

Studies in the Autoxidation of Monolayers II. Catalysts and Inhibitors

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narrow. A series of measurements has been carried out on acid substrates at $F=10$, at the two temperatures 4°C and 17°C , analogous to the series at $F=8$. The general effect of increasing the pressure from $F=8$ to 10 is to depress the whole of the $K \sim pH$ curve, but there is in addition a tendency to displace the maximum to a higher pH (especially at 4°C) and to produce a flatter maximum. In Fig. 2 the results of this series of experiments are summarized by plotting the ratio K_8/K_{10} as a function of pH at each temperature, and it will be noted that the inhibitory effect of pressure disappears for substrates of pH 4 at 4°C . It was found impossible to obtain data sufficiently reliable to permit

the quantitative analysis of the effect of pressure of the individual constants.

We may conclude finally that the reaction mechanism which has been put forward gives a satisfactory account of the effect of pH in the velocity of oxidation of monolayers of maleic anhydride β -elaeostearin, although it has not been found possible to make the experimental accuracy sufficiently high to permit a complete quantitative analysis of the effects of temperature and pressure on the separate reactions involved.

Thanks are due to Imperial Chemical Industries (Dyestuffs Group) for a grant to one of us (G. G.).

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Studies in the Autoxidation of Monolayers

II. Catalysts and Inhibitors

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An account is given of the effect of metallic catalysts and organic pro- and anti-oxygens added to the substrate on the rate of oxidation of monolayers of maleic anhydride α -elaeostearin. The catalytic effect depends both in direction and magnitude on the pH of the substrate. The results are discussed in the light of the autoxidation mechanism proposed in Part I, and a semi-quantitative kinetic treatment developed which accounts successfully for the principal features of the results.

IN discussing the general behavior of monolayers of maleic anhydride β -elaeostearin it was noted¹ that the oxidation process is accelerated by adding to the substrate a small amount of CoSO_4 , and retarded by a similar addition of hydroquinone. In this paper we shall examine these effects in more detail, especially in the light of the oxidation mechanism discussed above.

METALLIC CATALYSTS

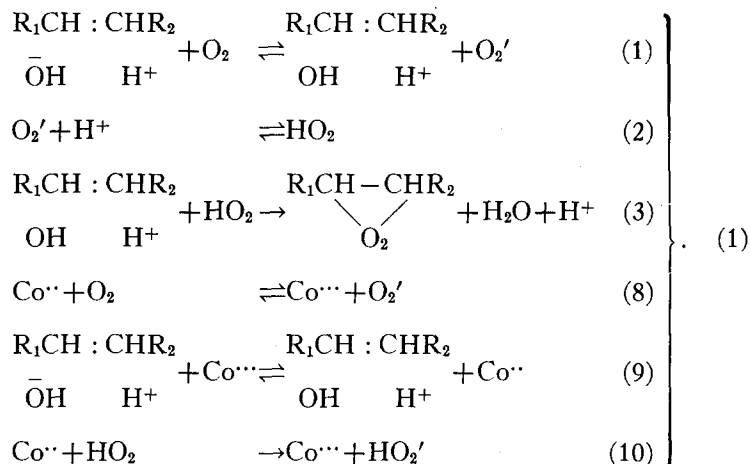
The experiments to which reference has been made were concerned with the effect of CoSO_4 on the rate of oxidation on $N/100$ H_2SO_4 substrates, and the behavior found was entirely in accord with expectation, the oxidation rate increasing progressively as the cobalt concen-

tration was raised. Replacement of cobalt by other metals however leads to more complex results. Thus MnSO_4 in $N/100$ H_2SO_4 gives only small accelerations, while high concentrations cause a reversal of the sign of catalysis, the metal becoming an inhibitor. Similar results were found for lead acetate in $N/100$ acetic acid and also for CoSO_4 in $N/10$ H_2SO_4 , while CoSO_4 in $N/100$ acetic acid gives more marked catalysis. It is evident that the catalytic effect of metals is complicated and is a function of both the concentration of the metal and the pH of the substrate. We have now to enquire therefore whether this behavior can be explained on the basis of the reaction mechanism given above, and we shall consider Co^{++} as a typical example. No experiments have been made on alkaline substrates so that the only oxidizable

¹ Proc. Roy. Soc. A153, 123 (1900).

material to be considered is $\text{R}_1\text{CH} : \text{CHR}_2$. As an additional simplification we shall restrict our attention to $p\text{H} \leq 2$, so that the concentration of the acid complex can be neglected, and the unoxidized film treated as consisting entirely of the neutral complex. The positive catalytic effect

of the metal we shall represent in the usual way as an alternative oxidation of the metal (by air) and reduction (by the film), while the negative catalytic effect is most simply accounted for by loss of HO_2 by oxidizing the metal. Combining these reactions with the normal oxidation mechanism we obtain the following set of reactions:²



(Followed by $\text{HO}_2' + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2$, and the catalytic decomposition of the H_2O_2 produced.)

These reactions are now to be analyzed kinetically so as to obtain an expression for the oxidation rate V , in terms of the concentration (c) of $\text{R}_1\text{CH} : \text{CHR}_2$, $[\text{O}_2]$, $[\text{H}^+]$ and the concentration (c_c) of cobalt added. The derivation follows the same general method as has been employed in Part I, and will only be given in outline. The unknowns which have to be

eliminated are $[\text{O}_2']$, $[\text{HO}_2]$, $[\text{Co}^{\cdot\cdot}]$, $[\text{Co}^{\cdot\cdot\cdot}]$ and c_c , the concentration of $\text{R}_1\text{CH} : \text{CHR}_2$. The five equations necessary are obtained by writing down:

- (i) the dissociation equilibrium of HO_2
- (ii), (iii), (iv), stationary state equations for HO_2 , O_2' and $\text{R}_1\text{CH} : \text{CHR}_2$
- (v) $[\text{Co}^{\cdot\cdot}] + [\text{Co}^{\cdot\cdot\cdot}] = c_c$.

A slight simplification is introduced by writing c_c instead of $[\text{Co}^{\cdot\cdot}]$ in obtaining the rate of reaction (10). The problem is readily reduced to the following quadratic equation for $[\text{HO}_2]$:

$$\begin{aligned}
 & [\text{HO}_2]^2 \cdot x \cdot \frac{k_{2e}k_{8r}}{[\text{H}^+]} \left(1 + \frac{k_{1r}k_{2e}}{k_3[\text{H}^+]} \right) + [\text{HO}_2] \left[\left(k_{9c} + \frac{k_{9r}}{k_3} x \right) \left(\frac{k_{1r}k_{2e}}{k_3[\text{H}^+]} x + k_2k_{2e} - k_{2r} + \frac{k_{2e}k_{8r}}{[\text{H}^+]} c_c \right) \right. \\
 & \left. - \frac{k_{2e}k_{8r}}{[\text{H}^+]} c (k_1[\text{O}_2] + k_9c_c) + k_8x[\text{O}_2] \left(1 + \frac{k_{1r}k_{2e}}{k_3[\text{H}^+]} \right) \right] - c \cdot [\text{O}_2] \left\{ k_1k_{9c} + \frac{k_1k_{9r}}{k_3} x + k_1k_8[\text{O}_2] + k_8k_9c_c \right\} = 0, \quad (2)
 \end{aligned}$$

where

$$x = k_3c_2 = k_2k_{2e} - k_{2r} - k_{10}c_c. \quad (3)$$

The velocity of oxidation is given by

$$V = k_3c_2[\text{HO}_2] = x[\text{HO}_2]. \quad (4)$$

² The nomenclature adopted is the same as in Part I (*q.v.*) and identical reactions are given the same number in both papers.

Also, from Eq. (5) of part I we know that the rate of oxidation V_0 in the absence of catalyst is given by

$$V_0 = \frac{k_1 c [\text{O}_2] [\text{H}^+]}{[\text{H}^+] + k_1 k_{2e} / k_3} \quad (5)$$

We now employ Eqs. (4) and (5) to change the variable in Eq. (2) from $[\text{HO}_2]$ to K/K_0 , remembering that $V/V_0 = K/K_0$, by the substitution

$$[\text{HO}_2] = \frac{K}{K_0} \cdot \frac{k_1 k_3 c [\text{O}_2] [\text{H}^+]}{x (k_1 k_{2e} + k_3 [\text{H}^+])} \quad (6)$$

We thus obtain the following quadratic equation for K/K_0 :

$$\begin{aligned} \left(\frac{K}{K_0} \right)^2 \cdot \frac{k_1^2 k_{2e} k_{8r} c [\text{O}_2]}{x} + \frac{K}{K_0} \cdot \frac{k_1}{x} \left[\left(k_3 c + \frac{k_{9r}}{k_3} x \right) \left\{ x \left([\text{H}^+] + \frac{k_1 k_{2e}}{k_3} \right) + c_c (k_{10} [\text{H}^+] + k_{2e} k_{8r}) \right\} \right. \\ \left. - k_{2e} k_{8r} c (k_1 [\text{O}_2] + k_3 c_c) + k_3 x [\text{O}_2] \left([\text{H}^+] + \frac{k_1 k_{2e}}{k_3} \right) \right] - \left([\text{H}^+] + \frac{k_1 k_{2e}}{k_3} \right) \\ \times \left\{ k_1 k_3 c + \frac{k_1 k_{9r}}{k_3} x + k_1 k_3 [\text{O}_2] + k_3 k_9 c_c \right\} = 0. \quad (7) \end{aligned}$$

This equation is now to be used to discuss the variation of the catalytic effect as a function of $[\text{H}^+]$ and c_c .

VARIATION WITH pH

At constant c_c , (7) may be written in the empirical form:

$$(K/K_0)^2 + (K/K_0)(A + B[\text{H}^+]) - (D + E[\text{H}^+]) = 0, \quad (8)$$

where A , B , D , E are independent of $[\text{H}^+]$. This may be further modified by changing to a new variable

$$Y = (K/K_0) - 1 \quad (9)$$

when we obtain an equation of the same form as (8):

$$Y^2 + Y(A' + B'[\text{H}^+]) - (D' + E'[\text{H}^+]) = 0. \quad (10)$$

As $c_c \rightarrow 0$, $Y \rightarrow 0$ so that for small values of c_c the solution of (10) is

$$Y \cong \frac{D' + E'[\text{H}^+]}{A' + B'[\text{H}^+]}. \quad (11)$$

This equation requires that the catalytic effect of the metal will, in general, be a function of pH, but does not enable us to predict the direction of the effect. In order to apply it to the experimental data it is necessary to compare values of

Y at the same (very small) value of c_c and this is most conveniently done by comparing values of

$$\left(\frac{\partial(K/K_0)}{\partial c_c} \right)_{c_c=0}$$

at different pH's. It is clear that the variation should be of the form

$$\left(\frac{\partial(K/K_0)}{\partial c_c} \right)_{c_c=0} = \frac{\alpha + \beta[\text{H}^+]}{\gamma + [\text{H}^+]}, \quad (12)$$

where α , β , γ are constants. In Fig. 1 plots of

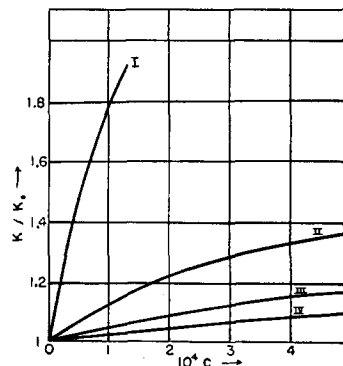


FIG. 1. Effect of pH on catalytic. Effect of cobalt. I, pH 4.7; II, 3.8; III, 3.0; IV, 2.0.

TABLE I. Variation of catalytic effect with pH.

[H ⁺]	$\left(\frac{\partial(K/K_0)}{\partial c_c}\right)_{c_c=0}$	[c _c in g % Co.]
	obs.	calc.
2.0×10^{-5}	12,000	12,000
1.6×10^{-4}	2,000	2,060
1.0×10^{-3}	450	495
1.0×10^{-2}	250	230

K/K_0 against c are given for a number of pH's, and in Table I the observed values of

$$\left(\frac{\partial(K/K_0)}{\partial c_c}\right)_{c_c=0}$$

are compared with the values calculated from Eq. (12) by putting $\alpha=0.298$, $\beta=200$, $\gamma=5.2 \times 10^{-6}$. The agreement is certainly within experimental error over the range of pH 2.0 to 4.7. It was not found practicable to extend the measurements to higher pH's as it was impossible to obtain sufficiently consistent velocity constants in this region, probably owing to the presence of traces of metallic impurity in the substrate. (At pH 5.3, a 10 percent acceleration would be produced by the presence of 3×10^{-6} percent Co.).

EFFECT OF COBALT CONCENTRATION

We have next to enquire whether the observed change of sign of catalysis at high metal concentrations is also explicable by this analysis. For this purpose Eq. (7) may be rewritten to give K/K_0 as an empirical function of c_c , in the form

$$(K/K_0)^2 + (K/K_0)(A + B \cdot c_c + D \cdot c_c^2) - (E + F \cdot c_c + G \cdot c_c^2) = 0, \quad (13)$$

where A , B , D , E , F , G are independent of c_c . The condition for a reversal of sign of catalysis is given by $K/K_0 = 1$, whence

$$1 + A - E + (c_c)_r(B - F) - (c_c)_r^2(G - D) = 0, \quad (14)$$

where $(c_c)_r$ is the value of c_c for $K/K_0 = 1$. Also since $(c_c)_r = 0$ must be a solution of (14),

$$E = A + 1$$

and we find

$$(c_c)_r = (B - F)/(G - D) \quad (\text{or } 0). \quad (15)$$

The existence of a critical concentration at which

reversal of catalysis occurs is therefore predicted, but it is not possible to predict the variation of $(c_c)_r$ with pH.

ORGANIC PRO- AND ANTI-OXYGENS

The phenomena associated with the use of organic pro- and anti-oxygens in bulk have been widely studied and we are in particular indebted to Moureu and his collaborators³ for the collection of a great deal of empirical information on this subject. A wide diversity of behavior is shown by the many systems investigated and examples have been found of almost every conceivable type of behavior, including the following:—

- (i) Simple acceleration or retardation of the oxidation,
- (ii) Acceleration by small amounts of catalyst and retardation by larger amounts, or *vice versa*,
- (iii) Reversal, i.e., acceleration during the early stages of the oxidation followed by retardation of the later stages, or *vice versa*.

A few experiments soon showed that the results obtained in monolayers, when pro- and anti-oxygens are added to the substrate, are likely to prove almost as complex, although no example of reversal (class (iii)) has yet been found. Some typical results are given in Fig. 2, in which the effect of concentration on catalytic activity is shown for several oxidation catalysts at pH 1.

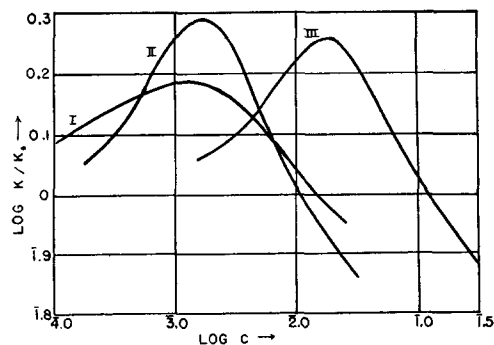
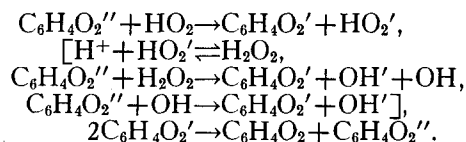
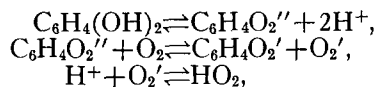


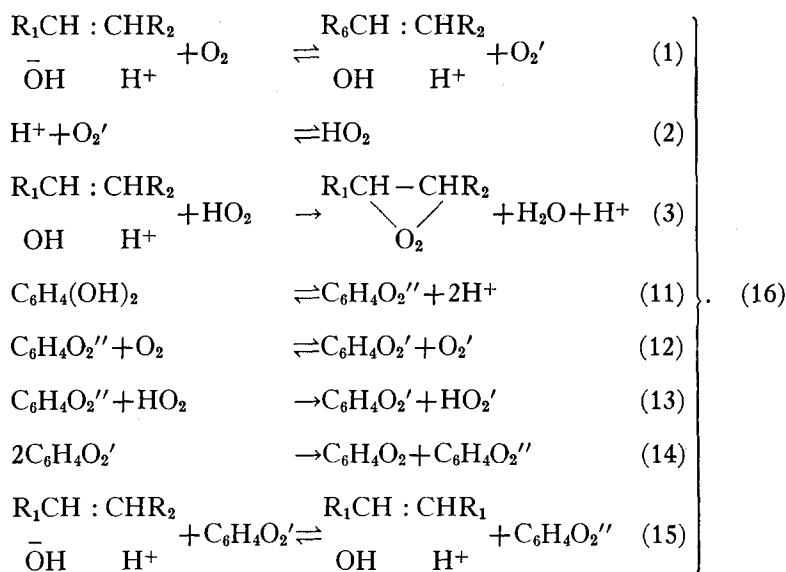
FIG. 2. Effect of organic pro- and anti-oxygens. I, iodo-aceric acid; II, *p*-nitraniline; III, piperidine.

³ For reviews see Chem. Rev. 3, 113 (1926); Chem. and Ind. 47, 819, 848 (1928).

Instead of examining the behavior of a large number of catalysts it was considered preferable to study a selected system in some detail and the catalyst chosen was hydroquinone, the autoxidation of which has been extensively studied.⁴ This material is stable to oxygen at pH 's below 7, its rate of oxidation being proportional to $[OH']^2$. In terms of a free radical mechanism the oxidative process may be formulated as follows.⁵



The bracketed equations we shall omit from our analysis as they introduce no fundamental differences. We have now to formulate the interaction of this system with maleic anhydride β -elaeostearin, and we shall confine ourselves—as in the case of catalysis by cobalt—to the pH range 2–7, so that the complete system to be examined is as follows:



Let c_i = concentration of $C_6H_4(OH)_2$,
 c_6 = concentration of $C_6H_4O_2''$,
 c_7 = concentration of $C_6H_4O_2'$,

the remainder of the nomenclature being as defined above. Since hydroquinone is very slightly ionized in the pH range considered c_i may be identified with the total hydroquinone concentration. The analysis follows the same lines as before, the necessary equations being derived by writing down:

(i), (ii) dissociation constants for reactions (2) and (11). (iii), (iv), (v) stationary state equations for $R_1CH : CHR_2$, HO_2 and $C_6H_4O_2'$. The

problem may now be reduced to an equation for $[HO_2]$ but the expression obtained is much too cumbersome to handle. It can be greatly simplified if we neglect the term in c_7^2 , a process which is justified to a first approximation since c_7 is small. The equation now becomes:

$$\begin{aligned} [HO_2]^2 &\left\{ \frac{k_{2e}k_{12r}(k_{1r}k_{2e} + k_3[H^+])}{k_3k_{15}c[H^+]^2} \left(k_2k_{2e} - k_{2r} - \frac{k_{11e}k_{13}c_i}{[H^+]^2} \right) \right\} + [HO_2] \left\{ \left(k_2k_{2e} - k_{2r} - \frac{k_{11e}k_{13}c_i}{[H^+]^2} \right) \right. \\ &\cdot \frac{1}{k_3[H^+]} \left(k_{1r}k_{2e} + k_3[H^+] + \frac{k_{2e}k_{11e}k_{12r}k_{15r}c_i}{k_{15}c[H^+]^2} \right) - \frac{k_{11e}k_{13}c_i}{[H^+]^2} - \frac{k_1k_{2e}k_{12r}}{k_{15}[H^+]} [O_2] \left. \right\} - [O_2] \left\{ k_1c + \frac{k_{11e}k_{12}c_i}{[H^+]^2} \right\} = 0. \quad (17) \end{aligned}$$

⁴ La Mer and Rideal, J. Am. Chem. Soc. **46**, 223 (1924). Reinders and Dingemans, Rec. trav. chim. Pays-bas **53**, 209 (1934).

⁵ Cf. Weiss, Naturwiss. **23**, 64 (1935).

A first approximation to the solution of this equation can be obtained by neglecting the term in $[\text{HO}_2]^2$, since we know that $[\text{HO}_2]$ must be small, and our confidence in this procedure is increased by noting that we obtain the correct value of $[\text{HO}_2]_0$ by putting $c_i=0$. From the value of $[\text{HO}_2]$ we readily obtain the following expression for the catalytic ratio V/V_0 .

$$\frac{V}{V_0} = \frac{(k_3[\text{H}^+] + k_{1r}k_{2e})\{k_{1c} + k_{11e}k_{12}c_i/[\text{H}^+]^2\}}{k_{1c}\left\{k_{1r}k_{2e} + k_3[\text{H}^+] + \frac{k_{2e}k_{11e}k_{12}r_{15}r_{16}c_i}{k_{15}c[\text{H}^+]^2} - \frac{k_3}{[\text{H}^+]} \frac{k_{1k_{1r}k_{2e}[\text{H}^+][\text{O}_2] + k_{11e}k_{13}k_{15}c_i}{k_{2k_{2e} - k_{2r} - k_{11e}k_{13}c_i/[\text{H}^+]^2}}\right\}} \quad (18)$$

This may be written in the form:

$$\frac{V}{V_0} = \frac{(A + [\text{H}^+])(B + D \cdot c_i/[\text{H}^+]^2)}{E + F[\text{H}^+] + G \cdot \frac{c_i}{[\text{H}^+]^2} - \frac{L + c_i/[\text{H}^+]}{M - N \cdot c_i/[\text{H}^+]^2}}, \quad (19)$$

where A, B, D, E, F, G, L, M and N do not involve $[\text{H}^+]$ or c_i . For small values of c_i we can expand the last term of the denominator. Then collecting similar terms and introducing the condition that $V = V_0$ for $c_i = 0$ we obtain finally (writing fresh constants):

$$\frac{V}{V_0} = \frac{(A + [\text{H}^+])(1 + B \cdot c_i/[\text{H}^+]^2)}{A + [\text{H}^+] + D \cdot c_i/[\text{H}^+] + E \cdot c_i/[\text{H}^+]^2 - F \cdot c_i^2/[\text{H}^+]^3}. \quad (20)$$

We have now to employ this equation to discuss the variation of V/V_0 with c_i and $[\text{H}^+]$ and we must remember in doing so that the equation has been derived on the basis of two assumptions

- (i) that c_i is small,
- (ii) that $10^{-2} \ll [\text{H}^+] \ll 10^{-7}$.

If $[\text{H}^+]$ is very small,

$$\frac{V}{V_0} \sim \frac{AB}{E - F \cdot c_i/[\text{H}^+]}. \quad (21)$$

At constant c_i , V/V_0 will therefore increase as

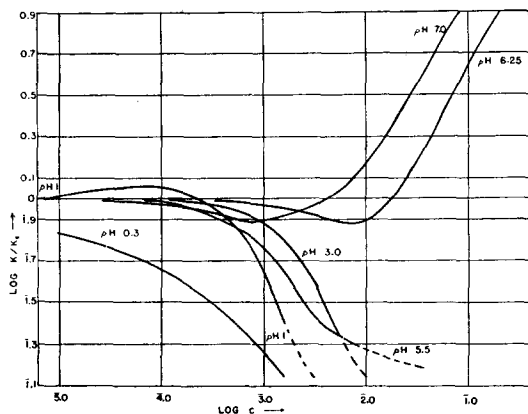


FIG. 3. Effect of hydroquinone on oxidation.

$[\text{H}^+]$ decreases, while at constant $[\text{H}^+]$, V/V_0 will increase with c_i . It is clear that this equation is meaningless for $c_i \geq E[\text{H}^+]/F$. If $[\text{H}^+]$ is large,

$$\frac{V}{V_0} \sim \frac{[\text{H}^+]}{[\text{H}^+] + D \cdot c_i/[\text{H}^+]}. \quad (22)$$

At constant c_i , V/V_0 will therefore increase as $[\text{H}^+]$ increases, the limit being given by $V/V_0 \rightarrow 1$; while at constant $[\text{H}^+]$, V/V_0 will decrease as c_i increases.

The condition for a reversal of sign of catalysis is found by putting $V = V_0$ in Eq. (20) and is easily seen to be of the form

$$(c_i)_r = \alpha[\text{H}^+]^2 + \beta[\text{H}^+], \quad (23)$$

where α, β are constants. Combining the various deductions we have been able to make from Eq. (20) we thus reach the following conclusions:

- (i) At constant c_i , V/V_0 approaches unity at low pH 's, decreases as the pH is raised, passes through a minimum and then increases again, finally becoming > 1 at sufficiently high pH 's.
- (ii) At constant $[\text{H}^+]$, the conclusions are less certain, but it seems most probable that the $(V/V_0 \sim c_i)$ curve should resemble in general form the $(V/V_0 \sim \text{pH})$ curve.

In Figs. 3 and 4 are plotted the results of an extensive series of measurements over a wide range of values of both c_i and $[H^+]$ and we observe that, within the limits defined above, the analysis is fairly successful. The decrease of V/V_0 at low pH 's is outside our restricted pH range, but the $(V/V_0 \sim pH)$ curves are in other respects essentially similar to the prediction. In the $(V/V_0 \sim c_i)$ curves a reversal of sign of catalysis is found only for the two highest pH 's but there is some evidence of a minimum in the next lowest pH . If we insert the two observed values of $(c_i)_r$ in Eq. (23) we find

$$\alpha = 10^{10}, \quad \beta = 3 \times 10^4,$$

whence we can calculate $(c_i)_r$ for other pH 's, and it is easily seen that for pH 5.5, $(c_i)_r \cong 0.2$ percent, while for the lower pH 's $(c_i)_r$ is impossibly high.

The mechanism advanced in Part I thus gives a reasonably satisfactory account of the behavior of metallic catalysts and organic pro- and anti-oxygens. The treatment given, while only approximate, nevertheless elucidates the principal features of the experimental results, and thus increases our confidence in the essential correctness of the mechanism proposed.

The author is indebted to Professor E. K.

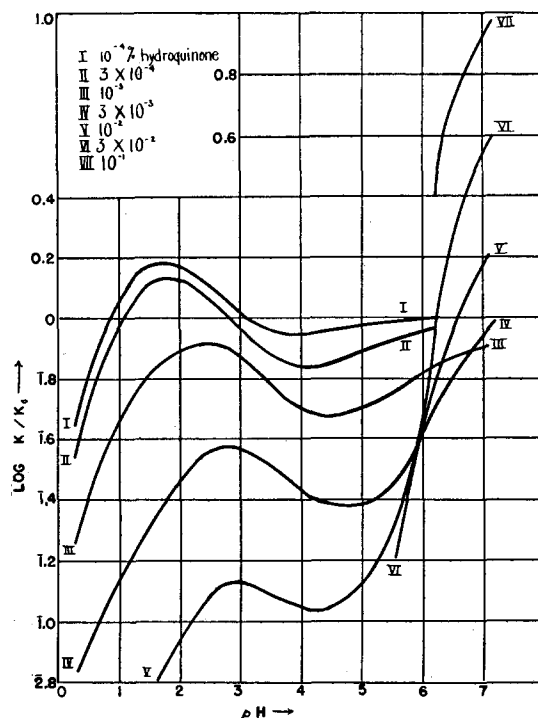


FIG. 4. Effect of hydroquinone on oxidation rate.

Rideal for much helpful advice and criticism, and to Imperial Chemical Industries (Dyestuffs Group) for financial aid.

Photochemical Studies. XXV. The Direct Photochemical Decomposition of Nitrous Oxide

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(Received June 2, 1937)

The number of molecules of gas uncondensed by liquid air formed per quantum absorbed by nitrous oxide has been determined both in the presence and absence of mercury. At least part of the primary dissociation must be into nitrogen molecules and oxygen atoms. A mechanism consistent with the facts involves the subsequent reactions $O + N_2O = 2NO$ and $O + O = O_2$. However, it is impossible to state definitely that none of the primary dissociation is into nitric oxide molecules and nitrogen atoms. The weakness of the absorption suggests that the absorption is "forbidden" and it is possible that the nitrogen molecules and oxygen atoms are produced in their normal electronic states (with perhaps some vibrational energy in the nitrogen molecule).

THE photochemical decomposition of nitrous oxide presents a real theoretical interest because the number of possible modes of primary dissociation is limited to two and because the

number of secondary reactions cannot be large. A study of the decomposition sensitized by mercury vapor was recently published,¹ but it

¹ Manning and Noyes, J. Am. Chem. Soc. **54**, 3907 (1932).