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THE MECHANISM OF THE PERIODATE OXIDATION OF AROMATIC SYSTEMS. II. THE FORMATION OF AN INTERMEDIATE DURING THE PERIODATE OXIDATION OF CATECHOL

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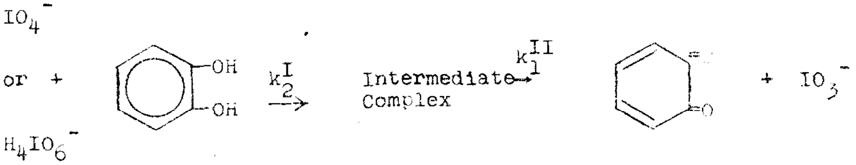
In a recent publication we reported the absence of any kinetic or spectrophotometric evidence for the formation of intermediates during the periodate oxidation of hydroquinone and its monomethyl ether, p-methoxyphenol, in aqueous solution over the pH range 0 - 4.[1] We have now extended this work to the oxidation of catechol, using stopped-flow methods.** We have found that in the periodate oxidation of catechol, over the pH range 1 - 6, an intermediate is formed in a second-order reaction and that this intermediate then decomposes to products in a first-order fashion.



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When equal volumes of 0.1 M $NaIO_4$ and 10^{-3} M catechol (containing 0.1 M $NaClO_4$) solutions both at pH 5 are rapidly mixed in a stopped-flow apparatus and the flow is suddenly stopped, observation of the change in transmittance at 390 mμ (λ max. of o-benzoquinone) shows the rapid formation of an intermediate species 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 1). The initial reaction was studied using periodate concentrations which were high enough to insure that the true infinity transmittance of the intermediate could be obtained before the second reaction (decomposition) became significant. The observed pseudo first-order rate constants, k_1^I, are tabulated in Table I and plotted as a function of the periodate concentration in Figure 2. The straight line in Figure 2 yields a second-order rate constant, k_2^I, of 1.7×10^3 M^{-1} $sec.^{-1}$ for the formation of the intermediate.*

The decomposition of the intermediate to products was studied by employing a $NaIO_4$ concentration of 0.05 M (after mixing) which was sufficient to assure that the intermediate would be formed rapidly (approximately 0.08 sec.). Also, the catechol concentration was raised in order to increase the difference in transmittance between the intermediate and products. First-order rate constants are shown in Table II. The average first-order rate constant, k_1^{II}, is calculated to be 0.65 $sec.^{-1}$, and it is clearly

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* The point at 0.05 M $NaIO_4$ was disregarded because the rate of the reaction there is simply too fast (half life of 6 millisec.) to follow it accurately.

TABLE I

KINETIC DATA FOR FORMATION OF INTERMEDIATE DURING OXIDATION OF CATECHOL BY PERIODATE AT pH 5.0.[a]

$NaIO_4$[a,b] M	Number of runs	Range of k_1^I (sec.$^{-1}$)	Average k_1^I (sec.$^{-1}$)	k_2^I (M^{-1} sec.$^{-1}$)[c]
0.0101	6	17.3 - 18.8	18.0±0.5	
0.0125	8	18.9 - 23.0	20.4±1.3	
0.0170	6	27.8 - 30.4	28.7±1.0	1.7×10^3
0.0251	10	38.8 - 45.6	42.1±1.9	
0.0499	7	95.1 - 122	108 ±9	

a) (HOAc) = 0.030 M, (NaOAc) = 0.070 M, ($NaClO_4$) = 0.10 M, ionic strength constant at 0.17 M (after mixing), temperature = 25.0°.

b) (Catechol) = 0.749×10^{-4} M.

c) Runs at 0.0499 M $NaIO_4$ excluded.

independent of the catechol concentration.*

Extensive kinetic studies of the periodate oxidation of -glycols have indicated that (for most simple glycols) a glycol-periodate complex is first formed in a rapid and reversible step.[2,3] This step is then followed by a rate-determining decomposition of the intermediate to products. The formation of the intermediate has been directly detected and followed spectrophotometrically, and it was concluded that the complex was a cyclic diester of periodic acid.[3]

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* The value at 0.75×10^{-4} M was disregarded because the difference in transmittance between the intermediate and products is not large enough to be followed accurately.

TABLE II

KINETIC DATA FOR DECOMPOSITION OF THE INTERMEDIATE TO PRODUCTS AT pH 5.0[a]

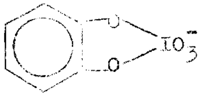
Catechol[a,b] 10^4 M	Number of runs	Range of k_1^{II} (sec.$^{-1}$)	Average k_1^{II} (sec.$^{-1}$)	Overall[c] average k_1^{II} (sec.$^{-1}$)
0.749	4	0.58 - 0.88	0.74	
2.03	10	0.59 - 0.74	0.67	
2.99	6	0.57 - 0.66	0.63	0.65±0.04
5.75	7	0.62 - 0.71	0.64	

a) (HOAc) = 0.030 M, (NaOAc) = 0.070 M, ($NaClO_4$) = 0.10 M, ionic strength constant at 0.17 M (after mixing), temperature = 25.0°.

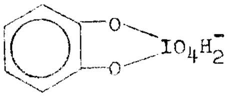
b) ($NaIO_4$) = 0.0499 M after mixing.

c) Runs at 0.749 x 10^{-4} M catechol excluded.

A number of possible structures can be postulated for the intermediate complex formed in the periodate oxidation of catechol. For example, this intermediate might be a cyclic diester, I or II, in analogy to the α-glycol case. Alternatively, the intermediate could be a closely related species, a dissociable o-benzoquinone-iodate complex.



I



II

Preliminary studies of the periodate oxidation of *o*-methoxyphenol have indicated that no observable intermediate is formed during the course of the oxidation. The kinetics of the periodate oxidation of catechol and of *o*-methoxyphenol as a function of pH and the structure of the intermediate formed in the oxidation of catechol are now under study in our laboratory.

References

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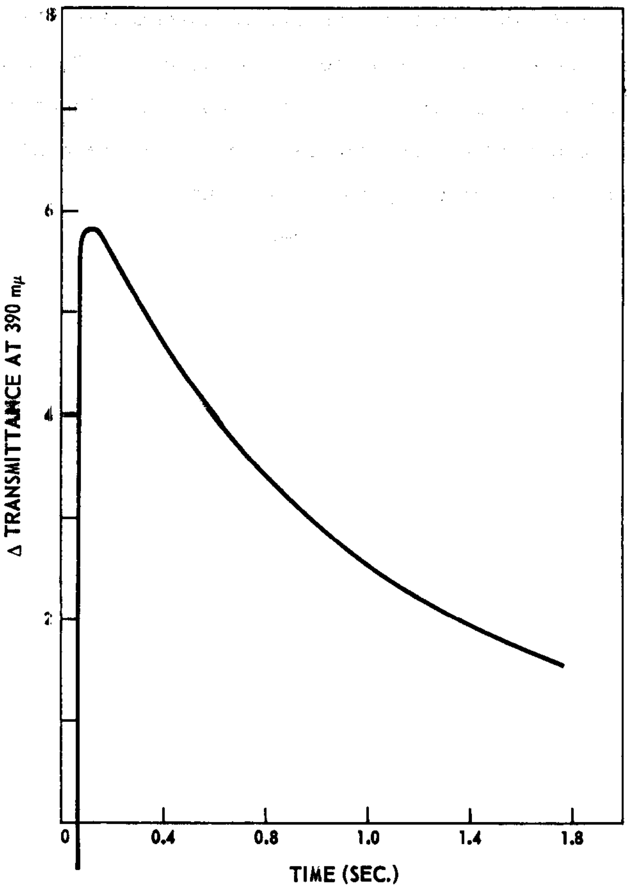

Fig. 1 Oscilloscope trace showing rapid formation and slower decomposition of an intermediate during periodate oxidation of Catechol at pH 5.

$(NaIO_4) = 0.0499\ \underline{M}$

$(\text{Catechol}) = 5.75 \times 10^{-4}\ \underline{M}$

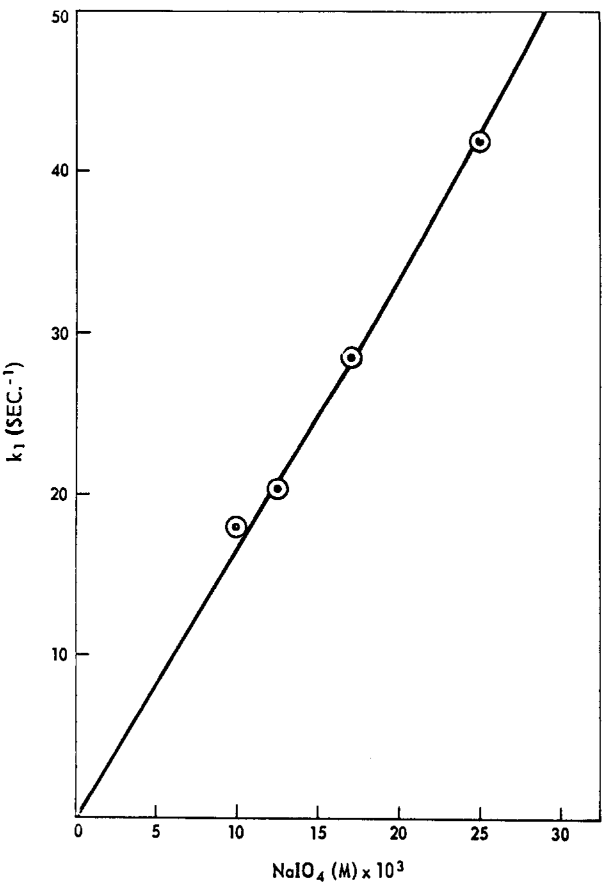

Fig. 2 The dependence of the observed first-order rate constant for intermediate formation on the periodate concentration at pH 5.0;

(Catechol) = 0.749×10^{-4} M