

# New Aspects of Ionic Catalysis in Oxidation of Organic Compounds by Oxygen

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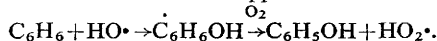
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The kinetics of methylethylketone oxidation in aqueous solutions has been studied. The catalysts used were  $\text{Fe}^{3+}$  ions and complexes:  $\text{Cu}^{2+}$ -pyridine,  $\text{Fe}^{3+}$ -phenanthroline,  $\text{Mn}^{2+}$ -phenanthroline. A mechanism has been proposed involving the following enolization,  $\text{RH} \xrightleftharpoons{\text{H}^+} \text{EnH}$  and oxidation steps,  $\text{EnH} + \text{Me}^{(n+1)+} \rightarrow \text{R}\cdot + \text{Me}^{n+} + \text{H}^+$ ,  $\text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$ ,  $\text{RO}_2\cdot + \text{Me}^{n+} \rightarrow \text{ROOH} + \text{Me}^{(n+1)+}$ ,  $\text{ROOH} + \text{Me}^{n+} \xrightarrow{\text{H}^+} \text{RO}\cdot + \text{Me}^{(n+1)+} + \text{H}_2\text{O}$ ,  $\text{HO}\cdot + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}\cdot$ ,



A general scheme of catalytic oxidation has been proposed on the basis of the scheme for the catalytic oxidation of ascorbic acid (non-chain oxidation with a cycle  $\text{Me}^{(n+1)+} \xrightarrow{\text{RH}} \text{Me}^{n+} \xrightarrow{\text{O}_2} \text{Me}^{(n+1)+}$ ), the scheme for catalytic chain oxidation of hydrocarbons and aldehydes, and the scheme for oxidation of methylethylketone. The  $\text{Br}^-$  and  $\text{H}^+$  catalysts may be those converting  $\text{ROOH}$  into free radicals.

A different mechanism of catalysis has been found for the oxidation of benzene in aqueous solution in the presence of  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$ . This reaction is autocatalytic. Autocatalysis is due to formation of free radicals in phenol oxidation. Benzene is supposed to be oxidized to phenol by a reaction



## CATALYTIC OXIDATION OF METHYLETHYLKETONE IN AQUEOUS SOLUTIONS

Oxidation of many organic compounds by molecular oxygen in the presence of transition metal ions is a chain reaction involving catalytic initiation of chains by reaction of the catalyst with hydroperoxide. Of interest is the catalytic oxidation under conditions when a usual chain reaction with propagation of chain by the reaction,  $\text{RO}_2\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}\cdot$ , is impossible.

Methylethylketone in aqueous solution has been chosen for study at 50–60°C. The activity of peroxy radicals in aqueous solution is low owing to the hydrogen bond formed by  $\text{RO}_2\cdot$  and water.<sup>1</sup> The ratio  $k(\text{RO}_2\cdot + \text{RH})/k^{\frac{1}{2}}(\text{RO}_2\cdot + \text{RO}_2\cdot) = a = 2.9 \times 10^{-4} \text{ M}^{-\frac{1}{2}} \text{ sec}^{-\frac{1}{2}}$  in water at 60°C.<sup>1</sup> The rate of oxidation is  $v = v_i + a[\text{RH}]\sqrt{v_i}$ , where  $v_i$  is the velocity of initiation of free radicals. The reaction is of a chain nature if  $v_i < a^2[\text{RH}]^2 = 2.1 \times 10^{-8} \text{ M sec}^{-1}$  at  $[\text{RH}] = 0.5 \text{ M}$ . The rate of a non-chain reaction will be higher than  $2a^2[\text{RH}]^2 = 4.2 \times 10^{-8} \text{ M sec}^{-1}$  at  $[\text{RH}] = 0.5 \text{ M}$ .

The rate of oxidation of methylethylketone has been measured manometrically. No oxidation was observed in the absence of a catalyst. The  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions and the  $\text{Fe}^{3+}$ -phenanthroline,  $\text{Cu}^{2+}$ -pyridine and  $\text{Mn}^{2+}$ -phenanthroline complexes have been found to catalyze oxidation of methylethylketone.<sup>2, 3</sup> The rates of oxidation were  $10^{-6}$ – $10^{-5} \text{ M sec}^{-1}$ , which is in agreement with a non-chain mechanism. Illustrative results of methylethylketone oxidation by oxygen with  $\text{Fe}^{3+}$  will be discussed.

To clarify the mechanism of this reaction, the oxidation of methylethylketone by  $\text{Fe}^{3+}$  has been studied also in the absence of oxygen. The rate  $v_{\text{Fe}^{3+}}$  of reaction was measured from the accumulation of  $\text{Fe}^{2+}$ . The  $\text{Fe}^{2+}$  concentration was determined by the phenanthroline method.<sup>4</sup> Methylethylketone was oxidized to biacetyl, reducing four  $\text{Fe}^{3+}$  ions to four  $\text{Fe}^{2+}$  per one molecule of ketone. Free radicals initiating polymerization of methyl methacrylate have been found to be formed in this reaction. The rate of the reaction between ketone and  $\text{Fe}^{3+}$  is lower than that of ketone enolization,  $v_{\text{en}}$  ( $v_{\text{en}}$  was measured iodometrically). The rate  $v_{\text{Fe}^{3+}}$  goes through a maximum with increasing pH (fig. 1).

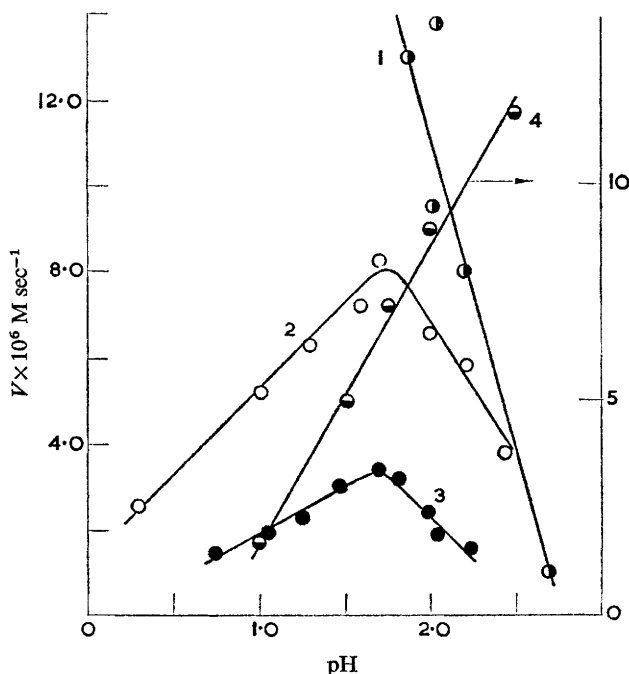
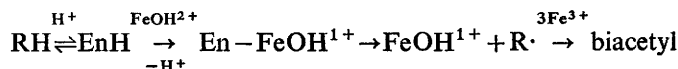


FIG. 1.—Dependence of reaction rates on pH at  $60.5^\circ$  and  $[\text{ketone}] = 0.5 \text{ M}$ . 1, the rate of enolization of methylethylketone; 2, the rate of oxidation of ketone by  $\text{O}_2$  at  $[\text{Fe}^{3+}]_0 = 0.05 \text{ M}$ ,  $p_{\text{O}_2} = 700 \text{ mm Hg}$ ; 3, the rate of oxidation of ketone by  $\text{Fe}^{3+}$ ; 4, the concentration of  $\text{FeOH}^{2+}$  at  $25^\circ\text{C}$  ( $10^3 \text{ M}$ ).

The dependence of  $v_{\text{Fe}^{3+}}$  on  $[\text{Fe}^{3+}]$  and  $[\text{RH}]$  is expressed as

$$V_{\text{Fe}^{3+}}^{-1} = (\alpha_1/[\text{RH}]) + (\beta_1/[\text{RH}][\text{Fe}^{3+}]).$$

The following scheme for ketone oxidation by  $\text{Fe}^{3+}$  in the absence of  $\text{O}_2$  has been proposed:

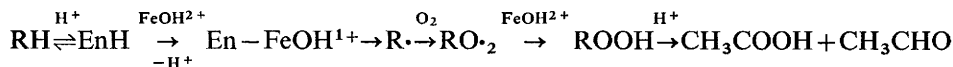


EnH is an enolic form of ketone. This scheme explains the dependence of  $v_{\text{Fe}^{3+}}$  on  $[\text{RH}]$  and  $[\text{Fe}^{3+}]$ , and that of  $v_{\text{Fe}^{3+}}$  on pH, as well as the formation of free radicals in this system. The maximum dependence of  $v_{\text{Fe}^{3+}}$  on pH seems to be due to the fact that at low pH the concentration of  $\text{FeOH}^{2+}$  is low and at high pH the rate is limited by enolization of ketone.

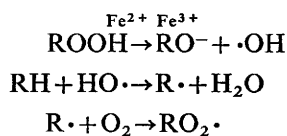
A similar dependence has been obtained for the rate of oxygen absorption,

$$V_{O_2}^{-1} = (a_2/[RH]) + (b_2/[RH][Fe^{3+}]),$$

The  $V_{O_2}^{-1}$  value goes through a maximum with increasing pH (fig. 1), and, at  $pO_2 > 400$  mm Hg,  $V_{O_2}$  does not depend on  $pO_2$ . The products of ketone oxidation by oxygen are acetic acid and acetaldehyde. The following scheme may be proposed for ketone oxidation by oxygen in the presence of  $Fe^{3+}$ :



The  $\alpha$ -ketohydroperoxides are decomposed to acid and aldehyde by acids.<sup>5</sup> In accordance with this scheme,  $V_{O_2} \approx V_i \approx \frac{1}{4}V_{Fe^{3+}}$ , where  $V_{Fe^{3+}}$  is the rate of reaction of methylethylketone with  $Fe^{3+}$  in absence of  $O_2$ . But it has been found experimentally that  $V_{O_2} > V_{Fe^{3+}}$  (fig. 1, table 1). Consequently a suggestion was made that  $\alpha$ -ketohydroperoxide decomposes to active free radicals (e.g., OH) by the action of ferrous and ferric ions



The formation of active free radicals has been proved by introducing isopropanol into ketone that was being oxidized. Acetone has been found among the products of oxidation. Isopropanol was not oxidized in the absence of ketone. Comparison

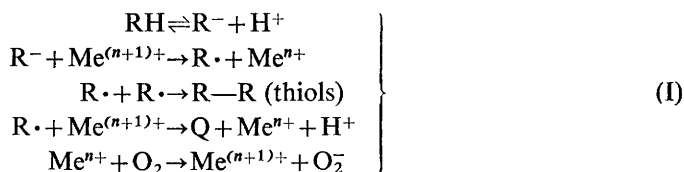
TABLE 1.—OXIDATION OF METHYLETHYLKETONE IN  $H_2O$  WITH VARIOUS CATALYSTS

catalyst	dependence of $V_{O_2}$ on pH	dependence of $V_{O_2}$ on $pO_2$ (mm Hg)	$V_{O_2} \times 10^6$ M sec <sup>-1</sup>	$\frac{1}{4}V_{Fe^{3+}} \times 10^6$ M sec <sup>-1</sup>	conditions
$FeOH^{2+}$	maximum at 1.75 [ $Fe^{3+}$ ] <sub>0</sub> = 0.50 M	const. at $pO_2 \geq 400$	8.3	1.4	60.5°, pH = 1.75 [ $Fe^{3+}$ ] <sub>0</sub> = 0.05 M, [ketone] <sub>0</sub> = 0.50 M
$CuPy_n^{2+}$ $n = 2, 3$	increases with increasing pH 5.8 < pH < 7.8	const. at $pO_2 \geq 300$	4.1	1.0	50°, pH = 6.00, [ $Cu^{2+}$ ] <sub>0</sub> = 0.10 M, [Py] <sub>0</sub> = 1.0 M, [ketone] <sub>0</sub> = 0.50 M
$Fe^{3+}$ (phen) <sub>2</sub>	maximum at pH = 0.90 [ $Fe^{3+}$ ] <sub>0</sub> = $2 \cdot 10^{-3}$ M [phen] <sub>0</sub> = $6.7 \cdot 10^{-2}$ M	increases	5.6	0.40	60.5°, pH = 1.00, [ $Fe^{3+}$ ] <sub>0</sub> = $2 \cdot 10^{-3}$ M, [phen] <sub>0</sub> = $3 \cdot 10^{-2}$ M [ketone] <sub>0</sub> = 0.50 M
$Mn^{3+}$ (phen) (autocatalytic reaction)	decreases with increasing pH 0.5 < pH < 2.7	const. at $pO_2 \geq 500$	1.85	0.20	60.5°, pH = 1.25 [ $Mn^{2+}$ ] <sub>0</sub> = 0.15 M [phen] <sub>0</sub> = 0.10 M [ketone] <sub>0</sub> = 0.50 M

of rate constants for the reactions:  $HO \cdot + Fe^{3+}$  ( $k = 8 \times 10^6$  M<sup>-1</sup> sec<sup>-1</sup>)<sup>6</sup>;  $HO \cdot + Fe^{2+}$  ( $k = 2.6 \times 10^8$  M<sup>-1</sup> sec<sup>-1</sup>)<sup>7</sup>;  $HO \cdot + CH_3COC_2H_5$  ( $k = 5.4 \times 10^8$  M<sup>-1</sup> sec<sup>-1</sup>)<sup>8</sup> shows that under experimental conditions the radical  $HO \cdot$  reacts mostly with ketone ([ $Fe^{2+}$ ]  $\approx 10^{-2}$  M; [ $Fe^{3+}$ ]  $\approx 5 \cdot 10^{-2}$  M; [ketone] = 0.5 M). Similar results have been obtained for ketone oxidation by other catalysts (table 1). It will be seen from the table that in all cases  $V_{O_2} > V_i$ , i.e., the scheme allowing for decomposition of ROOH into active radicals is valid.

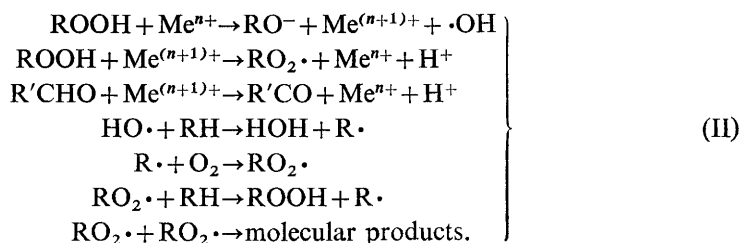
GENERAL SCHEME FOR CATALYTIC OXIDATION  
ORGANIC COMPOUNDS

The following scheme of oxidation was suggested for thiols<sup>9, 10</sup>:



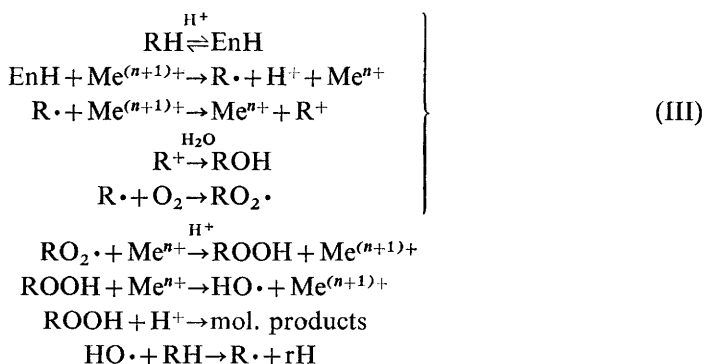
And a similar scheme was suggested for the oxidation of ascorbic acid.<sup>11, 12</sup> In reactions of this kind, catalysis is accounted for by the fast step  $\text{R}^- + \text{Me}^{(n+1)+}$  which limits the rate of the overall process. The only role of oxygen in such a process is to oxidize  $\text{Me}^{n+}$  to  $\text{Me}^{(n+1)+}$ .

The catalytic oxidation of aldehydes<sup>13, 14</sup> and hydrocarbons<sup>15</sup> is quite different:



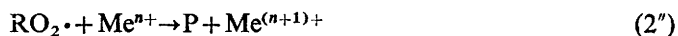
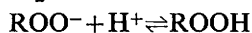
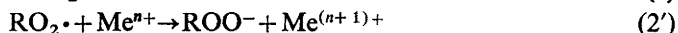
The catalyst initiates chains in processes of this kind.

The mechanism of methylethylketone oxidation differs from schemes (I) and (II) but some of its steps are similar:

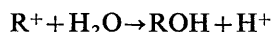
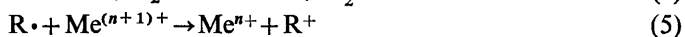
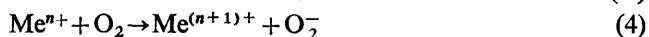
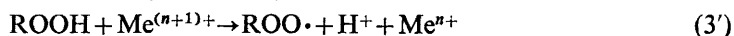
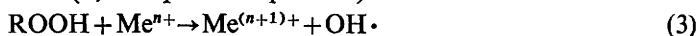


This scheme is intermediate between schemes (I) and (II). On the basis of schemes (I), (II) and (III), a general scheme for catalytic oxidation of organic compounds may be proposed. This scheme ought to be supplemented by the step,  $\text{RO}_2^\bullet + \text{Me}^{n+} \rightarrow \text{Me}^{(n+1)+} + \text{non-peroxide product}$ . This reaction takes place in the catalytic oxidation of hydrocarbons.<sup>15</sup> The ethylphenylperoxy radical has been shown to react with  $\text{Mn}^{2+}$  to form ketone.<sup>16</sup>

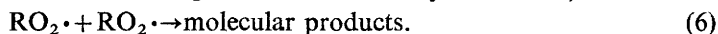
## GENERAL SCHEME OF CATALYTIC OXIDATION



(P, non-peroxide product)



(Q is the double-bond analogue of RH formed by loss of 2H)



Different variants of this scheme may take place depending on structure of RH, the catalyst and the conditions of oxidation. For example, catalytic oxidation of aldehydes involves the following steps: 0,1,2,3,6 (initiated chain reaction). The mechanism of hydroquinone oxidation with  $\text{Cu}^{2+}$  involves the steps: 0,4,5'; that for thiols the steps: 0,1',4 (non-chain oxidation with a cycle,  $\text{Me}^{(n+1)+} \xrightarrow{\text{RH}} \text{Me}^{n+} \xrightarrow{\text{O}_2} \text{Me}^{(n+1)+}$ ); that for methylethylketone with  $\text{Fe}^{3+}$  and with complexes  $\text{Cu}^{2+}$ -pyridine: enolization, 0,1,5,2',3; that for methylethylketone with complexes  $\text{Fe}^{3+}$ -phenanthroline: enolization, 0,1,5,2',3. This scheme explains the formation of alcohols and ketones (non-peroxide products) along with hydroperoxide by reactions 2'', 5 and 6. This was observed for the catalytic oxidation of cyclohexane,<sup>17</sup> n-decane<sup>18</sup> and cyclohexene.<sup>19</sup> The scheme explains the retarding action of transition metals.<sup>15, 19</sup> Retardation seems to be due to chain termination by reactions 2', 2'' and 5 dominating over initiation by reactions 0 and 3. Peroxy radicals react very rapidly with transition metal compounds in a hydrocarbon medium. For example, cobaltous acetylacetonate reacts with  $\text{RO}_2\cdot$  of oxidizing styrene in chlorobenzene with a rate constant<sup>20</sup>  $k = 2.9 \times 10^9 \exp(-7800/RT) \text{ M}^{-1} \text{ sec}^{-1}$ .

## NON-METALLIC CATALYTIC IONS

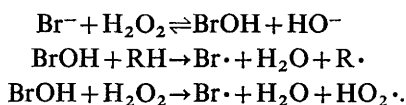
Not only metals but also anions may act as catalysts for liquid-phase oxidation. Decomposition of peroxides to free radicals under the action of  $\text{Br}^-$  has been found recently.<sup>21, 22</sup> Free radicals form by the bimolecular reaction between tert-butylhydroperoxide and  $\text{Br}^-$  in n-propanol. The rate constant was

$$k = 4.0 \times 10^8 \exp(-19500/RT)^{21}$$

The following reaction has been supposed to occur:  $\text{ROOH} + \text{Br}^- \rightarrow \text{RO}\cdot + \text{OH}^- + \text{Br}\cdot$ . The  $\text{Br}^-$  ion reacts also with hydrogen peroxide to form free radicals. The rate of free radicals formation is<sup>22</sup>

$$v_i = k_1[\text{Br}^-][\text{H}_2\text{O}_2] + k_2[\text{Br}^-][\text{H}_2\text{O}_2]^2.$$

At 70°C,  $k_1 = 1.21 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ ;  $k_2 = 1.27 \times 10^{-3} \text{ M}^{-2} \text{ sec}^{-1}$ . The following scheme has been proposed



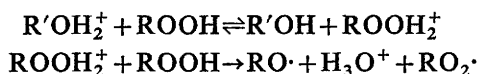
Hydrogen ions may catalyze oxidation, by decomposing hydroperoxides to free radicals.<sup>21</sup> The rate of free radical formation from  $\text{H}_2\text{O}_2$  and  $\text{HClO}_4$  in isopropanol has been found to be

$$\begin{aligned}v_i &= k_i[\text{H}_2\text{O}_2]^2[\text{HClO}_4], \quad ([\text{HClO}_4] < 0.01 \text{ M}), \\ k_i &= 3.3 \times 10^{15} \exp(-27,000/RT), \text{ M}^{-2} \text{ sec}^{-1}.\end{aligned}$$

The tert-butyl hydroperoxide decomposes to free radicals by action of  $\text{HClO}_4$  as well. The rate of free radical formation in isopropanol is  $v_i = k_i(\text{ROOH})^2(\text{HClO}_4)$ . At  $(\text{ROOH}) < 0.03 \text{ M}$ ,  $(\text{HClO}_4) < 0.01 \text{ M}$  the rate constant is

$$k_i = 4.0 \times 10^{15} \exp(-28,000/RT) \text{ M}^{-2} \text{ sec}^{-1}.$$

The following reaction mechanism has been proposed :



Thus, the number of catalysts that decompose peroxides into free radicals is great. The effect of  $\text{H}^+$  shows the ability of hydrogen ions to catalyze not only heterolytic, but also homolytic molecular reactions.

#### OXIDATION OF BENZENE CATALYZED BY FERROUS AND CUPRIC IONS

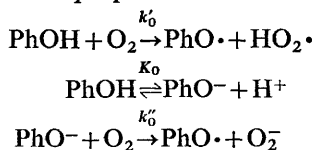
The above general scheme of catalytic oxidation is not universal. A different mechanism has been found for catalytic oxidation of benzene. Oxidation of benzene by oxygen in aqueous solutions in the presence of ions  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  has been established.<sup>23-29</sup> We have investigated in detail the kinetics of this reaction.<sup>30-32</sup>

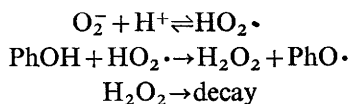
Benzene (2-10 ml in 100 ml of  $\text{H}_2\text{O}$ ) was oxidized in an autoclave in a glass reactor at 180-200°C,  $p\text{O}_2 = 0.35\text{-}35 \text{ atm}$ , in the presence of  $\text{CuSO}_4$   $10^{-4}$  to  $5 \times 10^{-2} \text{ M}$ , or  $\text{Fe}_2(\text{SO}_4)_3$ ,  $2.5 \times 10^{-2} \text{ M}$ , to  $2.0 \times 10^{-2} \text{ M}$ . Phenol was the main intermediate. The reaction is autocatalytic and is faster in the presence of  $\text{Fe}^{2+}$  than in that of  $\text{Fe}^{3+}$  (fig. 2). Phenol is responsible for the autocatalysis, as may be seen from experiments with different amounts of phenol introduced into the benzene (fig. 3).

The kinetics of phenol oxidation catalyzed by iron ions has been studied in the absence of benzene. Phenol was oxidized by  $\text{O}_2$ ,  $\text{Fe}^{3+}$  and by free radicals ( $\text{HO}\cdot$  and  $\text{HO}_2\cdot$ ) under these conditions (200°C,  $\text{H}_2\text{O}$ ,  $\text{Fe}_3(\text{SO}_4)_2$ ). The rate of phenol oxidation in reaction with oxygen, in the absence of  $\text{Fe}^{3+}$ , was

$$\begin{aligned}v &= k[\text{PhOH}][\text{O}_2], \quad k = a_3 + b_3[\text{H}^+]^{-1}, \\ a_3 &= 1.13 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}, \quad b_3 = 2.9 \times 10^{-5} \text{ sec}^{-1} \text{ at } 200^\circ\text{C}.\end{aligned}$$

The following mechanism has been proposed





It is seen from the scheme that  $k'_0 = \frac{1}{2}a_3$  and  $k_0 k'_0 = \frac{1}{2}b_3$ .

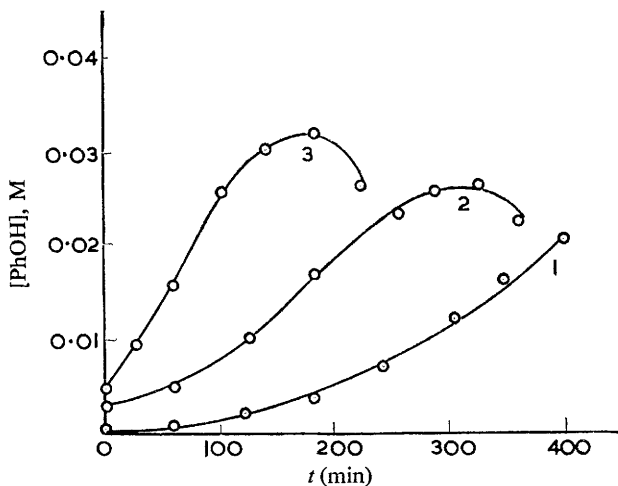


FIG. 2.—The kinetics of phenol formation by oxidation of benzene at 200°C; 4 ml benzene with 100 ml H<sub>2</sub>O, atm of air with different catalysts: 1, [Fe<sup>3+</sup>]<sub>0</sub> = 0.005 M; 2, [Fe<sup>2+</sup>]<sub>0</sub> = 0.005 M; 3, [Cu<sup>2+</sup>]<sub>0</sub> = 0.012 M and [Fe<sup>2+</sup>]<sub>0</sub> = 0.005 M.

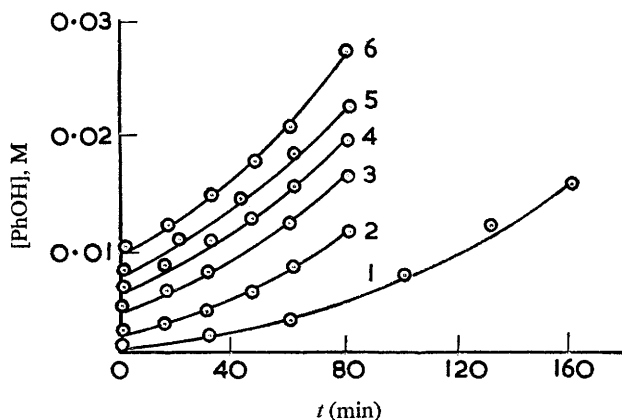
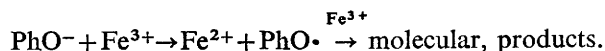


FIG. 3.—The kinetics of phenol formation at 200°C; 5 ml benzene with 100 ml H<sub>2</sub>O; pH = 1.2, [Fe<sup>3+</sup>]<sub>0</sub> = 0.006 with different amounts of phenol, added at the initial moment: 1, without phenol added; 2, [PhOH]<sub>0</sub> = 0.0018; 3, 0.0046 M; 4, 0.0074 M; 5, 0.0074 M; 6, 0.0100 M.

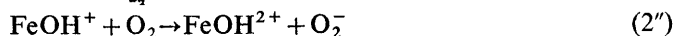
The reaction of phenol with Fe<sup>3+</sup> has been studied in the absence of oxygen. The rate of this reaction was  $v = k_1[\text{Fe}^{3+}][\text{PhOH}][\text{H}^+]^{-1}$ ,  $k = 3.5 \times 10^{-4} \text{ sec}^{-1}$  at 200°C. The following reaction is supposed to occur



The Fe<sup>2+</sup> ions are oxidized by oxygen at a rate of

$$v = (4.25 \times 10^{-3} + 9.0 \times 10^{-5}[\text{H}^+]^{-1})[\text{Fe}^{2+}][\text{O}_2] \text{ M sec}^{-1} (200^\circ\text{C}).$$

The following mechanism may be proposed :



As one  $\text{O}_2$  molecule oxidizes four  $\text{Fe}^{2+}$  ions, the rate of the reaction is

$$V = 4 k_2' [\text{Fe}^{2+}] [\text{O}_2] + 4 k_2'' K_2 [\text{Fe}^{2+}] [\text{O}_2] [\text{H}^+]^{-1}$$

$$k_2' = 1.06 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}; \quad k_2'' K = 2.25 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1} \quad (200^\circ \text{C}).$$

TABLE 2.—CONTRIBUTION FROM DIFFERENT REACTIONS TO THE PHENOL OXIDATION AT  $200^\circ \text{C}$

$[\text{O}_2]$ M	$[\text{H}^+]^{-1}$ $\text{M}^{-1}$	$[\text{Fe}^{3+}] \times 10^3$ M	$K k_0 [\text{O}_2] 10^5$ $\text{sec}^{-1}$	$k_1 [\text{Fe}^{3+}] 10^5$ $\text{sec}^{-1}$	$k_r [\text{OH}]$ $\text{sec}^{-1}$	$V \times 10^5 / [\text{PhOH}]$ $\text{sec}^{-1}$
0.022	12.6	2.2	0.52	0.97	1.26	2.75
0.022	12.6	1.1	0.52	0.48	1.00	2.00
0.022	12.6	0.5	0.52	0.22	0.56	1.30
0.044	6.0	17.0	0.60	4.10	6.30	11.00
0.022	52.4	0.2	1.50	0.36	2.31	4.17

$V$  = rate of disappearance of PhOH.

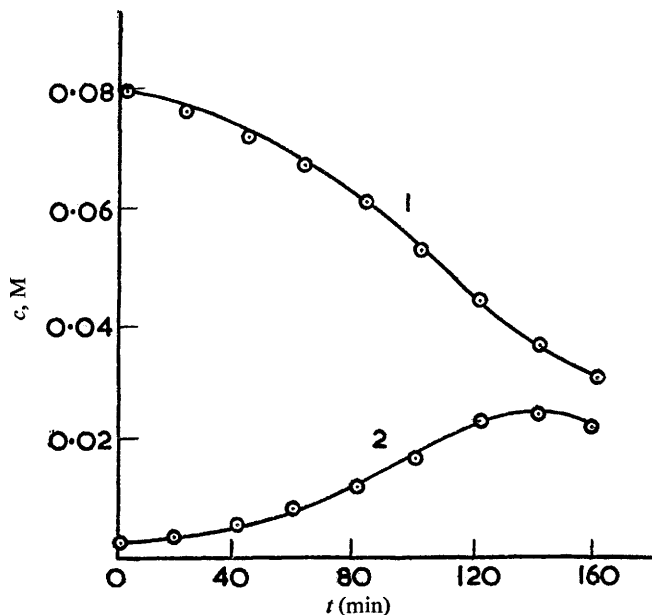


FIG. 4.—Kinetics of consumption of benzene (1) and formation of phenol (2) in benzene oxidation at  $200^\circ \text{C}$ ,  $\text{pH} = 1.90$ ;  $p_{\text{O}_2} = 35 \text{ atm O}_2$ ; 3 ml  $\text{C}_6\text{H}_6$  in 100 ml  $\text{H}_2\text{O}$ .

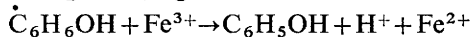
The  $\text{HO}\cdot$  and  $\text{HO}_2\cdot$  radicals react with phenol. Summarizing all reactions of phenol oxidation, we obtain for the rate of disappearance of PhOH,

$$V = (k_0 [\text{O}_2] + k_1 [\text{Fe}^{3+}] + k_r [\text{r}\cdot]) [\text{PhOH}]$$

where  $[\text{r}\cdot]$  is the total concentration of active radicals ( $\text{HO}\cdot$  and  $\text{HO}_2\cdot$ );  $k_r$  is an effective rate constant. The rates of each reaction in the phenol oxidation are given in table 2.



The radicals  $\text{HO}\cdot$  react with benzene. This reaction has been proved to occur by the addition mechanism<sup>33</sup>:  $\text{HO}\cdot + \text{C}_6\text{H}_6 \rightarrow \dot{\text{C}}_6\text{H}_6\text{OH}$ . Phenol is formed in the reaction of  $\text{C}_6\text{H}_6\text{OH}$  with  $\text{O}_2$  or  $\text{Fe}$ , e.g.,



The kinetics of phenol formation and benzene consumption are given in fig. 4.

The ratio of rate constants,  $k(\cdot\text{OH} + \text{C}_6\text{H}_6)/k(\cdot\text{OH} + \text{C}_6\text{H}_5\text{OH})$  has been calculated from concentrations and the rates of benzene and phenol consumption at a maximum phenol concentration. This ratio is unity. This is in agreement with the assumption of  $\text{HO}\cdot$  addition to benzene and phenol. Calculation of rates of free radical formation has shown that the reaction  $\text{Fe}^{2+} + \text{O}_2$  is predominant only at the initial stage of oxidation. In the presence of phenol in a concentration higher than 0.01 M, the main reaction of free radical formation is that between phenol and oxygen, i.e., the catalyst acts mainly as an initiator in this reaction.

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