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The Transfer of the Oxygen Atom of Water in an Aqueous Solution of Iron and Copper Sulfates*

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When an oxygen-18 enriched aqueous solution of ferrous, ferric and cupric sulfates was heated between 130 and 200°C, the oxygen-18 content decreased in the order of $\mathrm{Fe^{II}} > \mathrm{Fe^{III}} > \mathrm{Cu^{II}}$ in water; and it increased in the sulfate group and in the molecular oxygen of the gaseous phase. A transfer of oxygen from water to the sulfate group was also observed, even in a nitrogen atmosphere. The oxygen transfer was promoted in all the cases in the presence of molecular oxygen, and it increased further in the presence of benzene. Since the exchange reaction of oxygen does not occur between water and sulfate ions, the above facts may be attributed to the reactions between water and the thermal decomposition products of the sulfate group, and between water and the hydrogen peroxide produced. The peroxy species, produced by the oxidation of the decomposition products, are more reactive in such a transfer of oxygen, since the reaction is promoted in the presence of oxygen. The peroxides in the autoxidation of benzene seem also to be reactive in it.

The oxidation reaction of benzene to phenol in aqueous solutions of ferrous, ferric and cupric sulfates has previously been studied in our laboratory.[1-3] We showed that some of the oxygen atoms of the phenol produced originated in the water, using oxygen-18 enriched water.[4] In connection with this, the phenomena of the oxygen transfer in the oxygen-18 enriched aqueous solutions of these sulfates, which were studied with and without benzene, will be described in the present paper. Some properies of these solutions, studied without benzene under the same conditions as in the benzene oxidation, had already been reported in a previous paper.[5]

Experimental

Procedure.—The solutions of ferrous, ferric and cupric sulfates were prepared by dissolving 0.01 M of

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* Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. VIII.

[1] H. Hotta, A. Terakawa, K. Shimada and N. Suzuki, This Bulletin, **36**, 721 (1963).

[2] H. Hotta, N. Suzuki and A Terakawa, ibid., **36**, 1255 (1963).

[3] N. Suzuki and H. Hotta, ibid., **37**, 244 (1964).

[4] H. Hotta, N. Suzuki and T. Abe, ibid., **39**, 417 (1966).

[5] H. Hotta and N. Suzuki, ibid., **36**, 717 (1963).

metal ion in oxygen-18 enriched water (1.63 oxygen-18 atom%) obtained from the Weizman Institute of Science, Israel. These solutions were treated by the same procedure as was used in a previous paper.[5] That is, 15 cc. was put in a hard-glass tube in a 50 cc. stainless-steel reactor at an oxygen pressure of 30 atm. This system was then heated by a controlled heater and kept for 30 min. at a given temperature. Some of the experiments were performed under other conditions (see Table I). For example, experiments 44—47 were carried out at a nitrogen pressure of 30 atm., while 1 cc. of benzene was added for experiments 48—50. The experiments for the cupric sulfate solution were carried out only at 200°C under various conditions; experiment 40 was carried out under the standard condition described above; for experiment 40 the 0.001 M solution was used instead of the 0.01 M solution; experiment 42 was carried out in the presence of copper metal pieces alone[2]; and a 0.1 N sulfuric acid solution of 0.01 M cupric sulfate was used for experiment 43.

Although oxygen-18 7.56-atom-% enriched water was used to measure the change in the oxygen-18 content in the gaseous phase, the value in Table I is corrected as measured in 1.63-atom-% enriched water.

Analytical.—The oxygen-18 content in the water was determined as the atom percentage of oxygen-18 by the mass spectrum of carbon dioxide after equilibration with it by shaking it at 30°C for four hours.[6]

The oxygen-18 content in the sulfate group was also determined by the mass spectrum of carbon dioxide according to the method of Rittenburg and Ponticorvo after it was precipitated as barium sulfate and dried in vacumm for 48 hr.[7,8]

Although the observed values for the original enriched water as the standard fluctuated within ±0.02 atom %, the decrements after experimentation were in good agreement within ±0.001 atom% between the different runs. Therefore, the decrements or the differences between the values after and before experimentation are shown in the present paper.

Since the decomposition of the sulfate group must be expected at higher temperatures,[5] its concentration in the solutions after the above procedure was determined roughly as the residual ratio of the sulfate group:

$$R = \frac{(\mathrm{BaSO_4})_{\mathrm{treated}}}{(\mathrm{BaSO_4})_{\mathrm{untreated}}} \times 100 \qquad \text{(i)}$$

where $(\mathrm{BaSO_4})_{\mathrm{untreated}}$ and $(\mathrm{BaSO_4})_{\mathrm{treated}}$ represent the weights of dry barium sulfate precipitated from 50 cc. of the original and treated solutions respectively.

Results

The Decrements of the Oxygen-18 Atom Percentage in Water.—The results are shown in Table I. The decrements in the ferrous sulfate solution mount with increasing temperature (experiments 31—35). The decrements in the ferric sulfate solution are somewhat smaller than in the ferrous solution. When the solution was irradiated by 13000 r. of cobalt-60 gamma rays,[5] the decrements were nearly the same or a little larger than in the unirradiated solutions (experiments 37 and 39). The decrement in the cupric sulfate solution is smaller than in the iron sulfate solutions.

The results in 0.1 N sulfuric acid solutions are not very different from those in aqueous solutions (experiments 34 and 43); the effect of sulfuric acid is considerable in a nitrogen atmosphere (experiment 47).

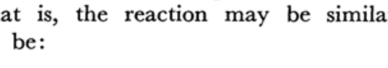
The results in Table Ib) show that the decrement is appreciable even in a nitrogen atmosphere, although it is smaller than in an oxygen atmosphere. The results in Table Ic) will be discussed later.

Oxygen-18 in the Sulfate Group.—The increments of the oxygen-18 atom percentage in the sulfate group, less by 0.20 than the observed value, are shown in Table I. They are larger in an oxygen atmosphere than in a nitrogen atmosphere, except in the cupric sulfate solution (experiment 46). The value in the presence of benzene is the largest among experiments 40, 46 and 50.

Iron sulfates are precipitated as ferric oxides at temperatures higher than 150°C in aqueous solutions[5] while few precipitates are found in an aqueous solution of cupric sulfate, even at 200°C. However, the concentration of the sulfate group in the iron sulfate solutions does not decrease so much as iron ions are precipitated, as is shown by the residual ratio of Eq. i in Table I.

Discussion

The results in Table Ib) show that there is some exchange reaction of oxygen between water and the sulfate group, independent of the presence of molecular oxygen. Brodsky and Vysotskaya have suggested the following scheme:



$$-\mathrm{X{=}O} + \mathrm{H_2O^*} \rightarrow -\mathrm{X}\begin{matrix}\mathrm{O^*H}\\ \mathrm{OH}\end{matrix} \rightarrow -\mathrm{X{=}O^*} + \mathrm{H_2O} \qquad (1)$$

for a similar reaction.[9] Since the exchange of the oxygen atom does not occur between water and sulfate ions,[10] the transfer of oxygen may be supposed to be due to the reaction not with the sulfate ion but with the sulfur trioxide produced by the thermal decomposition of the sulfate group; that is, the reaction may be similarly assumed to be:

$$\mathrm{MSO_4} \rightarrow \mathrm{MO} + \mathrm{SO_3} \qquad (2)$$

$$\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\mathrm{S{=}O} + \mathrm{H_2O^*} \rightarrow \begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\mathrm{S}\begin{matrix}\mathrm{O^*H}\\ \mathrm{OH}\end{matrix} \qquad (3)$$

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[6] M. Cohn and H. C. Urey, *J. Am. Chem. Soc.*, **60**, 679 (1938).

[7] D. Rittenburg and L. Ponticorvo, *J. Appl. Rad. Isotopes*, **1**, 208 (1956).

[8] I. Maass, *Kernenergie*, **5**, 402 (1962).

[9] A. E. Brodsky and N. A. Vysotskaya, *Zh. Fis. Khim.*, **32**, 1521 (1958).

[10] T. C. Hoering and J. M. Kennedy, *J. Am. Chem. Soc.*, **79**, 56 (1957).

TABLE I. CHANGE OF OXYGEN-18 ATOM PERCENTAGE AND RESIDUAL RATIO OF SULFATE

No.	Sulfate	Temp °C	Decrement in water	Increment in SO_4	Residual ratio of SO_4, R, %	Increment in gas phase	Remark
a) Aqueous solutions under oxygen pressure							
31	$FeSO_4$	130	0.006	—	—	—	—
32	$FeSO_4$	150	0.010	—	—	—	—
33	$FeSO_4$	180	0.015	0.78	85	0.0012	—
34	$FeSO_4$	180	0.014	—	—	—	0.1 N H_2SO_4 soln.
35	$FeSO_4$	200	0.014	—	—	—	—
36	$Fe_2(SO_4)_3$	150	0.006	—	—	—	—
37	$Fe_2(SO_4)_3$	150	0.007	—	—	—	Irradiated
38	$Fe_2(SO_4)_3$	180	0.013	1.07	85	—	—
39	$Fe_2(SO_4)_3$	180	0.014	—	—	—	Irradiated
40	$CuSO_4$	200	0.011	0.53	94	0.0018	—
41	$CuSO_4$	200	0.002	—	—	—	0.001 M $CuSO_4$
42	Cu-metal pieces	200	0.001	—	—	—	No sulfate
43	$CuSO_4$	200	0.009	1.09	97	—	0.1 N H_2SO_4 soln.
b) Aqueous solutions under nitrogen pressure							
44	$FeSO_4$	180	0.009	0.12	89	—	—
45	$Fe_2(SO_4)_3$	180	0.006	0.94	83	—	—
46	$CuSO_4$	200	0.004	0.68	91	—	—
47	$CuSO_4$	200	0.007	0.96	96	—	0.1 N H_2SO_4 soln.
c) Aqueous solutions with benzene under oxygen pressure							
48	$FeSO_4$	180	0.022	—	—	—	—
49	$Fe_2(SO_4)_3$	180	0.020	—	—	—	—
50	$CuSO_4$	200	0.015	0.97	98	0.0018	—

In fact, the increment of the oxygen-18 content in the sulfate group is larger in experiment 45 than in experiment 46 (in the order of the unstability of sulfates) and larger in experiment 47 than in experiment 46 (in the order of the concentration of the sulfate group). It is also explained by reactions 2 and 3 why the concentration of the sulfate group does not decrease in spite of the precipitation of ferric oxides, as is shown by the residual ratio of Eq. i. However, the result of experiment 44 is still obscure.

When the results in the oxygen and nitrogen atmospheres are compared, it may be seen that the transfer of the oxygen atom from water is promoted in the oxygen atmosphere, although the oxygen atom is not necessarily transferred from water to the sulfate group. Although the thermal decomposition of iron sulfates is independent of the presence of the molecular oxygen,[5] the decomposition products from the sulfate group are oxidized to peroxy acids, which are capable of exchanging oxygen with water, in the presence of oxygen.[11-13]

It has been assumed so far that hydrogen peroxide is formed in the oxygenated solution of iron and copper sulfates, as a result of the reaction:[1,14]

$$O_2 + M^+ = O_2^- + M^{2+} \tag{4}$$

Furthermore, it is known that the oxygen exchange reaction between hydrogen peroxide and water is induced in the presence of iron and copper ions (which are represented by M^+):

$$HOOH + M^+ = MOOH + H^+ \tag{5}$$

$$MOOH + H_2O^* = HOO^*H + MOH \tag{6}$$

and that reaction 6 is also induced by sulfur trioxide.[15,16] The oxygen exchange reaction might also occur between water and sulfur peroxides resulting from the oxidation of the decomposition products, in a manner similar to reaction 6.[10,13] These products, labeled by oxygen-18 as the result of these exchange reactions, namely, the labeled hydrogen peroxide and sulfur peroxides, provide not only the labeled sulfate and molecular oxygen, but also various products containing oxygen-18 which were not detected in the present study. In fact, even in experiment 46, the amount of oxygen-18 transferred from water (0.6 mg.) is fairly large in comparison with that transferred to the sulfate group (0.1 mg.); the amount transferred into gaseous oxygen, in experiment 40, is 0.1 mg. at most.

In summarizing the above discussion, the oxygen transfer reactions from water may be classified

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[11] J. M. Monger and O. Redlich, *J. Phys. Chem.*, **60**, 797 (1956).

[12] M. Tsao and W. K. Wilmarth, ibid., **63**, 346 (1959).

[13] C. R. Giuliano, N. Schwarz and W. K. Wilmarth, ibid., **63**, 353 (1959).

[14] G. Czapski and M. Dorfman, ibid., **68**, 1169 (1964).

[15] M. Anbar, *J. Am. Chem. Soc.*, **83**, 2031 (1961).

[16] M. Anbar and S. Guttmann, ibid., **83**, 2035 (1961).

into 1) reaction 3 through the thermal decomposition products of the sulfate group, independent of the presence of molecular oxygen; 2) some reactions through peroxy products from the above decomposition products in the presence of oxygen; and 3) reaction 6 through the formation of hydrogen peroxide.

As was pointed out in the foregoing paper,4) the concentration of iron species in the solution is about 0.0001 M at 180°C and 200°C as a result of the precipitation of ferric oxides.5) Although this is much smaller than in experiment 41 (0.001 M $CuSO_4$), the observed value of the decrement of the oxygen-18 content in water is much larger in experiments 33 and 38 than in experiment 41. The efficiency for the decrement is in the order of $Fe^{II} > Fe^{III} > Cu^{II}$. This suggests that the oxidation of metal ion, as well as the decomposition of sulfate, plays an important role in the transfer of the oxygen atom from water.

The Effect of Benzene Oxidation.—The results in Table I c) show that the decrement of the oxygen-18 content in water increases in the presence of benzene by 0.007 atom% at 180°C in either ferrous or ferric sulfate, and by 0.004 atom% at 200°C in cupric sulfate, in addition to the decrement when there is no benzene (Table I a), (experiments 33, 38 and 40), and that the increment of the oxygen-18 content in the sulfate group also increases considerably (experiments 40 and 50).

Since phenyl peroxide and its hydroperoxide are accumulated in the chain process of the benzene oxidation,4) the above effect may be attributed to some reaction with them. For example, phenyl peroxide and its hydroperoxide might exchange oxygen with water in a manner similar to reaction 6:

$$PhOOM + H_2O^* = PhOO^*H + MOH \qquad (7)$$

When M is sulfur trioxide, it may give the labeled sulfate group or its precursor.

When the results in Table I a) are compared with those in the previous papers,1-3) it may be seen that a large amount of benzene is oxidized to phenol when the decrement of the oxygen-18 content in water is greater than 0.010 atom% in Table I, independent of the other conditions. This suggests that the initiation process of the benzene oxidation is related to one of the oxygen-transfer process discussed above. Especially, the oxidation of benzene above 180°C in the unirradiated ferric and cupric sulfate solutions is considered to be initiated by the decomposition products of the sulfate group and their peroxides, since such decomposition is confirmed by the present study using oxygen-18. It has been reported that various aromatics, as well as benzene, are oxidized by sulfuric acid17) and aqueous sulfate18), which are decomposed to oxidizing reagents.

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17) M. Kilpatrick, M. W. Meyer and M. L. Kilpatrick, *J. Phys. Chem.*, **64**, 1433 (1960).

18) W. G. Toland, *J. Am. Chem. Soc.*, **82**, 1911 (1960).