

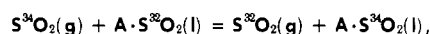
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Some Isotope Fractionation Factors for Sulfur

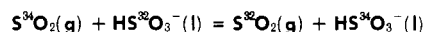
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Isotopic fractionation factors were measured for the reaction:



where **A** was aniline, dimethylaniline, triethylamine, pyridine, and ethylene oxide.

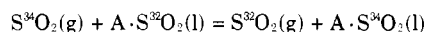
Similar measurements were made for the KH_2PO_4 buffered reaction:



and for the distillation of SO_3 . The fractionation factors ranged from 1.0005 to 1.005 with the heavy isotope concentrating in the liquid phase.

ALTHOUGH the fractionation of sulfur isotopes has been studied by a number of investigators (2, 5-7), no satisfactory separation method has been developed. This situation provided the incentive for further studies of the isotopic fractionation which may be achieved in sulfur systems.

A group of reactions, interesting for this purpose, is described by the equation:



where $A \cdot SO_2$ is a 1:1 molecular addition compound of SO_2 . A number of amines, ethers, and heterocycles are known to form such compounds (1, 3, 4). In the first part of this study, the isotopic fractionation achievable was measured through the exchange of sulfur between these compounds and SO_2 . In succeeding parts of the study, the isotopic fractionation resulting from the distillation of SO_3 , and the exchange of sulfur between SO_2 and HSO_3^- in a buffered solution (from which the SO_2 could be recovered thermally) was measured.

EXPERIMENTAL

Materials. Matheson's Anhydrous Grade SO_2 was used; the SO_3 was B & A Sulfan B sulfuric anhydride. The following were J.T. Baker Reagent Grade, Fischer Scientific

Reagent Grade, or Eastman White Label: aniline, dimethylaniline, triethylamine, pyridine, ethylene oxide, propylene oxide, tetrahydrofuran, dimethyl sulfide, thiophene, phenol, and KH_2PO_4 . All were used without further purification.

Apparatus and Procedure. MOLECULAR ADDITION EXCHANGE REACTIONS. A vacuum jacketed, borosilicate glass, 30-plate bubble cap exchange column, 84 cm. long and 2.5 cm. I.D., was used. Its plate efficiency was 50 to 55% for a wide variety of aqueous and organic systems. Above the exchange column was a jacketed glass tube 26 cm. long and 3.4 cm. I.D., packed with 0.3 cm. glass helices. In this recombiner, SO_2 gas from the exchange column was reacted with fresh solvent to form the liquid molecular addition compound. The liquid flow rate (under gravity) was set at a fixed value; the SO_2 flow was adjusted to maintain the recombination interface at the desired level in the recombiner.

Gradient studies established that seven hours was sufficient to achieve isotopic equilibrium. Samples of SO_2 gas were collected in evacuated tubes at a capillary sampling port between the column and the recombiner. These were frozen in liquid nitrogen, evacuated, and then distilled from dry ice to a liquid nitrogen trap. Representative samples were analyzed with a mass spectrometer and found essentially free of impurities.

Isotopic analyses were obtained from the m/e 64 and

66 peaks. The m/e 66 peak (mostly $S^{34}O_2^{16}$) was corrected for naturally occurring $S^{32}O^{16}O^{18}$; contributions to this peak owing to fractionation of oxygen-18 were negligibly small.

DISTILLATION OF SO_3 . The borosilicate glass distillation apparatus consisted of a flask of a condenser sealed to a 1.3-cm. diameter column packed to a height of 74 cm. with 0.16-cm. glass helices. The top was vented to the atmosphere through P_2O_5 . Enough SO_3 was used to provide 70 ml. in the pot during operation. The distillation was performed at 44° C., and samples were withdrawn over a seven-hour period. These were sealed in glass tubes with powdered, outgassed, spectrographic-grade graphite, and heated to 400° for 14 hours. The SO_2 from this treatment was analyzed as previously described.

BUFFERED SO_2 - HSO_3^- SYSTEM. Solutions of 1.5 to 1.8M KH_2PO_4 were equilibrated with gaseous SO_2 at 30, 40, and 58° C. in the equipment described previously.

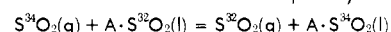
RESULTS AND DISCUSSION

Molecular Addition Exchange Reactions. At room temperature aniline, dimethylaniline, triethylamine, and pyridine formed stable solutions with SO_2 in which excess SO_2 dissolved. The ethylene oxide complex was less stable, but could be studied at 15°. The propylene oxide, tetrahydrofuran, dimethylsulfide, thiophene, and phenol complexes were too unstable to be considered further. The observed isotopic fractionation, and the derived equilibrium constants for the isotopic exchange reactions are given in Table I. Each estimate of the total separation (S) was obtained from a single distillation experiment by averaging results from at least three samples obtained during a two-hour interval following the attainment of isotopic equilibrium. The equilibrium constants were computed by means of the Fenske equation from the observed separation after correcting the latter for the effect of excess dissolved SO_2 . The results are based upon a 50% plate efficiency for the bubble cap column. The confidence interval given for the total separation indicates the precision of the isotopic analysis, and not the reproducibility of the entire experiment.

The fractionation of sulfur isotopes in the systems listed in Table I was quite small. The largest separation factors were associated with the most stable complexes. Thus, the aniline, triethylamine and pyridine complexes gave separation factors between 1.002 and 1.003. The less stable dimethylaniline complex gave an enrichment factor ($\alpha-1$) only half as large as its aniline analog. The least stable ethylene oxide complex yielded the smallest separation factor.

Distillation of SO_3 . A total separation, $(S^{32}O_3/S^{34}O_3)$ top/ $(S^{32}O_3/S^{34}O_3)$ bottom, of 1.022 ± 0.012 (95% C.I.) was observed. As expected, the heavy isotope concentrated in the liquid phase. Based on operational characteristics, the column was estimated to contain approximately 20 theoretical plates: the estimated single stage isotopic fractionation factor for the distillation process was thus 1.001.

Table I. Fractionation of Sulfur Isotopes by the Reaction



SO_2 Adduct	Temp., ° C.	Sol.	Total Sep. S ^a	95% C.I.	K_{eq}
		Comp. (SO_2 / Organic)			
Aniline	30	1.47	1.028	± 0.002	1.002 ₇
Dimethylaniline	24	1.55	1.013	0.003	1.001 ₄
Triethylamine	30	1.82	1.022	0.004	1.002 ₆
Pyridine	30	1.24	1.027	0.003	1.002 ₂
Ethylene oxide	15	0.6	1.008	0.009	1.000 ₃

^a ($S^{32}O_2/S^{34}O_2$) column top/ $(S^{32}O_2/S^{34}O_2)$ column bottom.

Table II. Fractionation of Sulfur Isotopes in the Buffered

SO_2 - HSO_3^- System

Exp. No.	KH_2PO_4 Concn. M	Temp., ° C.	Total Sepn., S ^a	95% C.I.	Effective
					Single Stage Sepn., Factor ^b
1	1.8	30	1.070	± 0.003	1.005
2	1.5	40	1.067	0.003	1.004
3	1.5	58	1.059	0.005	1.004

^a ($S^{32}O_2/S^{34}O_2$) column top/ $(S^{32}O_2/S^{34}O_2)$ column bottom.

^b Based upon 15 theoretical stages in exchange column.

Buffered SO_2 - HSO_3^- System. The isotopic fractionations observed in the SO_2 - HSO_3^- system are shown in Table II. At 30° the effective separation factor was 1.005. At this temperature a large fraction of the sulfur in the liquid phase existed as dissolved SO_2 (as distinguished from HSO_3^-), decreasing the effective isotopic separation factor of the system. The SO_2/HSO_3^- ratio in the liquid phase was reduced by increasing the temperature at which the exchange occurred. However, at 40° and 58° C., less, rather than more, separation was observed: The inverse temperature dependence of the isotopic equilibrium constant affected the separation factor to a greater extent than did the change in composition of the liquid phase.

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