are subject to greater error due to the absorption effect; some of the higher d-values may be low by 0.01–0.05 Å.

Single crystals of $HgOHNO_3$ and $Hg_3O_2(NO_3)_2 \cdot H_2O$ were studied by Dr. C. E. Nordman of this Department. The crystal structure of $HgOHNO_3$ will be reported separately by him at a later date. In the case of the $Hg_3O_2(NO_3)_2 \cdot H_2O$, his results are as follows: the unit cell is triclinic with a, b and c = 6.92, 10.10 and 6.87 Å. and α, β and γ = 97° 39′, 119° 31′ and 100° 07′, respectively. The volume of the unit cell is 398 Å.^{3} and the calculated density is 6.48 g. cm.$^{-3}$, assuming two formula units of $Hg_3O_2(NO_3)_2 \cdot H_2O$ per unit cell. The density of a powder sample of this compound was determined with a pycnometer using both CCl_4 and "Halocarbon" oil, resulting in values of 6.37 and 6.34 g. cm.$^{-3}$, respectively.

Using Nordman's values for the cell parameters of $HgOHNO_3$ and $Hg_3O_2(NO_3)_2 \cdot H_2O$ a number of d-values were computed, all of which agreed (within experimental error) with the powder data.

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[Contribution from the Chemistry Department, Oregon State College]

Radiosulfur Exchange Reactions between Sulfur Oxyhalides[1]

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The sulfur-35 exchange reaction between thionyl chloride and thionyl bromide has been studied at −20 and −50°, both in liquid sulfur dioxide solution and in the two pure mixed compounds. The exchange is rapid and complete, except for the pure compounds at −50°, where a measurable rate is observed. The results are interpreted as demonstrating the probable existence of ionic dissociation processes for thionyl halides, both pure and in liquid sulfur dioxide solutions. The sulfur-35 exchange between thionyl chloride and sulfuryl chloride is insignificant in five days at 0°, in line with the lack of a readily available ionization pathway. A further reason for the slowness of this type of exchange is suggested.

The rapidity of radiochlorine exchange reactions between solute chloride salts and thionyl chloride, both as a solvent and dissolved in liquid sulfur dioxide,[3] attests to the participation of thionyl chloride, under such circumstances, in some type of ionization processes. Although these results seem to suggest a dissociation equilibrium[4] to $SOCl^+ + Cl^-$, it is possible that they could alternatively be explained in terms of an association equilibrium to $SOCl_3^-$. We have now undertaken to distinguish between these two possibilities by studying the radiosulfur exchange between thionyl chloride and thionyl bromide. In such solutions, containing no halide salts, no association equilibrium could occur (except possibly by virtue of dissociation-produced halide ions). A rapid exchange, taken to imply an ionization process, would then indicate the occurrence of dissociation to SOX^+ for one or both of the thionyl halides (the apparently unstable species $SOClBr$[5] being assumed as an intermediate). Continuing the earlier work,[3] we have studied this exchange both between the two pure mixed compounds and between the two dissolved together in liquid sulfur dioxide.

As a related system, but one in which ionization would not lead directly to exchange, the radiosulfur exchange between sulfuryl chloride and thionyl chloride (pure liquids, no other solvent) has also been investigated. Besides their pertinence in the present context, the results in this case are of interest in their relation to earlier observations[6] on exchange in the related S(IV)–S(VI) system, sulfur dioxide–sulfur trioxide.

Results and Discussion

Thionyl Bromide–Thionyl Chloride Exchange.—The results are summarized in Table I. In the case of the experiments done in liquid sulfur dioxide solutions, although the separation method was such as to make difficult calculation of precise exchange percentages, it seems certain that the exchange was substantially complete within a few minutes, even at −50°, either with excess of thionyl bromide or of chloride. With the two pure mixed compounds the exchange is also fast, being essentially complete within a few minutes at ~ −20°. However, the rate does appear to be somewhat lower than in sulfur dioxide solutions, only partial exchange occurring at −50°.

The rapidity of the exchange appears to support, at least so far as sulfur dioxide solutions are concerned, the previously indicated[3] occurrence of some type of ionization process involving the thionyl halide solutes. It further satisfies the initial objective of this research by demonstrating the probable formation in these solutions of dissociated ionic species of the type SOX^+. Thus the ionization process might consist either of a simple dissociation of one or both of the thionyl halides (*e.g.*, $SOCl_2 \rightleftarrows SOCl^+ + Cl^-$), or alternatively of a direct halide ion transfer between two thionyl halides (*e.g.*,

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(1) Oregon State College, Research Paper No. 308, School of Science, Department of Chemistry.

(2) Taken from the M.S. thesis of LeRoy F. Johnson, Jr., at Oregon State College, June, 1956.

(3) B. J. Masters, N. D. Potter, D. R. Asher and T. H. Norris, This Journal, **78**, 4252 (1956).

(4) Dissociation to $SO^{++} + 2Cl^-$ has previously been shown not to occur, R. E. Johnson, T. H. Norris and J. L. Huston, *ibid.*, **73**, 3052 (1951).

(5) H. A. Mayes and J. R. Partington, *J. Chem. Soc.*, 2594 (1926).

(6) J. L. Huston, This Journal, **73**, 3049 (1951).

TABLE I

EXCHANGE OBSERVATIONS

Temp., °C.	$SOCl_2$, mole fr.	$SOBr_2$, mole fr.	Exch., %	Time,[h] min.	Estd. $t_{1/2}$,[i] min.
$SOCl_2$–$SOBr_2$ exchange in SO_2					
−23	0.04[a]	0.16	~100[c]	5	<2
−50	.04[a]	.16	~100[c]	8	<2
−50	.16	.04[b]	~100[c]	17	<5
$SOCl_2$–$SOBr_2$ exchange, pure compounds					
−18	0.10[a]	0.90	98[e]	34	<8
−50	.10[a]	.90	~23[f]	31	~80
−20	.91	.09[b]	100[d]	12	<3
−50	.91	.09[b]	71[e]	6	~3
$SOCl_2$–SO_2Cl_2 exchange, pure compounds					
0	0.09[a]	..	<25[g]	5	>70 days
0	.09[a]	..	<12[g]	60	
0	.09[a]	..	<5[g]	7200	

[a] $SOCl_2$ initially labeled. [b] $SOBr_2$ initially labeled. [c] Estimated uncertainty ±10. [d] Estimated uncertainty ±5. [e] Estimated uncertainty ±3. [f] Based on approximate fractionation data. [g] High because of separation error. [h] Distillation half-time for first sample in first two exchange systems. [i] Based on estimated exchange uncertainties.

$SOCl_2 + SOBr_2 \rightleftarrows SOCl^+ + SOBr_2Cl^-$), either process yielding the observed exchange (*via* SOClBr as an intermediate)—and either process bespeaking the formation of ionic species of the type SOX^+.

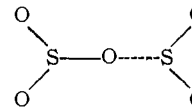
In contrast to the foregoing results, the occurrence of a measurable exchange rate in each of the pure thionyl halides, acting as solvents, presents a less clear-cut situation, with various possible interpretations. Conceivably ionic processes are no longer operating, a change in mechanism with change in solvent being a logical possibility. Alternatively it does not seem entirely unreasonable that ionization mechanisms might still be involved, since only at −50° are measurably slow rates observed; these might possibly be related to modified solvation effects in the different solvents or possibly to a somewhat modified ionization scheme (*cf.* the two alternative schemes suggested in the preceding paragraph).[7]

The observation of a measurable rate in the thionyl halide solvents invites re-examination of the previously reported[3] "rapid" radiochlorine exchange rates, the experiments on which were done at 0 and −20°. At such temperatures the present exchanges are also fast; it would be interesting to find whether the chloride exchanges (*e.g.*, Me_4NCl and $SbCl_3$ with $SOCl_2$ solvent) might, as was previously suggested,[3] be measurable at significantly lower temperatures, such as −50°.[9] If such were the case a more detailed kinetic study would suggest itself, both of these exchanges and of the $SOBr_2$–$SOCl_2$ sulfur exchange. Such a study would help to establish the mechanistic relationships between the two types of exchange systems and in particular to show whether the Me_4NCl–$SOCl_2$ exchange goes *via* a dissociation mechanism similar to that here tentatively postulated for the sulfur exchange. Such a mechanism should show a rate independent of solute chloride concentration; a concentration dependence would suggest an association mechanism. The further relationship of such results to our investigations of halide catalysis of the thionyl halide–sulfur dioxide exchange[10,11] is, in addition, self-evident.[12]

Thionyl Chloride–Sulfuryl Chloride Exchange.—Table I gives no evidence of any significant exchange between thionyl chloride and sulfuryl chloride solvent in five days at 0°, and clearly shows that at best the rate must be very low. This result contrasts markedly with that discussed in the preceding section, and is to be related to the fact that simple ionic dissociations of the two compounds involved (*e.g.*, to $SOCl^+$ and SO_2Cl^+) do not lead to identical or readily exchanging species.

The present lack of exchange recalls results previously reported for the sulfur dioxide–sulfur trioxide (liquid phase) exchange system, where it was found that, in contrast to a very rapid oxygen exchange,[13] the sulfur exchange rate was essentially negligible.[6] The explanation offered[4,6] in that case for the apparently conflicting results visualized the two compounds entering into an acid–base type of equilibrium with the strong acid sulfur trioxide accepting an oxide ion from the base sulfur dioxide, a process the reversal of which would yield oxygen but not sulfur exchange. The latter exchange would require a different, slower mechanism, involving an oxidation–reduction interaction between the two compounds.

In explanation of this slowness, it is perhaps worth extending the foregoing line of thinking. A reasonable process for the necessary oxygen atom transfer in this sulfur exchange might involve the formation of the symmetrical activated complex.



One might conveniently relate the reluctance toward formation of such a complex to the fact that here the stronger acid SO_3 must act as a base toward the weaker acid SO_2, in contrast to the "normal" acid–base interaction above referred to which gave rapid oxygen ion exchange. This qualitative

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(7) Since the rates of reactions leading to the production of ionic species would be expected in general to decrease with decreased dielectric constant, it is tempting in the present instance to try to relate the lower exchange rates in thionyl halides solvents to their lower dielectric constants (SO_2, 14.1; $SOCl_2$, 9.25; $SOBr_2$, 9.06, all at 20°.)[8] The decrease in their values from that of sulfur dioxide is not, however, great and is probably inadequate by itself to account entirely for the decreased exchange rates. This point is further emphasized by the fact that, although the two thionyl halides have very nearly the same dielectric constants, the rate in thionyl bromide appears to be definitely lower than that in thionyl chloride.

(8) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," Nat. Bur. Standards Circ. 514, 1951, p. 4.

(9) It may or may not be significant to note, relative to the above attempted partial correlation of rates with dielectric constants, that comparatively slow chlorine exchange occurs even at 0 and 25° between aluminum chloride and the solvent phosgene, with its somewhat lower dielectric constant of 4.34 (at 22°; ref. 8, p. 5) (J. L. Huston, *J. Inorg. Nucl. Chem.*, **2**, 128 (1956); also private communication).

(10) R. H. Herber, T. H. Norris and J. L. Huston, THIS JOURNAL, **76**, 2015 (1954).

(11) B. J. Masters and T. H. Norris, *ibid.*, **77**, 1346 (1955).

(12) Comparison of the different systems with reference to the effect of changing solvent would be of particular interest. Whereas the present $SOCl_2$–$SOBr_2$ sulfur exchange goes faster in SO_2 than in $SOCl_2$ solvent, the reverse is true of the chloride-catalyzed $SOCl_2$–SO_2 sulfur exchange, where the rate is about threefold greater in $SOCl_2$ solvent.[11]

(13) S. Nakata, *J. Chem. Soc. Japan*, **64**, 635 (1943).

type of reasoning can, of course, be applied to other slow oxidation–reduction processes (including exchange reactions), since in general the oxidizing agent will be the stronger acid of the two reacting species. And in particular such an explanation may possibly be advanced for the slowness of the present thionyl chloride–sulfuryl chloride exchange.

The foregoing picture would predict that these latter two compounds should probably undergo rapid exchange of isotopic oxygen or chlorine. The experimental demonstration of this would be of real interest. A point of further interest in this system would be the elucidation of conditions under which sulfur exchange would go at a reasonable rate, since other S(IV)–S(VI) exchanges are known to go at sufficiently high temperatures (*e.g.*, SO_2–concd. H_2SO_4[14] and SO_2–SO_3 (gas phase).[15]

Experimental

Radioactivity.—Sulfur-35 was obtained from the Atomic Energy Commission as neutron-irradiated potassium chloride. For radioassay all samples were converted to barium sulfate to be counted in thin layers with an end window Geiger tube, all appropriate corrections being applied.

Materials.—Sulfur dioxide, thionyl chloride and thionyl bromide were purified or prepared as previously described.[10,11] A fraction consisting of only about one-eighth of the total thionyl bromide was collected for use.

Anal. Calcd. or reptd. for $SOBr_2$: S, 15.42; Br, 76.8; d^{23}_4 (interpolated), 2.675.[5] Found: S, 15.20; Br, 76.0; d^{23}_4, 2.67.

Sulfuryl chloride (Eastman, practical) was fractionated on the vacuum system, the middle third being collected in sealed tubes. The clear, colorless liquid was stored in darkness until used. A slight color, appearing on long storage, was eliminated easily by evaporating and discarding a small portion of the material just prior to use.

Anal. Calcd. or reptd. for SO_2Cl_2: S, 23.7; Cl, 52.6; d^0_4, 1.708.[16] Found: S, 23.9; Cl, 52.9; d^0_4, 1.69.

Labeled thionyl chloride and labeled thionyl bromide, prepared as previously described,[10,11] had initial specific activities of 2,500 c.p.m./mg. (as barium sulfate) and 2,200 c.p.m./mg., respectively, and were used for one to two sulfur half-lives.

Analytical.—Sulfur was determined gravimetrically as barium sulfate. Total halide, chloride plus bromide, was determined by potentiometric titration with standard silver nitrate. Bromide in the presence of chloride was determined by the method of Willard and Heyn.[17] Chloride was obtained by difference.

Run Procedures.—These involved standard high vacuum techniques, generally similar to those of previous work.[10,11] Transfers were effected by distillation, the receivers being cooled with liquid nitrogen. Reaction mixture components were measured out as liquid in calibrated dosage volumes. Reaction temperatures were maintained reasonably constant with appropriate cold baths, the quoted temperatures being maintained until separation of reactants by fractionation had been completed.

$SOCl_2$–$SOBr_2$ Exchange in Liquid Sulfur Dioxide.—Three experiments were done in stopcock-equipped tubes. After initial mixing of the contents, successive small samples were evaporated off over periods of time, converted to barium sulfate and counted. The samples consisted mostly of sulfur dioxide (inactive, since it does not exchange with thionyl halides[4]), with small contaminating amounts of thionyl chloride and smaller amounts of the less volatile bromide. Since exchange appeared to be complete even with the first sample in all cases, the recorded times correspond to half the distillation time for these initial samples.

In the first two experiments (thionyl chloride labeled), the vapor samples' specific activities were compared, respectively, to specific activities roughly approximating zero and 100% exchange (the latter activity being only $^1/_5$ the former), both sets derived from a blank run in which thionyl bromide had been omitted. In both cases the observed activities were consistently *lower* than the 100% exchange figures (apparent exchange >100%, the presence of bromide modifying the volatility of the chloride), and showed no significant trend with time. In the third experiment the actual vapor samples were analyzed for sulfur, bromide and total halide, so that apparent percentage exchanges might be calculated. The resulting figures, while scattering somewhat, showed no increasing trend and averaged close to 100%. Although separation difficulties inherent in work with a three volatile component system hampered the obtaining of precise quantitative data (an approximate limit of error of ±10% is quoted in Table I, based on reasonable considerations of the uncertainties involved), it seems clear that exchange was complete before the first sample in all three experiments.

$SOCl_2$–$SOBr_2$ Exchange, Pure Compounds.—Experiments were done with excess of each compound, respectively. Partial separation of the reactants at the end of a run was achieved by fractional distillation, the more volatile thionyl chloride concentrating in the vapor phase. The quoted run times correspond to half the distillation time.

In the first experiment the distillate ($\sim^1/_3$ of the total material) composition was approximated by bromide and halide analyses on a blank, run in exactly comparable manner, so that a percentage exchange might be calculated. The calculated exchange (23%) for the second experiment serves only as an approximation, being based on the fractionation data of the first run (at higher temperature). The relative vapor pressure trend with temperature for the two reactants suggests the figure might be somewhat low (an upper limit, however, is set at 75%, corresponding to perfect reactant separation). In the third experiment, the mixture was fractionated into ten approximately equal cuts. Bromide and total halide analyses made possible, for each sample, calculation of the apparent percentage exchanges, all of which approximated 100%. The observed specific activities, all closely similar (±4%), showed no trend with time, indicating the exchange to have been complete before the initial sample. In the fourth experiment, about two-thirds of the mixture was distilled off, and the percentage exchange calculated on the basis of sulfur and bromide analyses.

SO_2Cl_2–$SOCl_2$ Exchange, Pure Compounds.—Three experiments were done, using labeled thionyl chloride and excess sulfuryl chloride. The volatilities of the reactants being too similar, partial separation was achieved by hydrolysis with a small portion of water (sulfuryl chloride hydrolyzes quite slowly) and removal of the water layer from the sulfuryl chloride layer with a pipet. The specific activity of the latter was consistently very low compared to the water fraction, and apparent exchanges were calculated on the unrealistic assumption of complete removal of thionyl chloride from the sulfuryl chloride. The figures so obtained (Table I) evidently constitute upper limits. The decreasing percentages derive from the fact that hydrolysis was allowed to proceed further and manipulative technique improved in the order given. The exchange appears triflingly slow, the half-time at 0° certainly exceeding 70 days.

Acknowledgment.—This research has been carried out under Contract AT(45-1)-244 between the U. S. Atomic Energy Commission and Oregon State College.

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(14) T. H. Norris, THIS JOURNAL, **72**, 1220 (1950). It is interesting to note that oxygen-18 exchange between sulfur dioxide and concentrated sulfuric acid is rapid (J. L. Huston, private communication).

(15) (a) H. H. Voge, *ibid.*, **61**, 1032 (1939); (b) J. L. Huston, Ph.D. Thesis, University of California, Berkeley, 1946; (c) ref. 14, footnote 3.

(16) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., p. 22.

(17) H. H. Willard and A. H. A. Heyn, *Ind. Eng. Chem., Anal. Ed.*, **15**, 321 (1943).