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Some Observations on the Oxygen Exchange of Sulfur Dioxide

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Infrared spectral data show that $S^{16,16}O_2$ and $S^{18,18}O_2$ exchange oxygen rapidly with each other in solution in CCl_4 or cyclohexane and in the gas phase. Gaseous SO_2 exchanges oxygen with Pyrex more slowly. Catalysis by water of exchange in solution and catalysis by Pyrex of exchange in the gas phase are not rigorously excluded but neither is direct exchange *via* a dimeric intermediate or activated complex.

The only direct[2] study of oxygen exchange of SO_2 molecules with each other appears to be that of Huston,[3] who adduced mass spectrometric evidence that a heterogeneous exchange occurs on Pyrex surfaces. In order to avoid complications arising from known[3-5] memory effects in the mass spectrometry of SO_2, we have employed infrared spectrometry, taking advantage of the isotope effect on the ν_3 frequency.[6] Labeled SO_2 was prepared from molecular oxygen of 97.55 atom % ^{18}O content and mixed with tank SO_2 in solutions in CCl_4 and cyclohexane and also in the gas phase in such a way that the samples were exposed to room temperature for 10–20 min. from the instant of mixing until completion of the spectral measurement. In all cases exchange equilibration appeared to be complete by this time. The significance of these observations is discussed below. A slower exchange, presumably with Pyrex, was also observed.

Experimental

All operations involving the preparation of $S^{18,18}O_2$, purification of $S^{18,18}O_2$ and $S^{16,16}O_2$, preparation of solutions, and filling of the gas infrared cell were performed on a high-vacuum line fabricated of Pyrex and operating at a pressure of *ca.* 2×10^{-6} mm. Apiezon N was used throughout. $S^{18,18}O_2$ was prepared by the "slow" reaction[7,8] of oxygen with sulfur in order to minimize formation of SO_3. A 16.6-mmole portion of sulfur (technical flowers, twice resublimed under high vacuum) was heated in a cylindrical, Pyrex wool-packed, resistance wire-wound, insulated 0.5-l. Pyrex reactor with 11.6 mmoles of gas composed of oxygen containing a small indeterminate amount of water vapor. The isotopic composition of the O_2 was ^{16}O, 1.84%; ^{17}O, 0.61%; and ^{18}O, 97.55%, according to mass spectrometric analysis. The temperature was maintained at 261 to 272° for 33 hr. The pressure was approximately 50 cm. at this temperature. Approximately 1.5 hr. after reaction temperature was reached an orange-pink flash, accompanied by a *ca.* 2-cm. drop in pressure, was observed. Trapping of the product in liquid N_2 immediately thereafter revealed that the reaction had reached about 60% of completion. This phenomenon, which was also observed in preliminary preparations of natural abundance SO_2, was not investigated further. Heating was stopped when the pressure of noncondensable gas had fallen to *ca.* 1 mm. The product was then degassed by multiple freeze (liquid N_2), pump, expand cycles and 6 g. of Hg admitted from an evacuated chamber *via* a break-off seal. The absence of significant amounts of SO_3 was indicated by the fact that the Hg remained bright overnight. The SO_2 was further purified by three bulb to bulb distillations at a "pot" temperature of −95° (acetone slush), a procedure designed to remove H_2O but not capable of removing CO_2, if it was present. The $S^{18,18}O_2$ was stored in the reactor in the presence of Hg and was degassed routinely before each aliquot was taken.

Ordinary SO_2 was taken from a cylinder of Matheson Anhydrous grade material and passed slowly through a 25-mm. tube packed with 1 m. of G. Frederick Smith granular anhydrous $Mg(ClO_4)_2$ into a 1-l. reservoir containing 5.6 g. of Hg to a pressure of 40 cm. The Hg surface remained bright for several days. The SO_2 was degassed and purified as described above and was stored in the reservoir throughout these experiments.

Aliquots were measured manometrically. Different sections of the vacuum line were used for $S^{18,18}O_2$ and $S^{16,16}O_2$ so that only the small section where solution sample tubes or the infrared gas cell were filled was exposed to both. For preparation of solution samples, an aliquot of solvent was first transferred to a flask containing several granules of $Mg(ClO_4)_2$ which was then attached to the line *via* a ₸ joint and its contents degassed. A measured aliquot of $S^{18,18}O_2$ was condensed at liquid N_2 temperature into the tip of a weighed tube, the lower half of which was conical. The solvent was then condensed above it at the same temperature. The tube was pumped to 2×10^{-6} mm. to remove traces of gas evolved during distillation of the solvent and a measured aliquot of $S^{16,16}O_2$ condensed above it as before. The tube was then sealed off at a constriction. It was very slowly removed from the liquid N_2 bath so that almost all the solvent had melted before the $S^{18,18}O_2$ was allowed to warm up. The tube was then quickly mixed, weighed, refrozen in liquid N_2, and stored in acetone slush while being transported to the infrared laboratory. The frozen sample was warmed to room temperature immediately before the tube was opened. Transfers to the infrared cell of solutions 0.06 to 0.12 *M* in each isotopic SO_2 were effected with a hypodermic syringe whereas the *ca.* 30 cc. volumes required with 0.001 *M* solutions were poured. The tube containing one 0.06 *M* aliquot was filled, before sealing, with air which had been dried by passage through a 40-cm. column of silica gel so that the pressure at room temperature was above 1 atm.

Solvent CCl_4 was BDH "Special for Spectroscopy" grade stored over $Mg(ClO_4)_2$. Cyclohexane was Eastman "Spectrograde." All spectra were measured on a Beckman IR-7 instrument. Path lengths of the liquid cells were 0.4 mm. and 2 cm.; that of the gas cell was 10 cm. The gas cell was tight to high vacuum and was pumped at high vacuum for several hours before each use. Neither CO_2 nor SO_3 was detectable in the infrared spectra of $S^{18,18}O_2$ and $S^{16,16}O_2$.

Results

In CCl_4 solution the isotopic ν_3 bands are well resolved with sharp maxima for $S^{18,18}O_2$, $S^{16,18}O_2$, and

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[2] The possibility of exchange *via* self-ionization has been studied by T. H. Norris and his associates: *cf. J. Phys. Chem.*, **63**, 383 (1959).

[3] J. L. Huston, *ibid.*, **63**, 389 (1959).

[4] T. C. Hoering and J. W. Kennedy, *J. Am. Chem. Soc.*, **79**, 57 (1957).

[5] K. Clusius, K. Schleich, and R. B. Bernstein, *Helv. Chim. Acta*, **40**, 252 (1962).

[6] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **22**, 900 (1954).

[7] R. G. W. Norrish and E. K. Rideal, *J. Chem. Soc.*, **123**, 3202 (1923).

[8] L. A. Sayce, *ibid.*, 1767 (1935).

$S^{16,16}O_2$ at 1302.5, 1327, and 1345 cm.$^{-1}$, respectively. Since, in addition, the bands have very little fine structure, they are convenient for qualitative estimation of the extent of isotopic exchange and purity. Spectra in this solvent revealed that SO_2 prepared from O_2 containing 97.6 atom % of ^{18}O was heavily contaminated with ^{16}O. The ratio of the optical density of the $S^{18,18}O_2$ band to that of $S^{16,18}O_2$ was 3 for samples taken 3 and 27 days after the material was prepared. Since the isotope effect on the absolute intensities is not known, isotopic composition cannot be determined precisely from these data.[9] If the effect is assumed to be small, approximately 15% ^{16}O was present. The constancy of the ^{16}O content over a 24-day period suggests that isotopic contamination took place during the preparation of SO_2, most probably by exchange with the Pyrex wool and reactor walls, since the reactor was separated from the nearest greased stopcock by 17 cm. of 8-mm. i.d. tubing, rendering diffusion a slow process.

Solutions in CCl_4 containing equal concentrations of synthetic and tank SO_2, each 0.06 to 0.12 M, were apparently fully equilibrated as soon as they were measured, *i.e.*, after 20 min. at room temperature, *e.g.*, for an experiment in which the sample tube was filled with dry air before sealing, the relative optical densities of the maxima, uncorrected for the small degree of overlap of the ν_3 bands, were 16,16:16,18:18,18 = 0.78:1.24:0.61. If the isotope effect on intensities and the correction for band overlap are ignored, this yields $K_{\text{exchange}} = (S^{16,18}O_2)^2/(S^{16,16}O_2)\cdot(S^{18,18}O_2) = 3.2$. On statistical grounds, ignoring presumably small isotope effects, K_{exchange} should be 4. Similar results were obtained when the sample was sealed under vacuum so that the solution became saturated with ambient air when the cell was opened; *e.g.*, $K_{\text{exchange}} = 2.9$. The spectra did not change significantly when the solutions stood at room temperature in the infrared cell.

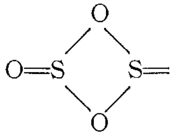
The isotopic ν_3 bands are not well resolved in cyclohexane solution. The maxima of the $S^{18,18}O_2$, $S^{16,18}O_2$, and $S^{16,16}O_2$ bands are at 1305, 1329.5, and 1343.5 cm.$^{-1}$, respectively. Overlap of these broad bands is so extensive, however, that only a qualitative conclusion was possible. Since the $S^{16,18}O_2$ band was most intense and no significant change took place on standing, it can be concluded that, with each variety of SO_2 0.12 M in this solvent, isotopic equilibration had occurred in less than 15 min.

It was not possible, with the procedures employed, to study the exchange at low concentration of SO_2, since 0.0012 M $S^{18,18}O_2$ underwent extensive exchange, presumably with atmospheric water introduced upon opening the sample tube and during transfer to the infrared cell.

Isotopic exchange of *ca.* 20 mm. of $S^{18,18}O_2$ with the gas cell was appreciable on first observation. After 1 day the ratio of the intensity of the sharp Q branch maximum of $S^{18,18}O_2$ to that of $S^{16,18}O_2$ (at 1318.5 and 1342 cm.$^{-1}$) was approximately 1. It decreased gradually over a period of 1 week. Although exchange with vacuum grease cannot be excluded, it is probable that the major reaction was with the Pyrex cell. When $S^{16,16}O_2$ was subsequently introduced into the thoroughly pumped out cell, it quickly became contaminated with $S^{16,18}O_2$. This heterogeneous exchange and the extensive overlap of the R branch of $S^{18,18}O_2$ with the P branch of $S^{16,18}O_2$, and analogous overlap of the spectra of the latter and $S^{16,16}O_2$, complicate observation of oxygen exchange of gaseous SO_2, particularly in a Pyrex cell. Within these limitations, the spectrum of a mixture made up of 10 mm. of each variety of SO_2 indicated complete equilibration within a period of 10 min.; after correction for overlap, the optical density of the $S^{16,18}O_2$ Q branch was more than twice that of each isotopically pure SO_2.

Discussion

Although rapid exchange of the oxygen of SO_2 has been established for the conditions of these experiments, the data are not discriminating as to mechanism. The exchange of SO_2 with Pyrex is consistent with Huston's observation of catalysis of the exchange of gaseous SO_2 by Pyrex but does not require that exchange of the gas proceed solely *via* a heterogeneous process.

In view of the slow rate of diffusion in solution it is improbable that exchange in solution is surface catalyzed. The possibility of participation of water has not been thoroughly excluded. Water is known[10] to exchange oxygen rapidly with SO_2 and no experiment was performed in a way which rigorously excluded atmospheric water. Water contamination was, however, reduced substantially (by saturating the solution with dry air prior to sealing the sample tube) without detectably inhibiting exchange. The data do not *exclude* the possibility that exchange occurs without the intervention of water or other species. Such exchange could take place *via* a cyclic transition state or intermediate, *e.g.*,  a possibility which is supported by the evidence that SO_2 is slightly associated in both liquid and gaseous states.[5,11] This picture is, of course, not in disagreement with Norris' evidence[2] excluding the self-ionization of SO_2.

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[9] An attempt to apply the isotopic analytical method of M. Anbar and S. Guttmann, *Intern. J. Appl. Rad. Isotopes*, **5**, 233 (1959), did not succeed since decomposition of SO_2 was only partial under the standard conditions.

[10] J. Halperin and H. Taube, *J. Am. Chem. Soc.*, **74**, 375 (1952).

[11] *Cf.* "Gmelins Handbuch der Anorganischen Chemie," System No. 9, Vol. B-1, Verlag Chemie, Weinheim/Bergstrasse, 1953, p. 208.