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Reports of the Academy of Sciences of the USSR

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1963

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Figure 1

Figure 1: Figure 1

Abstract**Full Text**

Reports of the Academy of Sciences of the USSR
1963. Volume 149, No. 5

PHYSICAL CHEMISTRY

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RADIOLYSIS OF SULFURIC ACID

(Presented by Academician A. N. Frumkin on 25 XII 1962)

In solutions of medium and high concentrations, simultaneously with the transformation of the dissolved substance as a result of the direct action of radiation, its transformation also occurs as a result of interaction with the products of radiolysis of the solvent. By investigating transformations over a wide range of concentrations, these two effects can be reliably separated.

In the present work this method was applied to the study of the radiolytic transformations of sulfuric acid. Water was used as the solvent. The main part of the experiments was carried out in the presence of Fe^{2+} ions, which, as is known, effectively interact with various radicals and whose mechanism of radiation-chemical transformations has for the most part been studied. The work used thrice-distilled sulfuric acid and ferrous sulfate recrystallized three times. All solutions were prepared with bidistillate. Irradiation was performed with x-rays of maximum energy 65 keV and with Co^{60} gamma rays. The dose rate was determined with a ferrous sulfate dosimeter, with the corresponding recalculation depending on the acid concentration, taking for both types of radiation the value $G(\text{Fe}^{3+}) = 15.6$ ions/100 eV. Irradiation was carried out in glass cells at dose rates from 5×10^{15} to 2×10^{16} eV/ml · sec. The concentration of ferric ions and sulfur dioxide ⁽¹⁾ was determined by a spectrophotometric method. The concentration of sulfuric acid was varied from 0.4 to 18 M.

Fig. 1. Dependence of the yields of oxidation of Fe^{2+} ions on the electron fraction of sulfuric acid in solution. Solutions saturated with air (1), oxygen (2), hydrogen (3), nitrogen (4). Open points – irradiation with x-rays; filled points – gamma rays.

Over the entire concentration range of sulfuric acid investigated, oxidation of Fe^{2+} ions to Fe^{3+} was observed. At Fe^{2+} ion concentrations from 0.002 to 0.004 M, the yield of iron oxidation does not depend on its concentration. Oxidation

Fig. 2

Figure 2: Fig. 2

yields in 0.002 M FeSO₄ solutions, calculated from the initial linear portions of the accumulation curves, are shown in Fig. 1 as a function of the electron fraction of sulfuric acid. As can be seen, the oxidation yields are the same in solutions saturated with nitrogen and with hydrogen. When oxygen is introduced into the system, the yields of iron oxidation increase considerably. The value of the ratio $G(\text{Fe}^{3+})_{\text{O}_2}/G(\text{Fe}^{3+})_{\text{N}_2}$, as the concentration of H₂SO₄ increases from 0.4 to 17.3 M, decreases from 1.9 to 1.8. The straight lines shown in Fig. 1 were calculated by the method of least squares.

Investigation of the formation of sulfur dioxide showed that its yield under irradiation reaches a measurable value only in solutions with an acid concentration above 10 M (Fig. 2). The yield values obtained are close to those published in Ref. (1). In a 17.3 M solution of H₂SO₄, the influence of the concentration of Fe²⁺ ions on the yield of SO₂ formation was investigated in the presence and absence of oxygen (Fig. 3). As can be seen, Fe²⁺ ions and molecular oxygen do not affect the yield of SO₂ formation. According to data available in the literature (2, 3), radicals H, OH, and HSO₄ are formed in an aqueous solution of sulfuric acid upon irradiation. All three radicals are capable of oxidizing Fe²⁺ ions. Of the stable radiolysis products of aqueous sulfuric acid solutions (1-5)—H₂, SO₂, H₂SO₅, H₂S₂O₈, and H₂O₂—only H₂O₂, H₂SO₅, and H₂S₂O₈ oxidize Fe²⁺ ions. Consequently, in solutions not containing oxygen, the yield of iron oxidation should be equal to

$$G(\text{Fe}^{3+}) = G_{\text{H}} + G_{\text{OH}} + G_{\text{HSO}_4} + 2(G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{SO}_5} + G_{\text{H}_2\text{S}_2\text{O}_8}).$$

Fig. 2. Dependence of $G(\text{SO}_2)$ on the concentration of sulfuric acid. The solution is saturated with nitrogen.

Of the radiolysis products listed above, only the H atom is capable of interacting with oxygen (the reaction between O₂ and SO₂ at the low SO₂ concentrations corresponding to radiolysis proceeds very slowly and may be neglected).

Since $G(\text{Fe}^{3+})_{\text{O}_2}/G(\text{Fe}^{3+})_{\text{N}_2}$ at high acid concentrations retains the same value as in a 0.4 M solution, it may be assumed that the HO₂ radical is also capable of oxidizing three Fe²⁺ ions under these conditions. Then for 17.3 M

$$G(\text{Fe}^{3+})_{\text{O}_2} = 3G_{\text{H}} + G_{\text{OH}} + G_{\text{HSO}_4} + 2(G_{\text{H}_2\text{O}_2} + G_{\text{H}_2\text{SO}_5} + G_{\text{H}_2\text{S}_2\text{O}_8}),$$

$$G(\text{Fe}^{3+})_{\text{O}_2} - G(\text{Fe}^{3+})_{\text{N}_2} = 2G_{\text{H}}.$$

Fig. 3

Figure 3: Fig. 3

For H_2SO_4 the calculation gives a value of G_{H} equal to 2.85 atoms per 100 eV*. If it is assumed that atomic hydrogen is formed only as a result of the action of radiation on water, an improbably high yield of H atoms in the radiolysis of water is obtained, approximately 40 atoms per 100 eV. This leads to the conclusion that in 17.3 M H_2SO_4 the H atoms are formed mainly as a result of the action of radiation on sulfuric acid. At lower acid concentrations, H atoms are formed at the expense of both the acid and water.

Fig. 3. Dependence of $G(\text{SO}_2)$ on the concentration of Fe^{2+} ions in the presence (1) and absence (2) of oxygen.

Using the value of G_{H} thus found, it is possible to determine the yield of the oxidation products of sulfuric acid, since the electron fraction of water in a 17.3 M solution of H_2SO_4 is small; to a first approximation, one may neglect the yields of the water radiolysis products OH and H_2O_2 . Then one obtains

$$G_{\text{HSO}_4} + 2(G_{\text{H}_2\text{SO}_5} + G_{\text{H}_2\text{S}_2\text{O}_8}) = G(\text{Fe}^{3+})_{\text{N}_2} - G_{\text{H}} = 4.15.$$

* All yields are given per 100 eV absorbed by the solution. The root-mean-square error of the given yield values does not exceed 10%.

Since the yield of oxidation products must be equal to the yield of reduction products, the yield of sulfuric acid decomposition in this solution is 4.15 molecules per 100 eV.

Using the stoichiometric relation

$$G_{\text{H}_2} + 2(G_{\text{H}_2} + G_{\text{SO}_2}) = G_{\text{HSO}_4} + 2(G_{\text{H}_2\text{SO}_5} + G_{\text{H}_2\text{S}_2\text{O}_8}),$$

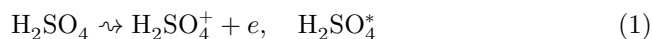
we obtain

$$G_{\text{H}_2} + G_{\text{SO}_2} = \frac{1}{2}[G(-\text{H}_2\text{SO}_4) - G_{\text{H}}] = 0.65.$$

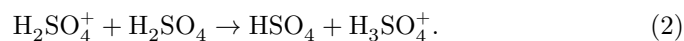
The yield of molecular hydrogen according to the data of (4) does not exceed 0.04 molecule per 100 eV in this system. For the yield of SO_2 , respectively, a value $G = 0.61$ molecule per 100 eV is obtained, which, within the experimental error, agrees with the experimental value given in Fig. 3.

The composition of sulfuric acid solutions depends substantially on their concentration (6). In a 17.3 M solution the main component (15-16 M) is undissociated sulfuric acid; in addition, at a concentration of $\sim 1\text{M}$ the ions HSO_4^- and H_3SO_4^+ or H_3O^+ are present.

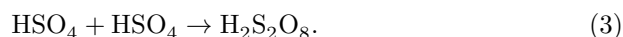
Taking ionization and excitation as the primary acts in the action of radiation on sulfuric acid, one may write:



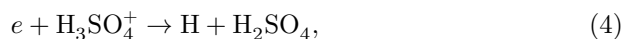
with subsequent formation of the HSO_4 radical, for example, by the reaction



In regions of high radical density, recombination of HSO_4 radicals to persulfuric acid will apparently occur:

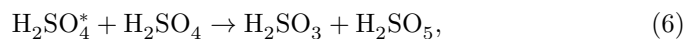


In strongly acid solutions, the free electrons knocked out by radiation from sulfuric acid molecules will be efficiently captured by positive ions with formation of atomic hydrogen, according to

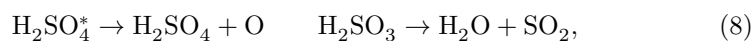


at a considerable distance from one another (the mean distance between positive ions in 17.3 *M* H_2SO_4 is of the order of 10 Å), and the probability of their recombination to molecular hydrogen must be small. This agrees with the low yield of molecular hydrogen (4).

Since $G(\text{SO}_2)$ does not depend on the concentration of atomic-hydrogen acceptors (Fig. 2), one may conclude that the reduction of sulfuric acid to sulfur dioxide does not proceed at the expense of H atoms. It may be assumed that SO_2 is formed by the interaction of sulfuric acid molecules excited by radiation with neighboring molecules, according to the reactions:



or





In solutions of medium sulfuric-acid concentration, the main component of the solution will be HSO_4^- ions. In these solutions the mechanism of radiochemical transformations is more complex, since the radiolysis of water plays a substantial role and, consequently, so does the transformation of sulfuric acid as a result of indirect action.

According to the data obtained, the yield of sulfuric acid decomposition is 4.15 molecules per 100 eV absorbed by sulfuric acid. This yield value is close to the decomposition yields of other inorganic compounds irradiated in the liquid state or in solutions—water (4.5 molecules (7)), perchlorate ions (5.5 ions (8)), nitrate ions (3.7 ions (9)).

The mechanism of radiolysis of sulfuric acid, as of other inorganic acids, has considerable similarity to the mechanism of radiolysis of water. Thus, in water, in sulfuric acid, and in pure liquid hydrogen chloride¹⁰, atomic hydrogen is formed in high yield. Livingston and Weinberger¹¹ found that atomic hydrogen is also formed in frozen solutions of hydrochloric, phosphoric, and sulfuric acids. Apparently, atomic hydrogen is formed in the radiolysis of any inorganic acids.

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Received
19 XII 1962

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Note: Figure translations are in progress. See original paper for figures.

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