. The experimental data do not allow a choice to be made between the two possibilities. The kinetic data were fitted by assuming values of k_{10}^I and k_{-10}^I of 116 and 352 $M^{-1} \text{sec}^{-1}$, respectively; with either k_{-20}^I equal to $4.33 \times 10^5 M^{-1} \text{sec}^{-1}$ and k_{-1-1}^I equal to zero, or k_{-1-1}^I equal to $2.17 \times 10^7 M^{-1} \text{sec}^{-1}$ and k_{-20}^I equal to zero. The data were fitted equally well by either possibility.

Intermediate Decomposition. The kinetic data obtained for intermediate decomposition at pH 5 are summarized in Table V. The average first-order rate constant, k_1^{II} , was 0.65 sec^{-1} , and it is clearly independent of the catechol concentration.¹⁶

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(14) G. J. Buist and J. D. Lewis, *Chem. Commun.*, 66 (1965).

(15) E. J. Fuller, *J. Am. Chem. Soc.*, **85**, 1777 (1963).

(16) The value at $0.75 \times 10^{-4} M$ catechol was disregarded because the

Table V. Kinetic Data for Intermediate Decomposition at pH 4.97

Catechol, ^a 10 ⁴ M	No. of runs	Range of k_1^{II} , sec ⁻¹	Av k_1^{II} , sec ⁻¹
0.749	4	0.58–0.88	0.74
2.03	10	0.59–0.74	0.67
2.99	6	0.57–0.66	0.63
5.75	7	0.62–0.71	0.64

^a 0.0499 M NaIO₄, $\mu = 0.17$. ^b Over-all average $k_1^{II} = 0.65 \pm 0.04 \text{ sec}^{-1}$ with runs at $0.749 \times 10^{-4} M$ catechol excluded.

The kinetics of intermediate decomposition were studied further over the pH range 0.45–7.26 (at the two extremes the reaction became too fast to follow accurately). The ionic strength was constant at 0.17 M over the pH range 3.6–7.26, but rose from 0.17 M at pH 3.6 to 1.1 M at pH 0.45. However, the data given in Table VI at pH 1.95 indicate that the effect of in-

Table VI. Effect of Ionic Strength and Periodate Concentration on Intermediate Decomposition

pH	μ	NaIO ₄ , M	No. of runs	Range of k_1^{II} , sec ⁻¹	Av k_1^{II} , sec ⁻¹
1.9 ^a	0.17	0.17	15	0.44–0.56	0.50 ± 0.04
	0.34	0.17	17	0.43–0.76	0.53 ± 0.08
3.4 ^b	0.17	0.0085	12	0.25–0.30	0.28 ± 0.02
	0.17	0.085	15	0.20–0.28	0.25 ± 0.02

^a $2.0 \times 10^{-3} M$ catechol. ^b $5.1 \times 10^{-4} M$ catechol.

creasing ionic strength on the rate constant is very small. Also, Table VI illustrates that the first-order rate constant is independent of the periodate concentration. The effect of pH on the intermediate decomposition is summarized in Table VII and the pH-rate

Table VII. Summary of Kinetic Data for Intermediate Decomposition

pH	μ	Av k_1^{II} , sec ⁻¹	Calcd k_1^{II} , ^a sec ⁻¹
0.45	1.1	8.9 ± 1.4	9.5
1.02	0.50	3.2 ± 0.5	2.7
1.94	0.34	0.53 ± 0.08	0.54
2.92	0.23	0.36 ± 0.06	0.27
	0.17	0.27 ± 0.02	
3.61	0.17	0.24 ± 0.02	0.26
3.95	0.17	0.31 ± 0.02	0.26
4.40	0.17	0.37 ± 0.02	0.31
4.81	0.17	0.48 ± 0.04	0.41
4.97	0.17	0.65 ± 0.04	0.48
6.08	0.17	3.5 ± 0.3	3.4
6.58	0.17	8.1 ± 0.7	10.1
6.86	0.17	17.2 ± 1.4	19.1
7.21	0.17	56 ± 6	42
7.26	0.17	49 ± 6	48

^a Calculated from eq 6 with $k^{II} = 0.24 \text{ sec}^{-1}$, $k^{III} = 26 M^{-1} \text{sec}^{-1}$, and $k_{OH}^{II} = 2.6 \times 10^6 M^{-1} \text{sec}^{-1}$.

profile is shown graphically in Figure 7. As was the case with intermediate formation, the decomposition is rather sensitive to the acidity. There is a broad minimum in the rate constant between pH 2.5 and 4.6 with the rate constant rising sharply on either side.

difference in absorbance between the intermediate and products was not large enough to be followed accurately.

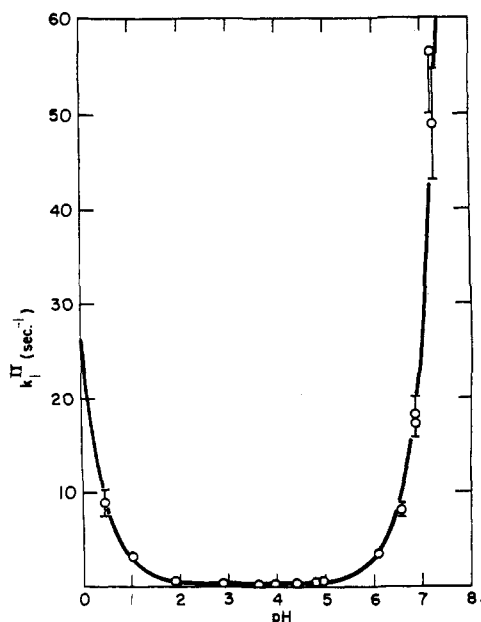


Figure 7. Dependence of first-order rate constant for intermediate decomposition on pH; \circ = experimental points.

The pH effects on the intermediate decomposition are explained by assuming an uncatalyzed reaction with rate constant k^{II} , an acid-catalyzed reaction with rate constant $k_{\text{H}^{\text{II}}}$, and a hydroxide-catalyzed reaction with rate constant $k_{\text{OH}^{\text{II}}}$. The expression for the observed first-order rate constant then becomes

$$k_1^{\text{II}} = k^{\text{II}} + k_{\text{H}^{\text{II}}}(\text{H}^+) + k_{\text{OH}^{\text{II}}}(\text{OH}^-) \quad (6)$$

Since the minimum of the pH-rate profile is rather broad, it was assumed that this value (0.24 sec^{-1}) represented k^{II} in eq 6.

On the high pH side of the rate profile, $k_{\text{H}^{\text{II}}}(\text{H}^+)$ is certainly negligible. Subtracting k^{II} from both sides of eq 6 then gives

$$k_1^{\text{II}} - k^{\text{II}} = k_{\text{OH}^{\text{II}}}(\text{OH}^-) \quad (7)$$

Taking the logarithm of both sides of eq 7 yields

$$\log(k_1^{\text{II}} - k^{\text{II}}) = \log k_{\text{OH}^{\text{II}}} + \log(\text{OH}^-) \quad (8)$$

Then a plot of the $\log(k_1^{\text{II}} - k^{\text{II}})$ against the $\log(\text{OH}^-)$ should yield a straight line with unit slope. Figure 8 shows the results of such a plot. The observation that the experimental rate constants yield a straight line with unit slope proves the validity of assuming a hydroxide-catalyzed decomposition. The evaluation of $k_{\text{OH}^{\text{II}}}$ was done using the relation

$$k_{\text{OH}^{\text{II}}} = \frac{(k_1^{\text{II}} - k^{\text{II}})}{(\text{OH}^-)} \quad (9)$$

at each pH above pH 6 and taking the average value of $k_{\text{OH}^{\text{II}}}$ thus calculated. The average value of $k_{\text{OH}^{\text{II}}}$ was $2.6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$. This value is not far below that for a diffusion-controlled reaction.

On the low pH side of the rate profile $k_{\text{OH}^{\text{II}}}(\text{OH}^-)$ is negligible. Thus, one is left with the relation

$$k_1^{\text{II}} = k^{\text{II}} + k_{\text{H}^{\text{II}}}(\text{H}^+) \quad (10)$$

Then, a plot of the observed rate constant, k_1^{II} , against the hydrogen ion concentration should yield a straight line with an intercept on the ordinate of k^{II} and a slope

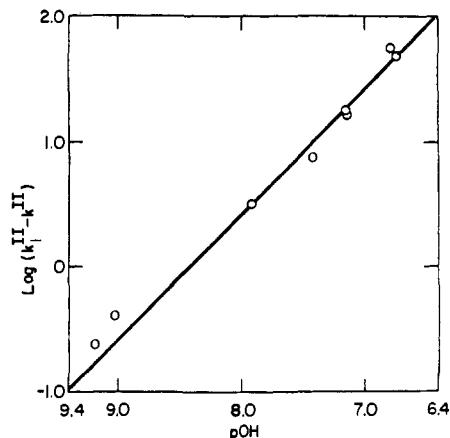


Figure 8. Dependence of first-order rate constant for intermediate decomposition on hydroxide ion concentration.

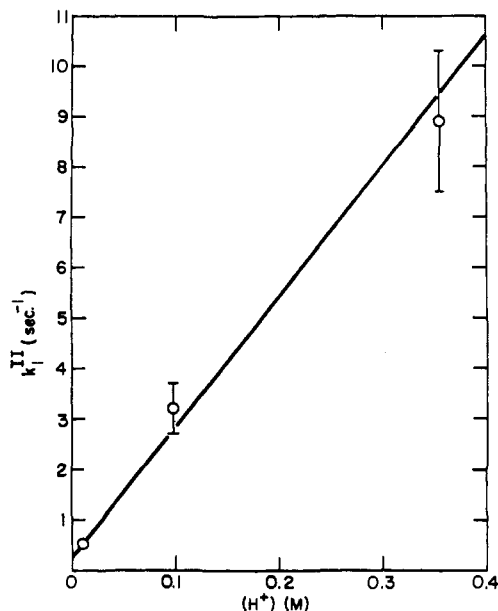


Figure 9. Dependence of first-order rate constant for intermediate decomposition on the hydrogen ion concentration.

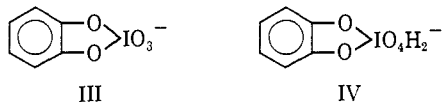
of $k_{\text{H}^{\text{II}}}$. The result of such a plot is seen in Figure 9. The limits indicated at the two points at 0.1 and 0.355 M H^+ are one standard deviation, while the vertical diameter of the lower circle is one standard deviation. Since the point at 0.01 M H^+ represents the average of 32 kinetic runs (13 runs at 0.1 M H^+ and 6 runs at 0.355 M H^+), the best fit straight line was drawn from 0.24 sec^{-1} on the ordinate through this point. The line passes through the standard deviation limits of the other two points at higher acidity. The $k_{\text{H}^{\text{II}}}$ was determined from the slope to be $26 \text{ M}^{-1} \text{ sec}^{-1}$.

With all the constants in eq 6 now in hand, it was possible to calculate the pH-rate profile for intermediate decomposition and compare it with the experimental values. This comparison is shown in Figure 7. The calculated rate constants agreed with the experimental quantities to within an average of 10%.

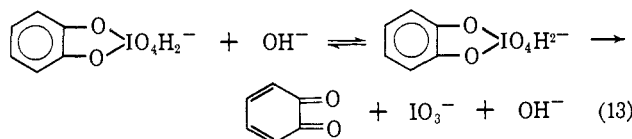
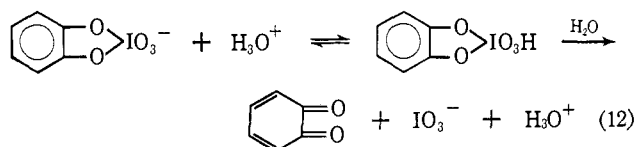
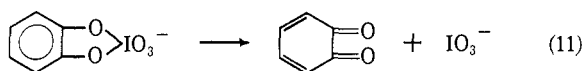
Mechanistic Considerations. The following kinetic studies of the periodate oxidation of aromatic systems have been completed: (1) hydroquinone and *p*-methoxyphenol, pH 0–4; (2) catechol, pH 0–10; and (3) *o*-methoxyphenol, pH 1–4. The kinetics of the oxida-

tion of *o*-methoxyphenol were found to be second order (first order in each reactant concentration).¹⁷ The rate constant does not vary by more than 18% from $2.0 M^{-1} \text{ sec}^{-1}$ over the pH range 1–4 and no intermediate was observable on the stopped-flow apparatus.

Since catechol was the only substrate for which an intermediate was detected and the only substrate which has two phenolic hydroxyl groups *ortho* to each other, it does seem reasonable to assume that the intermediate is a cyclic diester of periodic acid (III or IV). The

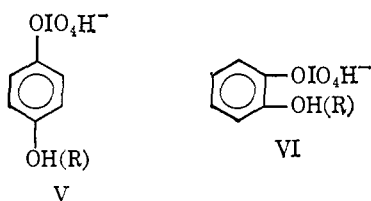


three paths of decomposition of this intermediate diester corresponding to the observed kinetic dependence on the hydrogen and hydroxide ion concentrations could then be formulated as shown in reactions 11–13. The cyclic diester is assumed to be a stronger



acid than periodic acid. This has been found to be the case for the cyclic intermediate in the periodate oxidation of aliphatic 1,2-diols.^{3,4} If mechanisms 11–13 are valid, it would be anticipated that if measurements could be made at lower and at higher pH values than were accessible in our experiments the rates of decomposition of the intermediate would level off (unless additional acid and base terms would intervene at the extremes of the pH-rate profile). Furthermore, the empirical eq 6 should not hold then at very low and very high pH values.

Although there is no evidence for intermediates for the other three substrates, this does not rule out the possibility that intermediate monoesters like V and VI



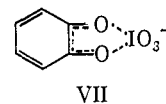
are formed in these oxidations if their formation, rather than their decomposition to products, is the rate-determining step. Stable monoesters of periodic acid are not known. If monoesters are found during the course of these oxidations, it would be expected that they would be very reactive and decompose rapidly.

There are some experimental data which seem to provide evidence against a cyclic diester intermediate

(17) E. T. Kaiser and S. W. Weidman, unpublished observations.

for catechol oxidation. The intermediate has a higher extinction coefficient than the product, *o*-benzoquinone, at $390 m\mu$. If one follows the oxidation of catechol on the stopped-flow apparatus in the spectral region $360\text{--}440 m\mu$ and then makes a plot of the difference in absorbance between the intermediate and *o*-benzoquinone against the wavelength, a curve with the same shape as the absorbance curve for *o*-benzoquinone in this spectral region is obtained. Thus, it appears that the intermediate has its wavelength of maximum absorption at the same wavelength as *o*-benzoquinone ($390 m\mu$). In the formation of cyclic esters of catechol with boric acid¹⁸ and sulfuric acid,¹⁹ the wavelength of maximum absorption of the cyclic ester is shifted to shorter wavelengths from $275 m\mu$, the wavelength of maximum absorption of catechol. It might be expected, therefore, that a cyclic ester of periodic acid would have little absorbance at $390 m\mu$. However, if the intermediate is a charged ester, it is possible that its wavelength of maximum absorption could be shifted to a longer wavelength. The successive ionizations of catechol and hydroquinone yield anions which have their wavelength of maximum absorption shifted to longer wavelengths.²⁰

If the assumption that the intermediate is a cyclic diester were rejected, we would be left with the problem of the nature of the intermediate. A labile charge-transfer complex between iodate and *o*-benzoquinone (VII) would conceivably explain the spectral data for



the intermediate. If this were the intermediate observed, there should be a charge-transfer absorption band in the ultraviolet region. The determination of the absorption spectrum of the intermediate is therefore needed. However, this is experimentally difficult to obtain. At acidities where the intermediate has its maximum half-life the ultraviolet region is blanked out by the absorption of periodate since the periodate concentration must be high enough to cause the intermediate to be formed rapidly compared to its half-life for decomposition. At acidities where the periodate concentration can be kept low enough to investigate the ultraviolet region, the rate of intermediate decomposition is too fast for the intermediate to be observed on the stopped-flow apparatus.

The possibility that the intermediate is a semiquinone must also be considered. The spectral data might support this, but no definite conclusions can be made because the visible and ultraviolet spectra of *o*-semiquinone are not known. In view of the difference in the spectra of the *p*-semiquinone anion and *p*-benzoquinone,²¹ it would seem somewhat unlikely that the wavelength of maximum absorption of *o*-semiquinone would be the same as that of *o*-benzoquinone. The kinetic observations would appear to provide evidence against a semiquinone intermediate, also. If a semiquinone is formed in an initial step, an iodine species with a +6 oxidation state would also be formed. If

(18) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

(19) T. F. Wulfers, personal communication.

(20) H. Staude and M. Teupel, *Z. Elektrochem.*, **61**, 181 (1957).

(21) H. Diebler, M. Eigen, and P. Matthies, *ibid.*, **65**, 634 (1961).

these two species react with each other to yield iodate and *o*-benzoquinone, second-order kinetics for intermediate decomposition would be observed, but this is contrary to the experimental observations. If the semiquinone reacts with the excess periodate, pseudo-first-order kinetics would be observed, but the apparent rate constant would be dependent on the periodate concentration. Again, this is contrary to the experimental observations. If the semiquinone lost an electron to the aqueous solvent, then this might correspond to the experimentally observed kinetics, but it would be highly unlikely that the solvent would act as an oxidizing

agent under these conditions. More definite evidence concerning the possibility that the intermediate is a radical species should be obtained from electron spin resonance experiments now in progress.

It will not be possible to write an exact mechanism for the periodate oxidation of aromatic diols and their monoethers until further information is available concerning the structure of the intermediate involved in the oxidation of catechol. Therefore, work on this problem is proceeding along such lines.

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The Kinetics of the Permanganate Oxidation of Alkenes¹

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Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut, and The University of Washington, Seattle, Washington. Received May 27, 1966

Abstract: The kinetics of the permanganate oxidation of alkenes was investigated at pH 6.5 and 13. The rate of the initial reaction showed a first-order dependence on the concentrations of alkene and permanganate, but was independent of the base concentration. Thus, although the products of the reaction do vary with pH, they are all probably derived from the same intermediate. Kinetic evidence was obtained for the appearance of a manganese(V) intermediate which is rapidly oxidized to a manganese(VI) species.

Bimolecular reactions characterized by rate constants in excess of 100 l. mole⁻¹ sec⁻¹ are of intrinsic interest in organic chemistry because of their relative rarity in other than proton-transfer reactions. A reaction of this type is the permanganate oxidation of alkenes. The reaction has received some previous study, particularly with regard to the products. It is known, for example, that a 1,2-diol is favored at high pH, that a ketol is favored at low pH, and that cleavage may also occur.^{2,3} The diol is formed *via* a *cis* addition,⁴ and the oxygen in the diol arises from the oxidant.³ A kinetic study of the oxidation of oleate ion has been made,⁵ but due to the high rates of reaction the kinetic data were not very detailed. Further, as will be shown below, oleate ion is an atypical substrate.

Results

The alkenes used in this study were largely the salts of unsaturated carboxylic acids in order to ensure having homogeneous aqueous solutions. The reaction was studied in both neutral and basic solutions. Because of the large rate constants, the rates of reaction were determined spectrophotometrically using a stopped-flow system. Reactions with a half-life as low as 0.4 sec could be studied satisfactorily with the apparatus used.

(1) This work was supported by the U. S. Atomic Energy Commission.

(2) G. King, *J. Chem. Soc.*, 1788 (1936).

(3) K. B. Wiberg and K. A. Saegbarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957).

(4) J. Böeseken, *Rec. Trav. Chim.*, **41**, 199 (1922).

(5) S. Wolfe, Ph.D. Dissertation, University of Ottawa, 1957.

A record from a typical kinetic run is shown in Figure 1. When the flow is started in the system, the per cent transmission decreases and levels off at a steady-state value. When the flow is stopped, the transmittance increases and approaches a constant value. Shortly thereafter, transmittance begins to decrease again as a result of the formation of colloidal manganese dioxide. The reactions were normally carried out under pseudo-first-order conditions. The rate constants were estimated from plots of $-\ln [\log (T_{\infty}/T)]$ against time where T_{∞} is the per cent transmission at a point just before colloidal manganese dioxide begins to form.

With most of the substrates investigated there was some curvature in the plots. Here, two slopes were obtained from the curves: m_i represents the slope near zero time and m_f represents the slope near the third half-life. An example of a curve where m_f is greater than m_i is shown in Figure 2a and is typical of many substrates when present in excess in alkaline solution. A case in which m_i is greater than m_f is shown in Figure 2b and is typical of many oxidations in neutral solution.

The reaction was found to be first order in permanganate at any pH as indicated by the data in Table I. Under the conditions used the kinetic plots were linear, and m is the slope of the line. For convenience, most of the following data were obtained at a permanganate concentration of $4.0 \times 10^{-4} M$.

Before considering the kinetic data in further detail we must first consider the stoichiometry of the reaction. In basic solution (above pH 12) the oxidant is reduced to manganate. The diol is the principal product, and thus a 2:1 ratio of permanganate:alkene is needed. Since the reaction is first order in permanganate, at