$k_2 = 2.7 \times 10^6$. In any event this value is to be compared with the values 1.2×10^3 for chloride and 3.4×10^4 for the bromide system.

We may conclude that the rates of these reactions are correlated with the ease of oxidation of the particular halide used. Since these reactions undoubtedly take place between complexed forms of the metal ions, and since the complexing ability of the halides decreases as the rates increase, we may also conclude that charge repulsion is not a primary consideration.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF OREGON STATE COLLEGE]

Isotopic Exchange Reactions of Liquid Sulfur Trioxide and Sulfur Dioxide[1]

BY J. L. HUSTON

No isotopic exchange of sulfur takes place at room temperature when sulfur trioxide is dissolved in liquid sulfur dioxide or when sulfur dioxide is dissolved in liquid sulfur trioxide, and exchange occurs only slowly at 132°. It is suggested on the basis of these results and of work of Nakata that the two compounds undergo rapid exchange of oxide ions at room temperature, interacting as a Lewis acid and a Lewis base but not undergoing oxidation–reduction interaction. Sulfur trioxide reacts with potassium pyrosulfite at room temperature, converting it to potassium sulfate and potassium dipyrosulfate. The process induces a small amount of exchange between sulfur dioxide and sulfur trioxide, indicating that some oxidation–reduction interaction takes place under these conditions. Isotopic exchanges of sulfur trioxide with barium sulfate and with potassium sulfate were observed. When potassium sulfate and sulfur trioxide react to form potassium dipyrosulfate substantial, and possibly complete, exchange occurs between excess sulfur trioxide and the sulfur originally in potassium sulfate.

Isotopic exchange of radiosulfur between compounds containing sulfur (IV) and sulfur (VI) has been investigated in a number of cases[2,3,4] and in no instance has a rapid exchange at room temperature been observed. In contrast with this generalization, Nakata,[5] using O^{18} as a tracer, thus labeling oxygen in place of sulfur, has reported a rapid, room temperature exchange for sulfur dioxide dissolved in excess liquid sulfur trioxide. The present work, done in part under conditions used by Nakata, was undertaken with S^{35} as tracer, to clarify the situation concerning isotopic exchange between these two compounds as well as to obtain information on the nature of liquid sulfur dioxide as an ionizing solvent.

Experimental

Preparation of Materials.—Sulfur dioxide from a cylinder was freed of sulfur trioxide and moisture by successive passage through concentrated sulfuric acid and phosphorus pentoxide. Freezing with liquid air and pumping to a high vacuum ensured the absence of permanent gases.

Radioactive sulfur dioxide was prepared by a method previously described.[6]

Sulfur trioxide was handled by all-glass technique without contact with stopcock grease. Kahlbaum material was vacuum distilled into several small containers fitted with break-off tips for use as needed. It was condensed at temperatures above 0° to obtain the low-melting α-form. Its only drying was that inherent in distillations of moderate temperatures (below 50°), but this sufficed to maintain largely the α-form for more than a year.

Radioactive sulfur trioxide was made by a heterogeneous exchange found to occur between the liquid and active barium sulfate. Since it developed that the presence of barium sulfate catalyzed polymerization to the high-melting β-form within a few hours, it was necessary, after solidification had occurred, to distil off the sulfur trioxide by warming; the liquid distillate was then poured or distilled back onto the barium sulfate. After repetition of this procedure eight times during three days, the sulfur trioxide was finally distilled off with liquid air into small containers with break-off tips. Using 127 mg. of barium sulfate, 28.5% of the activity was transferred to 3.9 g. of sulfur trioxide. The solid residue from the last distillation was washed with water and after filtration 89.6 mg. of barium sulfate was precipitated from the filtrate, containing 12% of the activity; this must have been present as relatively involatile trioxide and perhaps partly as barium pyrosulfate. The residual barium sulfate retained the rest of the activity. The exchange might better have been conducted at a higher temperature, perhaps *ca.* 60°, to avoid solidification of the trioxide.

Potassium pyrosulfite was made by a standard procedure,[7] modified to permit all operations, including terminal drying in high vacuum, to be done in the same container. Iodimetric determination of sulfur(IV) gave 99.1% of the calculated value, considerably better than results for commercial material.

Commercial potassium sulfate was recrystallized and dried at 150°.

Run Procedure.—High vacuum techniques were used for all gas handling operations, all-glass methods being applied for sulfur trioxide. Visually estimated quantities of sulfur trioxide were distilled into small ampules, which were sealed off and placed in an all-glass apparatus. Sulfur dioxide was condensed into a separate leg of this apparatus which was then sealed off and shaken to break the ampoule, after which the sulfur trioxide was condensed into the leg containing the sulfur dioxide. In certain cases appropriate amounts of potassium sulfate or potassium pyrosulfite had initially been weighed into this "reaction leg" before sealing onto the apparatus.

At the end of a run sulfur dioxide and trioxide were, if necessary, distilled away from solid material by warming to 100° for two hours and collecting the distillate at liquid air temperature in a different leg of the apparatus. Dilute hydrochloric acid was next admitted to this leg (the other having been sealed off) to dissolve the two reactants, and sulfur dioxide then distilled out of this aqueous solution into sodium hydroxide, care being taken to prevent bumping. The two fractions thus obtained were each converted to barium sulfate for radioassay.

Residual solid material from the first distillation was weighed *in situ*. Where potassium pyrosulfite was involved, it was then subjected to the dilute hydrochloric acid and vacuum distillation treatment described in the preceding paragraph. Thus was determined the degree of conversion of pyrosulfite to sulfate and of sulfate to dipyrosulfate.

Appropriate modifications were made for runs at 132°; these were executed in heavy-walled capillary tubing and were thermostated in the vapor of refluxing chlorobenzene.

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[1] Presented before the Physical and Inorganic Division of the American Chemical Society in Chicago, September, 1950. Published with the approval of the Oregon State College Monographs Committee. Research Paper No. 176, Department of Chemistry, School of Science.

[2] H. Voge, THIS JOURNAL, **61**, 1032 (1939).

[3] J. L. Huston, Thesis, University of California, Berkeley, 1946.

[4] T. H. Norris, THIS JOURNAL, **72**, 1220 (1950).

[5] S. Nakata, *J. Chem. Soc. Japan*, **64**, 635 (1943).

[6] R. E. Johnson and J. L. Huston, THIS JOURNAL, **72**, 1841 (1950).

[7] H. F. Johnstone, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 167.

Radioactivity Measurements.—All materials were counted as barium sulfate in "cupped planchets."[4] The expected error with this procedure, due to mounting irreproducibility, is around five to ten per cent., which normally exceeds the statistical error of counting. Experimental errors given hereafter are estimated on the basis of these figures.

Results and Discussion

Sulfur Dioxide–Sulfur Trioxide.—Liquid sulfur dioxide and liquid sulfur trioxide are miscible in all proportions and it has been claimed the compound $SO_2 \cdot 2SO_3$ is formed,[8] although the existence of this compound has been disputed. Jander[9] has reported that a solution of sulfur trioxide in liquid dioxide has appreciable electrical conductivity. This may be due to an oxidation–reduction interaction of the two compounds which could be represented by the example

$$2SO_2 \rightleftarrows SO^{++} + SO_3^{=}$$
$$SO_3 + SO_3^{=} \rightleftarrows S_2O_6^{=}$$

Mechanism I

If this process, or any other involving transfer of an oxygen *atom* from sulfur trioxide to sulfur dioxide should occur, isotopic interchange would be detectible with either tracer oxygen or sulfur. Nakata proposed this mechanism to explain his observed oxygen exchange.

Alternatively the two substances may react as a Lewis acid and Lewis base, the sulfur in each maintaining its oxidation state. For example

$$SO_2 + SO_3 \rightleftarrows SO^{++} + SO_4^{=}$$

or

$$SO_2 + 2SO_3 \rightleftarrows SO^{++} + S_2O_7^{=}$$

Mechanism II

Jander[9] offered this mechanism in explanation of the observed conductivity, though with little supporting evidence. Interaction of this sort, with transfer of an oxide *ion*, evidently would yield a detectable isotopic exchange with tracer oxygen but not with tracer sulfur.

Sets of exchange experiments were performed with respective, approximate sulfur dioxide:sulfur trioxide quantities (millimoles), and up to maximum times, as follows. At room temperature: (1) 5.2: 1.5, 336 hr.; (2) 10.3: 1.2, 329 hr.; (3) 1.9: 2.0, 792 hr.; and (4) 0.43: 2.9, 768 hr. Also at 132°: (5) 5.0: 1.9, 72 hr.; and (6) 0.32: 2.9, 624 hr. The proportions used in Groups (4) and (6) approximated those used by Nakata. In no case was any exchange apparent except for a small effect in Group (6). The use of labeled sulfur dioxide (Groups (1), (2) and (5)) yielded small apparent exchanges up to 1% (estimated counting error, ±0.1%). These, however, showing no tendency to increase with time or temperature, are presumably spurious and to be ascribed to a readily explained separation "blank." The effect was eliminated by the use of labeled sulfur trioxide (Groups (3), (4) and (6)).

In the single instance of Group (6) a small but probably genuine effect, increasing with time, appeared, to the extent of 1.6 ± 0.1% after 624 hr. Norris[4] observed a considerably greater exchange rate at 135° between sulfur dioxide and concentrated sulfuric acid. Although direct comparison of the two sets of data is not possible, it is likely that the rate he observed is not proportional to the concentration of sulfur trioxide in sulfuric acid.

The non-observance of exchange at room temperature with either excess sulfur dioxide or excess trioxide clearly implies that Nakata's results are to be explained with Mechanism II rather than Mechanism I. The rapid exchange of oxygen which he observed is thus indicative of rapid mobility of oxide ions in liquid sulfur dioxide, comparable with the mobility of protons in water. Further evidence in favor of this point of view is offered in the following paper.

Sulfur Dioxide–Sulfur Trioxide–Potassium Pyrosulfite.—In one run of Group (5) above a small amount (*ca.* 30 mg.) of potassium pyrosulfite was included to see if this might induce some exchange in accordance with Mechanism I. No significant effect was observed; however, the pyrosulfite was converted to a solid residue containing no sulfite but only inactive sulfur(VI). This reaction was then investigated in a series of five experiments at room temperature, using labeled sulfur trioxide instead of dioxide as in the previous run. Runs 1–4 lasting, respectively, for 5.5, 24, 42 and 96 hours, consisted of mixtures of about 0.31 mmole of sulfur dioxide, 2.5 mmoles of sulfur trioxide and 0.29 mmole of potassium pyrosulfite. Run 5, lasting 24 hours, consisted of 6.3, 3.4 and 0.30 mmoles of each of these substances, respectively. The observed per cent. conversions of pyrosulfite to sulfate, calculated according to Equation (1) below, amounted to 70, 93, 100, 88 and 100%, respectively, ±5%.

It is known that potassium dipyrosulfate, $K_2S_3O_{10}$,[10] can be made by exposing potassium sulfate to sulfur trioxide vapor for an hour or more, followed by removal of excess trioxide by warming to 100°. Reaction is always incomplete at room temperature, though it may be complete at higher temperature and in the presence of a little water. The present results indicate that similar treatment of potassium pyrosulfite at room temperature (using however liquid sulfur trioxide instead of vapor) also results in incomplete reaction of potassium sulfate with sulfur trioxide even though the potassium sulfate is formed *in situ* by reaction of sulfur trioxide. The five experiments showed, in order, 83, 63, 23, 89 and 24% reaction (±15%), calculated according to the equation

$$K_2S^*O_4 + 2S^*O_3 \longrightarrow K_2S_3^*O_{10}$$

Sulfur dioxide was present initially and was also generated during each run by reaction of sulfur trioxide and potassium pyrosulfite. The observed final specific activities of sulfur dioxide for the five runs were 1.9, 2.0, 2.6, 1.5 and 0.37 c./m./mg. as compared with an average final sulfur trioxide value of 161 c./m./mg. The low sulfur dioxide values indicate that this reaction is at least predominantly of acid–base type, *i.e.*

$$K_2S_2O_5 + S^*O_3 \longrightarrow K_2S^*O_4 + 2SO_2 \qquad (1)$$

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[8] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 10, Longmans, Green and Co., London, 1930, p. 345.

[9] G. Jander, *Naturwissenschaften*, **26**, 795 (1938).

[10] P. Baumgarten and E. Thilo, *Ber.*, **71**, 2596 (1938)

However, the activities differ from zero by more than the experimental error and there must be some small degree of oxidation–reduction interaction of hexavalent and tetravalent sulfur along the line of Mechanism I. It is to be noted that the activity enters sulfur dioxide as a consequence of reaction of sulfur trioxide with potassium pyrosulfite, that is to say, the momentary coexistence of these two compounds along with sulfur dioxide, and is not due to an exchange catalyzed by potassium sulfate or potassium dipyrosulfate, it being shown by the two room temperature experiments described in the next section that neither substance serves as such an exchange catalyst: in both these runs 0.0 ± 0.1% SO_2–SO_3 exchange was observed.

Since the presence of sulfite or pyrosulfite ion, even momentarily, leads to isotopic exchange between sulfur(IV) and sulfur(VI) in accordance with Mechanism I, we may conclude that the absence of exchange when only sulfur dioxide and sulfur trioxide are used bespeaks a low concentration of sulfite ions arising from self-ionization in liquid sulfur dioxide.

The percentages of isotopic exchange between all the tetravalent and all the hexavalent sulfur, calculated without regard to initial or final chemical forms, are, for the five runs, 1.7, 1.6, 2.2, 1.2 and 0.7% (±0.2%). But it is probable that exchange occurs only between that sulfur dioxide which was generated by reaction and the reacting sulfur trioxide which is itself converted to potassium sulfate and potassium dipyrosulfate. The corresponding exchange figures calculated on this assumption are 6.0, 6.1, 8.2, 4.4 and 8.1% (±1.0%). Some support for the validity of this assumption derives from the fact that in four cases out of five the specific activity of sulfur trioxide (average value 161 c./m./mg.) exceeded that of the solid residue (average value 154 c./m./mg.), the sulfur of which has presumably undergone exchange with inactive sulfur dioxide. These differences, however, do not exceed the experimental error inherent in the counting method.

It may be noted that when sulfur trioxide was distilled onto potassium pyrosulfite a blue-green color was observed to permeate the solid but to disappear within a few minutes. Presumably some unstable intermediate was formed.

Potassium Sulfate–Sulfur Trioxide.—The structure of the dipyrosulfate ion, $S_3O_{10}^=$, is not known though it is assumed[10] to be held together by sulfur–oxygen–sulfur bridges. Nor is it known whether it forms directly when potassium sulfate is brought in contact with sulfur trioxide or whether pyrosulfate is intermediate in the reaction. Some attention was paid to the possibility of obtaining information on these questions by tracer methods. Two runs, each lasting 24 hours, were done by exposing potassium sulfate to liquid sulfur trioxide at room temperature. The reaction mixture consisted of sulfur dioxide, sulfur trioxide and potassium sulfate in the millimole quantities: (1) 0.235, 3.62 and 0.319; and (2) 0.338, 2.58 and 0.341. In addition two runs were made at 50–53°, following the procedure of Baumgarten and Thilo, by exposing potassium sulfate to trioxide vapor, the vapor condensing on the solid to give partial solution of the solid to form a viscous liquid. These runs lasted 2 hours and contained sulfur trioxide and potassium sulfate in the millimole quantities: (3) 1.85 and 0.322; and (4) 2.10 and 0.338. The observed reaction percentages for the four runs, calculated according to the equation

$$K_2SO_4 + 2S^*O_3 \longrightarrow K_2SO_4 \cdot 2S^*O_3$$

were 75, 40, 43 and 52% (±10%). In each case values were obtained for the per cent. exchange between the sulfur originally present in potassium sulfate and sulfur trioxide, correction being applied for activity introduced directly into the solid material by reacting sulfur trioxide. The values so obtained were 60, 63, 77 and 67% (±10%). Evidently there is considerable exchange and, indeed, comparison with the preceding set of figures indicates that to such extent as potassium sulfate undergoes reaction, to that extent it probably undergoes complete exchange with sulfur trioxide. This is not surprising since Baumgarten and Thilo found they had to obtain complete solution of the solid to obtain complete reaction.

To verify the completeness of this exchange, the mixture of potassium sulfate and potassium dipyrosulfate obtained in the third run was extracted with a little water to produce the reaction $K_2S_3O_{10} + H_2O \longrightarrow 2H^+ + SO_4^= + K_2S_2O_7$. From the liquid were precipitated 0.336 millimole of barium sulfate with specific activity of 149 c./m./mg. while the residue gave 0.266 millimole with specific activity of 120 c./m./mg. These are to be compared with a specific activity of 157 c./m./mg. for the sulfur trioxide previously distilled from mixed solids. The mixture of sulfate and dipyrosulfate obtained in the last run was heated *in vacuo* for one hour, the temperature being raised from 200 to 250° during this time, and the sulfur trioxide evolved from the reaction $K_2S_3O_{10} \longrightarrow K_2S_2O_7 + SO_3$ being condensed with liquid air. This sulfur trioxide amounted to 0.139 millimole with specific activity of 149 c./m./mg., to be compared with specific activity of 156 c./m./mg. for the unreacted sulfur trioxide previously distilled at 100°. The pyrosulfite residue amounted to 0.547 millimole with specific activity of 123 c./m./mg. These results support the assumption that the specific activity of the dipyrosulfate is the same as that of the sulfur trioxide. It is thus not possible to investigate its structure or mode of formation by tracer techniques.

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