# *Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. I. The Thermal Behavior of Iron Sulfate and Chloride in Aqueous Solutions without Benzene*

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Benzene can be oxidized to phenol in an aerated aqueous solution by cobalt-60 gamma rays at room temperature[1]. The yield is improved in the presence of iron and copper ions[2,3]. It has been reported that the yield also increases somewhat above 130°C, even in the absence of any metal ions[4,5].

This subject has been studied also in this Laboratory in co-operation with a group of researchers at Showa Denko Co., Tokyo. Especially, the effect of metal ions on the oxidation reactions has been studied at elevated temperatures. The experiments were rather troublesome due to the corrosion of the reactor and the precipitation of metal ions. In order to clarify such complicated phenomena, the first problem was to understand the thermal behavior of metal salt aqueous solutions, used for benzene oxidation, without benzene at elevated temperatures. Therefore, the experimental methods employed in benzene oxidation were also used for this purpose. The results for iron sulfate and chloride aqueous solutions will be given in the present paper.

## Experimental

**Solutions.** — G. R. reagents without further purification were dissolved initially by 0.01 M-Fe[6] in 0, 0.01 and 0.1 N sulfuric acid for ferrous and ferric sulfates or in hydrochloric acid of these concentrations for these chlorides.

**Apparatus and Procedure.**—A hard-glass reaction tube with a stopper, having a small hole for gas, was set tightly in a 50 ml. stainless-steel reactor. Fifteen ml. of the solution was put in the glass tube under oxygen pressure of 30 atm. The temperature was varied in all cases by the same procedure, using an electric controlling-heater, that is, a) the reactor was heated up to the given temperature during 30 min. by the heater (first-stage), b) kept at that temperature within ±1°C for 30 min. (middle-stage), and c) cooled outside the heater by a fan (final-stage). For reference, the same experiments were carried out without the middle stage to find the contribution of reactions during the first and final stages[7]. The temperature was measured by thermocouple set in the wall of the reacter.

**Analytical.**—The solutions after reaction were analyzed by a spectrophotometer as follows: The concentration of total iron species dissolved was determined from the optical density of ferric-oxine complex in chloroform at 470 m$\mu$ at pH=3.5∼4.5 (0.0105 for 1 $\mu$g. iron species)[8], and the concentration of ferrous species in it from that of ferrous-$\alpha,\alpha'$-dipyridyl complex in an aqueous solution at 522 m$\mu$ at pH 3∼9 ($\varepsilon=8520$), adding some potassium fluoride if necessary. The amount of ferric species in the aqueous phase and the amount of precipitated iron species were evaluated from these observed values. The original impurities, ferrous species in ferric solutions and vice versa, were $2\sim4\times10^{-5}$ M respectively.

## Results

**Ferric Sulfate and Chloride.**—The ferric concentrations after experiment in ferric sulfate

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[1] P. V. Phung and M. Burton, *Radiation Research*, 7, 199 (1957).

[2] J. H. Baxendale and D. Smithies, *J. Chem. Soc.*, 1959, 779.

[3] H. Hotta and A. Terakawa, This Bulletin, 33, 335 (1960).

[4] M. A. Proskurnin and Y. M. Kolotyrkin, Proc. 2nd Conf. Peaceful Uses A. E., Geneva, 29, 52 (1958).

[5] E. J. Henley, J. Goodman and I. Tang, *Trans. Am. Nuclear Soc.*, 3, No. 2, 387 (1960).

[6] All the concentrations of solutions were initially 0.01 M of iron ion.

[7] Such experiments are represented by the "reference experiment" in this series.

[8] K. Motojima and H. Hashitani, *Japan Analyst* (*Bunseki Kagaku*), 151 (1960).

solutions dissolved by 0.01 M of ferric ion in 0, 0.01 and 0.1 N sulfuric acid respectively, are given by solid marks and solid lines in Fig. 1, with the results of the corresponding reference experiments given by open marks and dotted lines. The corresponding results for ferric chloride dissolved in hydrochloric acid are given in Fig. 2. The low values of the reference experiment at 75°C for the neutral ferric chloride solution was just equal to the value of the filtrate before experiment, namely, the saturated concentration at room temperature. All the ferrous concentrations after experiment for ferric salts were not so different from their initial concentration contained as impurities, namely, $(1\sim4)\times10^{-5}$ M.

The same results of ferric and ferrous concentrations as those in Fig. 1 were obtained within the range of experimental error between 130 and 200°C for the neutral ferric sulfate solution under the following conditions: a) with irradiation by cobalt-60 gamma rays for 25 min. at the middle-stage of the heating procedure (14000 r), and b) with and without the same irradiation under nitrogen pressure of 30 atm. Therefore, the precipitation

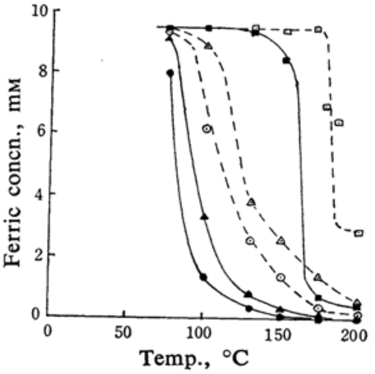

Fig. 1. Ferric concentration in 0.01 M-Fe ferric sulfate solutions after reaction (solid marks) with results of reference experiment (open marks); (⊙ and ●) in neutral, (△ and ▲) in 0.01 N and (⊡ and ■) in 0.1 N sulfuric acid.

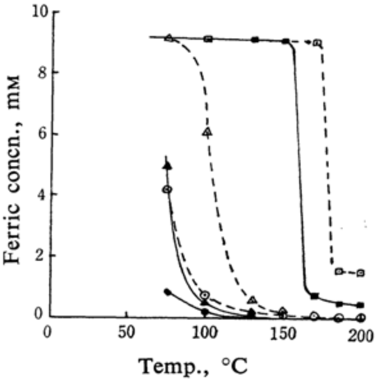

Fig. 2. Ferric concentration in 0.01 M ferric chloride solutions after reaction (solid marks) with results of reference experiment (open marks); (⊙ and ●) in neutral, (△ and ▲) in 0.01 N and (⊡ and ■) in 0.1 N hydrochloric acid.

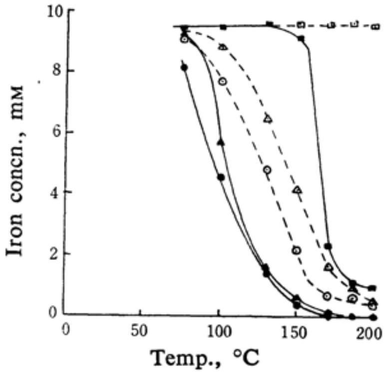

Fig. 3. Iron concentration in 0.01 M ferrous sulfate solutions after reaction with results of reference experiment; marks are the same with Fig. 1.

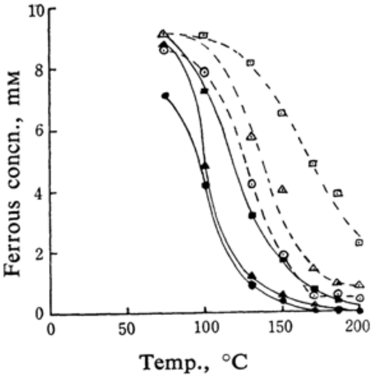

Fig. 4. Ferrous concentration in the results shown in Fig. 3; marks are the same with Fig. 1.

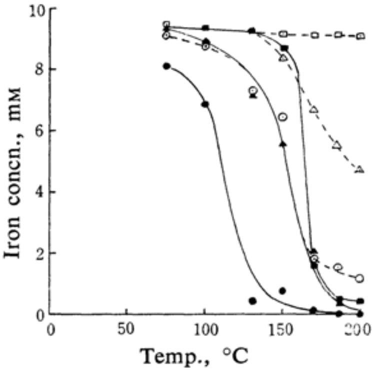

Fig. 5. Iron concentration in 0.01 M ferrous chloride solutions after reaction with results of reference experiment; marks are the same with Fig. 2.

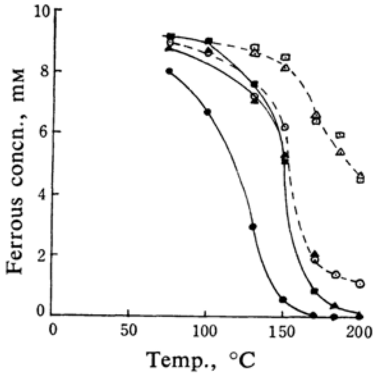

Fig. 6. Ferrous concentration in the results shown in Fig. 5; marks are the same with Fig. 2.

reaction is independent of oxygen and radiation. It is noted that the ferrous concentration dose not increase in all cases over that original impurities.

**Ferrous Sulfate and Chloride.**—The total iron and ferrous concentrations after experiment are shown in Figs. 3 and 4 for ferrous sulfate, and in Figs. 5 and 6 for ferrous chloride respectively.

## Discussion

**Oxidation of Ferrous Ions.** — The oxidation of ferrous ions by oxygen in an aqueous solution is usualy assumed to be[9,10]

$$Fe^{2+} + O_2 + H^+ = Fe^{3+} + HO_2 \qquad (1)$$

The concentration of hydrogen ion for reaction 1 is supposed to be fairly higher at elevated temperatures than at room temperature due to the higher dissociation of iron salt and water[11].

Since the ferrous sulfate solution in 0.1 N sulfuric acid gave no precipitate at temperatures lower than 150°C (Fig. 3), the rate of ferrous oxidation, $k_o$, in such a non-precipitated system can be expressed as

$$\frac{dx}{dt} = k_o(a-x)$$

at a given oxygen pressure from reaction 1; that is,

$$k_o = \frac{1}{t} \ln \frac{a}{(a-x)} \qquad \text{(i)}$$

where $a$ is the initial ferrous concentration, and $x$ the amount which is oxidized in time $t$. On putting the observed value of the reference experiments to $a$ and that of the actual experiments to $a-x$ in Eq. i, the oxidation rate, $k_o$, in 0.1 N sulfuric acid can be estimated as 1.24, 5.17 and $6.10 \times 10^{-4}$ sec$^{-1}$ at 100, 130 and 150°C respectively. Huffman and Davidson had estimated the rate to be $1.93 \times 10^{-5}$ atm$^{-1}$ sec$^{-1}$ at 159°C, i. e., $6 \times 10^{-4}$ sec$^{-1}$ at 30 atm. of oxygen[12]. The activation energy, estimated from the present values is also nearly equal to their value, 13.4 kcal./mol.[12]

Similarly, the oxidation rates of ferrous chloride in 0.1 N hydrochloric acid are estimated as 0.83 and $2.78 \times 10^{-4}$ sec$^{-1}$ at 130 and 150°C respectively. These rates are slower than the above values of ferrous sulfate. The rate seems to increase as the complexing affinity of the anion for ferric ion increases[12,13]. However, the high oxidation rate in sulfuric acid may be partially due to decomposed products of sulfate ion, which is ignored in Eq. i.

**Precipitation of Iron Species.**—Milburn concluded, in his study of the hydrolysis of ferric ion at 25°C, that the dimerization of ferric monohydroxide is predominant in a solution more concentrated than 0.001 M[14]. In fact, more precipitate was found in the lower acidic solution. Therefore, it can be assumed that the precipitation reaction is through the dimerization of partially hydrolyzed ferric ions, for the equilibrium constant of ferric hydrolysis is much higher[15] and the stability of ferric hydroxide is lower[16] in comparison with ferrous species.

When the rate-determining step of the precipitation reaction is assumed from these facts to be bimolecular for the formal concentration of iron species in the solution, the precipitation rate, $k_p$, can be expressed as

$$\frac{dx}{dt} = k_p(a-x)^2$$

That is,

$$k_p = \frac{x}{ta(a-x)} \qquad \text{(ii)}$$

where $a$ is the initial iron concentration in the solution, and $x$ the amount of iron precipitate during time $t$.

The rates of the precipitation reaction, $k_p$, for ferric sulfate, estimated from Eq. ii like Eq. i, are plotted against the reciprocal of the absolute temperature in Fig. 7. This figure suggests that the ratio of the rates is 1.00 : 0.47 : 0.105 in 0, 0.01 and 0.1 N sulfuric

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[9] A. M. Posner, *Trans. Faraday Soc.*, **49**, 382 (1953).

[10] M. Cher and N. Davidson, *J. Am. Chem. Soc.*, **77**, 793 (1955).

[11] Intern. Critical Table, **6**, 152, McGraw-Hill Co. (1926).

[12] R. E. Huffman and N. Davidson, *J. Am. Chem. Soc.*, **78**, 4856 (1956).

[13] H. Hotta and S. Ohno, This Bulletin, **34**, 1640 (1961).

[14] R. M. Milburn, *J. Am. Chem. Soc.*, **77**, 1352 (1955); **79**, 537 (1957).

[15] B. O. A. Hedslröm, *Arkiv Kemi*, **5**, 457 (1953); **6**, 1 (1954).

[16] W. F. Linke, "Solubilities of Inorganic and Metal-organic Compounds", Vol. **1**, D. Van Nostrand Co., New York (1958), pp. 1038-1039.

TABLE I. X-RAY ANALYSIS OF PRECIPITATE

| Solute | Solvent | Precipitation temp., °C<br>100 | <br>130 | <br>200 |
|---|---|---|---|---|
| $Fe_2(SO_4)_3$ | Water | Completely amorphous | — | $\alpha$-$Fe_2O_3$ |
| | 0.1 N $H_2SO_4$ | — | — | $\alpha$-$Fe_2O_3$ |
| $FeSO_4$ | Water | — | Amorphous<br>$\alpha$-$Fe_2O_3$ | $\alpha$-$Fe_2O_3$ |
| | 0.1 N $H_2SO_4$ | — | — | $\alpha$-$Fe_2O_3$ |

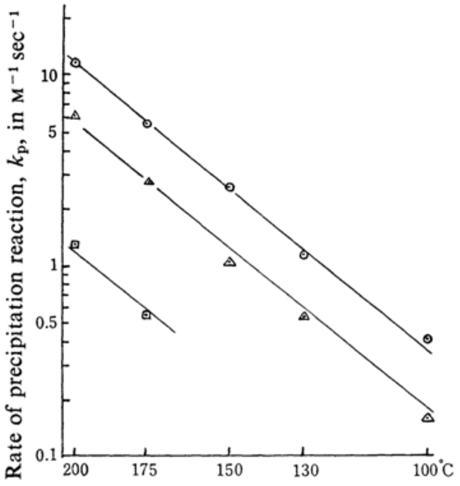

Fig. 7. Rate of precipitation reaction, $k_p$, from 0.01 M-Fe ferric sulfate aqueous solutions plotted against reciprocals of absolute temperature; (⊙) in neutral, (◬) in 0.01 N sulfuric acid and (▣) in 0.1 N sulfuric acid.

acid over a wide range of temperature, and that the activation energy of this reaction is 12.5 kcal./mol. in this range of acid concentration. When the precipitation reaction is assumed as above, this ratio means the ratio of the proportions of hydrolyzed ions at the respective acidities, i. e., the ratio of the true reactants.

The precipitation in the ferrous solution should also be attributed to ferric hydroxide oxidized from ferrous species, for the precipitate is the same from the ferric solution as shown in Table I. (See the next section). When the results for the 0.1 N acid solutions shown in Figs. 1, 2, 3 and 5 are compared, it is noted that precipitation is independent of either sulfate or chloride species, but dependent on either ferric or ferrous species, and that the precipitation is retarded in the ferrous solution compared with the ferric, but there is no difference between ferric and ferrous species in the iron concentration after experimentation. On the other hand, when the ferric solution is heated with benzene, the precipitation is somewhat retarded upon the reduction of ferric ions, as will be shown in detail in the next paper. These facts also support the assumption about the precipitation as mentioned already.

**Precipitates.** — Since the precipitates, when dried in a vacuum, gave no pattern for X-ray analysis, they were dried for one day at 70°C. The results of their X-ray analysis are given in Table I; the precipitate at 100°C still did not give any pattern, but the one at 130°C gave a weak pattern of $\alpha$-$Fe_2O_3$, and all the precipitates at 200°C gave a sharp pattern of $\alpha$-$Fe_2O_3$ independent of ferrous and ferric sulfates. Therefore, it is concluded that the precipitate at the lower temperature is completely amorphous. The color varied from orange to brown with rise of the precipitation temperature.

According to Shipko and Douglas[17], the precipitate of ferrous hydroxide containing $Ni(OH)_2$ is decomposed spontaneously in this manner;

$$3Fe(OH)_2 = Fe_3O_4 + H_2 + 2H_2O \qquad (2)$$

with the activation energy of 10.2 kcal./mol. below 100°C, and the pure ferrous hydroxide is more stable, decomposing with the activation energy of 30 kcal./mol. at 150∼200°C in the same manner. The former value for the amorphous precipitate is nearly equal to the activation energy from Fig. 7.

## Summary

The rate of the ferrous oxidation at 150°C is $6.10 \times 10^{-4}$ sec$^{-1}$ for sulfate, and $2.78 \times 10^{-4}$ sec$^{-1}$ for chloride at the oxygen pressure of 30 atm. The precipitation reaction of iron species is through hydrolyzed ferric ions even in the ferrous solution. The rate of precipitation for ferric sulfate is given in Fig. 7, with the activation energy of 12.5 kcal./mol. The precipitate is amorphous at 100°C and completely $\alpha$-$Fe_2O_3$ at 200°C.

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[17] F. J. Shipko and D. L. Douglas, *J. Phys. Chem.*, **60**, 1519 (1956).

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