Again applying the usual steady-state assumptions and Marcus' approach one obtains

$$-\frac{d(B_4H_{10})}{dt} = k_6\left[\left(\frac{k_5}{k_{-5}}\right)(B^{10}{}_2D_6)\right]^{1/2}[B_4H_{10}] \quad (5)$$

This series of reactions is compatible with the observed orders and at the same time could account

for the boron exchanges. In view of the fact that the first exchange reaction does not permit boron exchange, whereas the second one does, a significant test of the proposed mechanisms could be realized by careful B¹⁰ exchange studies and such work is under way.

BALTIMORE, MARYLAND

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. V. The Acid Halide-catalyzed S³⁵-Exchange between Thionyl Chloride and Sulfur Dioxide[1]

BY DAVID E. BURGE[2] AND T. H. NORRIS

A study has been made of the kinetics of catalysis by antimony pentachloride of the radiosulfur exchange reaction between thionyl chloride and liquid sulfur dioxide. The process is interpreted as a case of acid catalysis in contrast to the previously investigated basic chloride catalysis. Exchange rates are only about one-hundredth as large as in the basic catalysis. The indicated rate law is rate = $k(SO_2)(SOCl_2 \cdot SbCl_5)$, where the last term represents a complex formed in a rapid preliminary reaction with a formation equilibrium constant $K \approx 0.8$ at $0°$, and $\Delta H^0 \approx 3.6$ kcal./mole. The rate constant is given by $k = 0.875 \times 10^2 \exp(-10,400/RT)$ l. mole⁻¹ sec.⁻¹. The entropy of activation is -51.6 e.u. K and k appear to be essentially unchanged throughout the complete solvent range from excess sulfur dioxide to excess thionyl chloride. An activated complex involving a double chlorine, oxygen bridge between sulfurs is postulated, reminiscent of that proposed for the basic chloride case. The greater complexity of the acid complex may account for the lower exchange rates observed. The occurrence of catalysis by aluminum chloride at a ten-fold lower rate is confirmed and briefly discussed.

Previous work in this Laboratory,[3,4] has shown that the radiosulfur exchange between thionyl halides and liquid sulfur dioxide is subject to a strong basic catalysis by ionic halide solutes. Preliminary experiments in the same research[4] suggested that an acid catalysis might also occur. While no effect could be observed with hydrogen chloride, aluminum chloride appeared to show a weak catalysis for the thionyl chloride–sulfur dioxide exchange, giving rates of the order of one thousandth those with tetramethylammonium chloride. We have now investigated the kinetics of the catalysis of this exchange by antimony pentachloride, the occurrence of acid catalysis being confirmed. The experiments cover the entire range of solution composition from excess sulfur dioxide to excess thionyl chloride. The observed rates are much smaller than with basic chlorides but significantly greater than with aluminum chloride.

Results

The Rate Law.—The results of all the experiments are recorded in Table I. The first twenty-four form a set at one temperature in which the concentrations of all three reactants were varied over considerable ranges in an effort to arrive at a rate law. Although preliminary treatment of the data indicated that separate empirical rate laws could be demonstrated for excess sulfur dioxide[5] and excess thionyl chloride[6] solutions, respectively,

there was every indication in the case of the basic chloride catalysis of this exchange that the same mechanism prevails in excess of either substance.[4] It was tempting, therefore, to try to show a similar situation in the present instance. It develops that a quite simple interpretation of the reaction will suffice for this purpose. One may assume that antimony pentachloride tends to form a complex with thionyl chloride and that this complex then reacts with sulfur dioxide in the rate-determining step. The rate law thus becomes[7]

$$\text{Rate} = k(SO_2)(SOCl_2 \cdot SbCl_5) \quad (3)$$

where the concentration of the complex will be governed by the equilibrium constant expression

$$\frac{(SOCl_2 \cdot SbCl_5)}{(SOCl_2)(SbCl_5)} = K \quad (4)$$

In attempting a quantitative test of the validity of this interpretation, one is confronted with the problem that both k and K are unknown. This difficulty has been resolved by least squares analysis of the data[8] so as to obtain simultaneously optimum values for the two constants. In so doing, however, a further problem arises. It is by no means certain that these constants will be numerically the same both in excess sulfur dioxide and excess thionyl chloride. Such a situation, for example, was *not* found for the basic chloride catalysis. For this reason the two sets of data have first been treated separately. The excess sulfur dioxide data consist of all experiments where thionyl chloride was less than 2 molar and lead to the constants $k = 1.75 \times 10^{-3}$ l. mole⁻¹ hr.⁻¹ and $K = 0.6$ l. mole⁻¹. The excess thionyl chloride

(1) Oregon State College, Research Paper No. 348, School of Science, Department of Chemistry.

(2) Taken from the thesis of David E. Burge, submitted in partial fulfillment of the requirements for the Ph.D. degree at Oregon State College, June, 1958.

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

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

(5) Rate = $k(SbCl_5)(SOCl_2)(SO_2)^2$ (1).

(6) Rate = $k(SbCl_5)(SO_2)$ (2).

(7) Assuming the equilibrium constant K fairly close to unity, the consistency of this rate law with the preliminary rate laws 1 and 2 is readily shown.

(8) For details of calculation methods see the Ph.D. thesis of David E. Burge, Oregon State College, 1958.

TABLE I

RADIOSULFUR EXCHANGE RATES WITH ANTIMONY PENTACHLORIDE CATALYST

Expt. no.	Temp., °C.	SbCl₅, mole/l.	SOCl₂, mole/l.	SO₂, mole/l.	Rate × 10³, mole/l.-hr.	k^a × 10³, l./mole-hr.
1	0.0	0.027	1.14	20.5	0.45	1.69
2	.0	.052	1.14	20.4	0.81	1.59
3	.0	.100	1.13	20.3	1.38	1.45
4	.0	.126	1.12	20.2	1.40	1.19
5	.0	.078	1.13	20.4	1.00	1.36
6	.0	.735	1.04	18.6	7.46	1.44
7	.0	.139	1.90	19.0	2.86	1.79
8	.0	.553	0.562	20.2	3.60	1.27
9	.0	.018	1.14	20.5	0.33	1.79
10	.0	.359	3.24	16.2	10.7	2.61
11	.0	.723	0.539	19.4	4.21	1.30
12	.0	.310	5.99	12.0	7.75	2.54
13	.0	.619	6.34	10.6	8.60	1.58
14	.0	.497	6.44	10.7	8.10	1.84
15	.0	.856	1.02	18.3	9.86	1.74
16	.0	.720	1.04	18.7	8.13	1.59
17	.0	2.85	0.726	13.5	8.18	1.27
18	.0	2.29	2.40	12.0	24.5	1.78
19	.0	2.48	2.51	11.3	20.3	1.43
20	.0	0.629	12.6	0.314	0.216	1.21
21	.0	0.620	12.4	.620	.460	1.32
22	.0	1.18	11.8	.589	.942	1.52
23	.0	0.564	11.3	2.82	1.68	1.18
24	.0	0.402	8.04	8.44	4.91	1.68
25	.0	2.05	10.3	0.513	1.32	1.44
26	−15.0	0.051	1.16	20.9	0.16	
27	−15.0	.214	1.14	20.5	0.77	
28	−15.0	.497	1.10	19.7	1.55	
29	15.0	.381	1.11	19.9	14.4	4.16
30	15.0	.284	1.07	19.3	9.71	3.84
31	15.0	.618	12.4	0.618	1.37	3.92
32	15.0	1.15	11.5	.573	2.20	3.68
33	15.0	2.00	10.0	.500	4.40	4.99
34	23.0	0.494	1.07	19.3	28.6	5.61
35	23.0	.217	5.47	12.3	40.2	17.1
36	23.0	.498	4.94	12.4	34.4	6.45
37	23.0	.561	4.90	12.3	42.8	7.19
38	23.0	.613	12.3	0.613	2.10	5.93
39	30.0	.384	1.03	18.5	45.7	10.42
40	30.0	.608	12.2	0.608	3.71	10.47

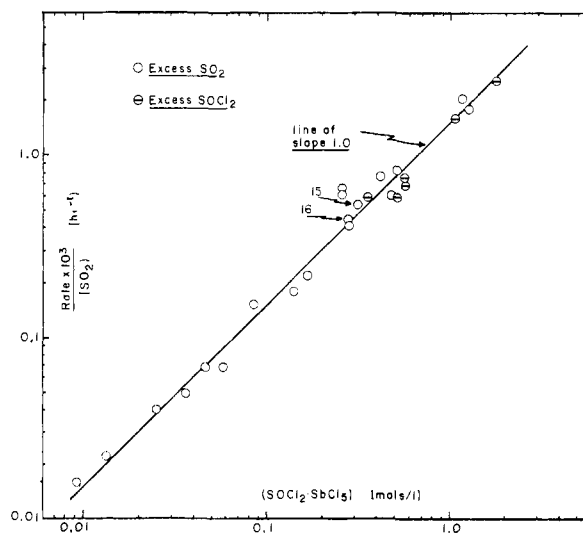^{a} Based on equations 3 and 4, K = 0.8(0°), 0.9(15°), 1.4(23°) and 2.0(30°).

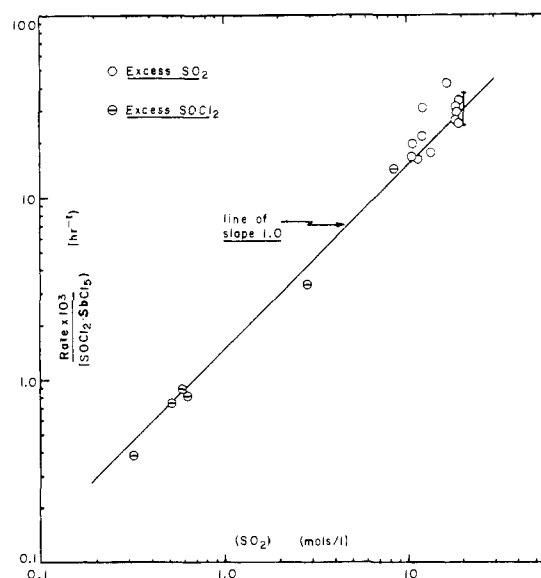Fig. 1.—Rate dependence on thionyl chloride–antimony pentachloride complex at 0.0°; expts. 1–25.

Fig. 2.—Rate dependence on sulfur dioxide at 0.0°; expts. 1–25. The vertical line at $(SO_2) \approx 20.3M$ represents the range of values for seven points.

experiments, embracing those where sulfur dioxide did not exceed 3 molar, give k = 1.35 × 10⁻³ l. mole⁻¹ hr.⁻¹ and K = 0.6 l. mole⁻¹.

In view of the somewhat modest precision associated with the present experiments, it appears that the close agreement shown by the above two equilibrium constants may well be fortuitous and, by the same token, the relatively small difference in the rate constants may be more apparent than real. For this reason all the 0° data taken as a whole, without regard to which material is in excess, have again been subjected to least squares treatment. The "best" values now found for the constants are k = 1.48 × 10⁻³ l. mole⁻¹ hr.⁻¹ and K = 0.8 l. mole⁻¹.

One may now make a test of the rate law here postulated. Using K = 0.8, concentrations of complex have been calculated for each of the 0° experiments. Figure 1 shows a log-log plot of rate (corrected for sulfur dioxide variation) versus complex concentration; Fig. 2 is a similar plot of rate (corrected for complex concentration variation) versus sulfur dioxide. In both cases the points fall nicely along lines of unit slope (drawn corresponding to k = 1.48 × 10⁻³) demonstrating the validity of the rate law (equation 3). One may further note that no significant difference is evident between the fit of the excess thionyl chloride and the excess sulfur dioxide points. It appears that the assumption that k and K have essentially the same values in either case is probably reasonably accurate. A final test is also provided by consideration of the k values recorded in the last column of Table I, calculated on the basis of equations 3 and 4 using the K appropriate for each

temperature as shown (see next section), together with the recorded reactant concentrations in each case. The 0° figures, averaging 1.58×10^{-3} l. mole^{-1} hr.$^{-1}$, not very different from the above calculated "best" value, show a reasonable constancy (experimental standard deviation $\pm22.2\%$) and appear to be substantially the same in excess of either material. The experiments at the other temperatures, except for one presumably "bad" run, seem likewise to agree well among themselves. It may be concluded that equations 3 and 4 represent a rate law and mechanism adequately descriptive of this exchange system and applicable throughout the entire solvent range.

Temperature Dependence.—In addition to those at 0°, experiments were run at -15, 15, 23 and 30°. Consideration of runs at each temperature at fairly similar reactant concentrations makes possible calculations of apparent activation energies. For this purpose the observed rates have been corrected for reactant concentration variation by application either of equation 1 or 2 as appropriate. The logarithms of the corrected rates then plotted against the reciprocal of the absolute temperature give good straight lines leading, by application of the conventional Arrhenius equation, to the apparent activation energies: (1) for excess sulfur dioxide, 12.3 kcal./mole[9] and (2) for excess thionyl chloride, 11.2 kcal./mole.[10]

The foregoing figures differ from each other and from the true activation energy since they take no account of the temperature dependence of the equilibrium constant, K (equation 4). Enough experiments were run at each temperature except $-15°$ so that both constants, k and K, could be determined. By least squares treatment (or at 30° by direct solution of simultaneous equations), the values found are: (1) for k: 1.48×10^{-3} (0.0°), 4.0×10^{-3} (15.0°), 6.3×10^{-3} (23.0°) and 10.5×10^{-3} l. mole^{-1} hr.$^{-1}$ (30.0°); (2) for K: 0.8 (0.0°), 0.9 (15.0°), 1.4 (23.0°) and 2.0 l. mole^{-1} (30.0°). A plot of log k versus $1/T$ (Fig. 3) gives a good
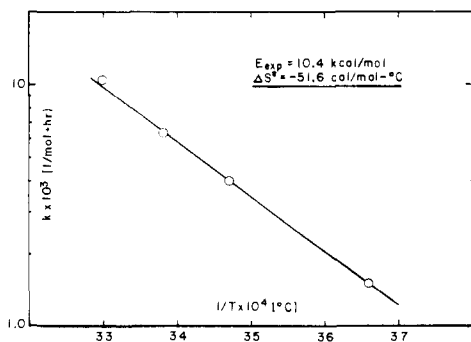

Fig. 3.—Temperature dependence of the rate constant.

straight line leading to the expression

$$k = 0.875 \times 10^2 e^{-10,400/RT} \text{ l. mole}^{-1} \text{ sec.}^{-1} \quad (5)$$

The activation energy is probably good to ca. $\pm$ 500 cal./mole. The corresponding entropy of activation, based on the equation

(9) Based on expts. 28, 16, 29, 34, 39.

(10) Based on expts. 21, 31, 38, 40.

$$k = e \frac{kT}{h} e^{-E \exp /RT} e^{\Delta S^{\ddagger}/R}$$

is calculated to be -51.6 cal. mole^{-1} deg.$^{-1}$.

On the basis of the van't Hoff equation

$$\Delta H^0 = -2.3 R \frac{\text{d log } K}{\text{d}(1/T)}$$

one may, from the recorded equilibrium constant values, calculate approximately the heat content change for the complex formation reaction (equation 7 below). The points in a plot of log K versus $1/T$ show considerable scatter since the K values are not very accurately known, but it is possible by least squares treatment to draw through them (appropriately weighted) a straight line from the slope of which one may estimate $\Delta H° \approx 3.6$ kcal./mole. The corresponding entropy change for equation 7 is then ~13 cal. mole^{-1} deg.$^{-1}$. The scatter of the points is such that no very great accuracy can be claimed for these figures; they are estimated to be good to perhaps about $\pm 25\%$.

It is of interest to observe how the activation energies and $\Delta H°$ value reported in this section are generally consistent with the assumed mechanism. Consider, for example, two extremes. If equilibrium 7 lay well to the right, the concentration of complex would simply be equal to that of either thionyl chloride or antimony pentachloride, whichever were limiting. A corresponding rate law would apply and the temperature coefficient of (7) would be without influence on the apparent activation energy. The latter would therefore approximate the true activation energy, 10.4 kcal./mole. At the other extreme, if equilibrium 7 lay well to the left the rate law would become

$$\text{Rate} = kK(SO_2)(SOCl_2)(SbCl_5) \quad (6)$$

and the apparent activation energy would be the sum of $\Delta H°$ and the true activation energy, i.e., 14.0 kcal./mole. Since K at 0.8 is neither very large nor very small, an intermediate situation should and does apply. The observed apparent activation energies lie numerically between the two extremes, with the figure for excess thionyl chloride, where equilibrium 7 would be shifted well to the right, having, as it should, a significantly smaller value.

Catalysis by Aluminum Chloride.—The work of Masters and Norris[4] indicated fairly clearly that aluminum chloride had a weak catalytic effect on the exchange system here under investigation. The data were such, however, as to give only an approximate indication of the rate. In the present work therefore a single additional experiment has been done to confirm the effect and obtain a better rate measurement. At 0.0° a bomb containing 0.617 M AlCl$_3$, 1.14 M SOCl$_2$ and 20.6 M SO$_2$ gave a rate of 4.5×10^{-4} mole l.$^{-1}$ hr.$^{-1}$. This is to be compared to a value of 5.2×10^{-4} mole l.$^{-1}$ hr.$^{-1}$ observed in the earlier work using nearly the same catalyst concentration and almost twice the thionyl chloride concentration. It may also be compared to a value of about 7.8×10^{-3} mole l.$^{-1}$ hr.$^{-1}$ to be expected under comparable conditions
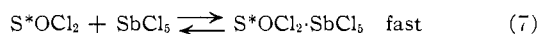
(11) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

with antimony pentachloride. The catalytic effect is definitely real, but much smaller than that of antimony pentachloride.

Discussion

The strong catalysis shown by ionic chlorides for the present exchange reaction might have suggested the weak antimony pentachloride catalysis to be related to a low chloride ion concentration arising from a slight dissociation of this material, a very weak electrolyte in sulfur dioxide.[12] It has been shown, however, that the experimental data support instead a mechanism and rate law in which undissociated molecular antimony pentachloride, $SbCl_5$, is itself the catalytically active material rather than any ionic derivative. Further important evidence to this same effect, based on experiments with mixed acid and basic chloride catalysts, is presented in an accompanying paper. Hence it seems reasonable to consider the process in terms of an acid catalysis in contrast to the previously observed basic chloride catalysis.

The proposed mechanism may be summarized in the equations

$$S^*OCl_2 + SbCl_5 \rightleftharpoons S^*OCl_2 \cdot SbCl_5 \quad \text{fast} \qquad (7)$$

$$S^*OCl_2 \cdot SbCl_5 + SO_2 \rightleftharpoons SOCl_2 \cdot SbCl_5 + S^*O_2 \quad \text{slow} \quad (8)$$

Here it is interesting to find independent indication furnished by kinetics data of the existence of the complex $SOCl_2 \cdot SbCl_5$, a species already previously suggested by others, on the basis of other evidence, as occurring both in sulfur dioxide and thionyl chloride solutions.[13] In general conformity with the views and observations of the earlier workers, we assume the postulated complex to be unionized[14] and to involve the formation of hexachloroantimonate by coördination to the antimony pentachloride of one chlorine from thionyl chloride. Thus antimony pentachloride serves as a Lewis acid in harmony with the acid catalysis interpretation and in contrast to the picture previously presented for the basic chloride catalysis wherein the first step involved coördination of chloride ion (base) to a sulfur dioxide molecule.

It is interesting to consider the nature of the activated complex involved in reaction 8. Here we may imagine a sulfur dioxide molecule coördinating to its sulfur a chloride adjacent, in the octahedral hexachloroantimonate complex, to the chlorine from thionyl chloride. The two sulfurs would then be in appropriate positions to form between themselves, without excessive strain of bond angles or lengths, a double oxygen, chlorine bridge, making a symmetrical structure. An interchange of bonds in the bridge and dissociation of the erstwhile thionyl chloride sulfur, now become sulfur dioxide, from its hexachloroantimonate attachment would complete the exchange.

An activated complex such as this bears a distinct similarity to that envisioned for basic chloride

catalysis.[4] In that case the species SO_2Cl^-, formed in low concentration by a rapid equilibrium between chloride ion (or an ion pair) and sulfur dioxide, was thought of also as forming a double chlorine, oxygen bridge to the sulfur of a thionyl chloride molecule. Redissociation of the symmetrical structure so formed, after interchange of bonding in the bridge, would produce exchange. On this basis one might expect a similarity in activation energies for the two cases. Unfortunately a direct comparison is not possible since for the basic chloride case only an apparent activation energy is available, the $\Delta H°$ for the combination of chloride and sulfur dioxide to form SO_2Cl^- being unknown. Assuming, as for the formation of $SOCl_2 \cdot SbCl_5$, this to be small, however, one might still expect the apparent activation energies for the two cases to be at least approximately similar. Such is indeed found to be the case, the "basic" value being (in excess sulfur dioxide) 14.7 as compared to the present value of 12.3 kcal./mole.

The equilibrium constant for the combination reaction forming SO_2Cl^- in the basic catalysis is also not known, but it appears to be small, much smaller than that for formation of $SOCl_2 \cdot SbCl_5$. Despite both this fact and the slightly lower apparent activation energy observed in the present case,[15] antimony pentachloride catalysis gives about one hundred-fold lower exchange rates than are to be observed in the basic chloride catalysis; in excess sulfur dioxide at one molar $SOCl_2$, 0.1 molar catalyst and 0°, tetramethylammonium chloride would give a half-time of ca. 5.1 hr., in contrast to ca. 530 hr. for antimony pentachloride. This low rate is clearly to be associated with a very small preexponential term (equation 5) or alternatively with the observed high negative entropy of activation, -51.6 e.u.[16] Possibly one might suppose that this large negative value is to be associated with the somewhat greater complexity of the activated complex in the acid as compared to the basic catalysis.

One further point of comparison between the basic and acid catalysis cases: in the former, although it was concluded that the same mechanism applied both in excess thionyl chloride and excess sulfur dioxide, the observed rate constant (which included an equilibrium constant) was about three times as great in the former as in the latter. In contrast, the indications are with antimony pentachloride that the equilibrium and rate constants involved have essentially the same values in excess of either material. While any explanation of this difference must be admittedly speculative at this juncture, it seems reasonable to suppose that it may possibly be related to the absence of ions from the acid catalysis mechanism in contrast to the basic case, where a change in solvent dielectric

(12) F. Seel, Z. anorg. Chem., **252**, 24 (1943).

(13) H. Spandau and E. Brunneck, Z. anorg. allgem. Chem., **270**, 201 (1952); **278**, 197 (1955).

(14) In sulfur dioxide the measured conductance (0.02 molar solution) was such as to imply less than 1% dissociation.[12] In pure thionyl chloride, antimony pentachloride gave conductances, in the concentration range involved in the present experiments, which would also indicate no more than about 1 or 2% dissociation of complex.[13]

(15) The higher value in the basic catalysis may in part be related to the difference in the association constants of the complexes SO_2Cl^- and $SOCl_2 \cdot SbCl_5$. If we assume the $\Delta H°$ values for the two association processes roughly equal in magnitude and sign, this suggested explanation presents itself, since, as discussed earlier in this paper, the smaller the degree of association of a reacting complex such as SO_2Cl^- or $SOCl_2 \cdot SbCl_5$, the more closely will the apparent activation energy approach the sum of the true activation energy plus $\Delta H°$.

(16) The lower figure observed with tetramethylammonium chloride, -28.1 e.u., is not strictly speaking comparable, being calculated on the basis of the third order rate law corresponding to the combination of the preliminary equilibrium with the rate-determining step.

constant might be expected possibly to affect either the equilibrium or rate constant. This situation merits further study.

Finally, what of the fact that aluminum chloride gives less than one tenth the rate of antimony pentachloride? Without knowledge of the mechanism involved in this case, interpretation of the difference is difficult. One may note, however, that Spandau and Brunneck[13] observed at comparable concentrations a much smaller conductance for aluminum chloride than antimony pentachloride in pure thionyl chloride, indicating a much smaller production of the dissociated aluminum chloride complex. A comparable relative behavior for the two compounds was observed by Seel and Bauer in sulfur dioxide solution[17] where a substance such as benzoyl chloride gave with aluminum chloride a much smaller conductance than with antimony pentachloride. While such considerations pertain of course to the tendency for the ionized complex to be formed in the solution, it may possibly be reasonable to take them also as an indication of the tendency towards *un-ionized* complex formation. On this basis aluminum chloride has clearly the smaller tendency.

In line with these observations, then, one might suppose that substitution of aluminum for antimony chloride in equation 7 would yield a pronounced equilibrium shift to the left. Assuming the same mechanism involved with both catalysts, such an effect might at least in part explain the rate decrease. It is to be recognized, however, that other factors may also play a role, such, for example, as tetrahedral in place of octahedral bonding in the tetrachloroaluminate formed, which might well affect the tendency toward activated complex formation. Alternatively it is of course possible that altogether different mechanisms apply in the two cases. In view of the points raised, a detailed study of the kinetics of catalysis by a series of acid chlorides including aluminum chloride (*e.g.*, $AlCl_3$, $SbCl_3$, BCl_3, etc.) appears quite inviting. One might hope thereby to resolve some of these ambiguities and to broaden our general insight into the nature of acid–base catalysis in this system.

Experimental

General.—Techniques were generally similar to those previously used, including both the methods of handling and counting the radiosulfur, S^{35}, obtained from the Atomic Energy Commission, and the high vacuum techniques employed in handling the volatile materials here involved.[4] In this work thionyl chloride and antimony pentachloride were never exposed to mercury. Halocarbon grease[18] was used for all stopcocks involving antimony pentachloride and, in most of the later experiments, those involving thionyl chloride, Apiezon "N" being otherwise employed. To minimize contamination by strongly adsorbed water, no transfers were made until the system had been pumped to high vacuum for at least 10 hr.

Run Procedures.—As before,[4] two types of procedures were employed. Experiments involving excess sulfur dioxide were done in glass vessels equipped with pressure stopcocks, thionyl chloride being labeled. Sulfur dioxide was dosed as gas, thionyl chloride as liquid from calibrated volumes. Antimony pentachloride, although also transferred by distillation into liquid air cooled receivers, proved difficult to handle because of its low volatility. It was

therefore dosed only approximately at the beginning of runs, its concentration being established by iodometric titration of antimony at the end of the experiments. The initial concentration of aluminum chloride, sublimed directly into the exchange bombs, could also only be estimated and was established by potentiometric titration of chloride in the final recovered aluminum chloride. The progress of the exchange was followed by withdrawal from the bombs (held at $-20°$) of five successive vapor samples (consisting predominantly of sulfur dioxide, the other solution components being relatively less volatile). The initial, zero time sample established the separation error. The exchange rate then was calculated by the same method previously used[4] to correct for the significant drain on total sulfur ($\sim$15–20 mmoles) that these samples ($\sim$0.5 mmole each) represented.

Experiments involving excess thionyl chloride (including expt. 24, about a 50-50 mixture) were done in all glass bombs equipped with break tips, sulfur dioxide being labeled. Each experiment consisted of a set of such bombs which were opened successively and fractionated as the exchange proceeded, the exchange being followed by growth of activity in a fraction of relatively pure thionyl chloride. The exchange rate was calculated from the slope of a log $(1 - F)$ *vs.* time plot according to the usual first order exchange rate law. In making these plots the minor variations of catalyst concentration between the bombs of a given set were corrected for on the basis of an assumed first order dependence of rate on this factor, an assumption justifiable on the basis of the final results.

Runs at $0°$ were carried out in ice baths, those at other temperatures in conventional liquid thermostats regulated to $\pm0.1°$. Normally the bombs were exposed only to subdued light, but it was possible to show that light was without effect on the rate. Experiment 15 was done with a fluorescent light placed immediately over the ice-bath containing the reaction vessel. Experiment 16 was kept in complete darkness except while samples were being taken. No significant difference in rates is apparent.

All rates and rate constants have been recorded in terms of molar concentration units. These have been computed from the amounts of the three solution components actually used on the basis of their densities,[19,20] the volumes of the mixed materials being assumed additive.

Preparation of Reactants.—Sulfur dioxide (Ohio Chemical), labeled sulfur dioxide, and labeled thionyl chloride were purified or prepared as previously described.[4,21] Thionyl chloride (Matheson, Coleman and Bell, b.p. range 75–76°) for use in the first experiments (all ones involving excess sulfur dioxide) was purified, as before, by successive distillation *in vacuo* from quinoline and raw linseed oil,[22] followed by fractionation of the resulting clear, colorless liquid, the middle one-half being retained. In the experiments with excess thionyl chloride, however, this product proved unsatisfactory, a precipitate, whose composition we did not succeed in establishing, forming on addition of antimony pentachloride to the exchange mixtures. Omission from the purification procedure of the distillation from quinoline eliminated this difficulty, suggesting it possibly to be related to some volatile impurity in the quinoline. (In the filling of a succession of reaction bombs by distillation from a common thionyl chloride supply, the precipitate had formed in least amount or not at all in the last bombs filled.) The modified purification procedure was therefore subsequently used. Vapor phase chromatography of the material so obtained showed the only significant impurity probably to be sulfur dioxide, present in quite small amounts, sufficiently so to be negligible compared to the amounts added in the exchange experiments.

Anal. Calcd. for $SOCl_2$: d^{-10}_4, 1.696[19]; S, 26.95; Cl, 59.60. Found: d^{-10}_4, 1.705; S, 26.23; Cl, 59.10.

(17) F. Seel and H. Bauer, *Z. Naturforsch.*, **2b**, 397 (1947).
(18) Halocarbon Products Corporation, Hackensack, N. J.

(19) "International Critical Tables," Vol. III, McGraw–Hill Book Co., Inc., New York, N. Y., 1928, pp. 22 ($SOCl_2$) and 236 (SO_2).
(20) Ref. 19, Vol. I, 1926, p. 111 ($SbCl_5$). For this component only a single density at 20° was available and so was used for all temperatures. Since antimony pentachloride made but a minor contribution to the total volume this would introduce only a small error, probably less than that due to the assumption of additivity of volumes.
(21) B. J. Masters and T. H. Norris, THIS JOURNAL, **74**, 2395 (1952).
(22) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1955, p. 345.

Antimony pentachloride (Baker and Adamson, Reagent Grade) was fractionated *in vacuo* the middle one-half being retained.

Anal. Calcd. for SbCl₅: Cl, 59.3. Found: Cl, 58.5.

Aluminum chloride (Baker, C.P., anhydrous) was purified by sublimation in the vacuum system, stored in small glass ampoules and sublimed directly into the exchange bombs without ever any exposure to air.

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[Contribution from the Department of Chemistry, Oregon State College]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. VI. Mixed Acidic and Basic Catalysts and the S³⁵-Exchange between Thionyl Chloride and Sulfur Dioxide[1]

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Antimony pentachloride has been shown to have a pronounced inhibiting effect on the catalysis by tetramethylammonium chloride of the radiosulfur exchange reaction between thionyl chloride and liquid sulfur dioxide, the catalysis reaching a minimum at an antimony pentachloride concentration corresponding to hexachloroantimonate, thus confirming the formation of this complex. Aluminum chloride similarly gives inhibition, suggesting the formation of tetrachloroaluminate complex. Hydrogen chloride gives no inhibition either of catalysis by tetramethylammonium chloride or of that by antimony pentachloride, signifying the absence of any important complex-forming interaction in either of these cases. The results support the previously offered acid–base interpretation of catalysis in this system.

The radiosulfur exchange reaction between thionyl chloride and liquid sulfur dioxide has been found subject to catalysis by both acidic and basic chlorides.[3,4] In view of the reported formation of various types of anionic chlorocomplexes in sulfur dioxide solutions,[5-7] it seemed particularly inviting to investigate the catalysis of this exchange reaction in solutions containing mixtures of such chlorides, in the hope of showing a correlation between complex formation and the exchange rates observed. We have now carried out experiments with four such mixtures involving combinations of the materials antimony pentachloride, aluminum chloride, tetramethylammonium chloride and hydrogen chloride. The results demonstrate a novel method of showing complex formation in sulfur dioxide solution, and in so doing serve to support most satisfactorily in a general way the previously offered acid–base interpretation of catalysis in the thionyl chloride–sulfur dioxide exchange system.

Results and Discussion

Antimony Pentachloride–Tetramethylammonium Chloride Mixtures.—In the investigation of this exchange reaction the catalysts tetramethylammonium chloride and antimony pentachloride have been studied in particular detail, the former giving about one hundred times the catalytic effect of the latter. Jander and Hecht[8] have reported the formation in mixtures of the two of a quite stable hexachloroantimonate complex. We have therefore studied exchange rates in a series

(1) Oregon State College, Research Paper No. 349, School of Science, Department of Chemistry.

(2) Taken from the thesis of David E. Burge, submitted in partial fulfillment of the requirements for the Ph.D. degree, Oregon State College, June, 1958.

(3) B. J. Masters and T. H. Norris, This Journal, **76**, 2015 (1954).

(4) D. E. Burge and T. H. Norris, *ibid.*, **81**, 2324 (1959).

(5) G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, pp. 299 ff.

(6) F. Seel, *Z. anorg. Chem.*, **252**, 24 (1943).

(7) F. Seel and H. Bauer, *Z. Naturforsch.*, **2b**, 397 (1947).

(8) G. Jander and H. Hecht, *Z. anorg. allgem. Chem.*, **250**, 304 (1943)

of such mixtures over a range of mole ratios of the two. It is to be anticipated that the strong ionic chloride catalysis should be inhibited by the presence of antimony pentachloride in proportion as chloride ion is converted to the complex.

The results are presented in Table I, the first two columns giving the concentrations of the two

TABLE I

RADIOSULFUR EXCHANGE RATES WITH ANTIMONY PENTACHLORIDE–TETRAMETHYLAMMONIUM CHLORIDE MIXTURES[a]

Me₄NCl, mole/l.	SbCl₅, mole/l.	Rate × 10³, mole/l.-hr. Cbsd.	mole/l.-hr.[b] Exptd.	$k^c × 10^3$, l./mole-hr.
0.104	0.018	104	153	
.069	.021	62	101	
.106	.033	136	155	
.118	.041	132	172	
.086	.039	49	126	
.068	.032	66	99	
.092	.079	18.4	133	
.115	.101	14.6	165	
.092	.086	10.2	132	
.086	.089	0.80	123	~30
.086	.115	0.50	123	1.80
.085	.207	2.11	118	1.89
.083	.327	4.03	112	1.89
.080	.632	7.73	99	1.86

[a] SOCl₂ (labeled 1.05–1.14 molar, SO₂ 18.9–20.6 molar. Temp., 0.0°. [b] Expected rate, calculated on the basis of catalysis by all the tetramethylammonium chloride present assuming no interaction with antimony pentachloride, using data of Masters and Norris.[3] [c] Calculated according to the rate law of Burge and Norris[4] ($K = 0.8$) on the basis of catalysis by SbCl₅ present in excess of that required for formation of (Me₄N)SbCl₆.

catalysts as put into the solution, calculated without regard to any possible complex formation. Column three records the experimentally observed exchange rates. The fourth column gives the rates to be expected on the basis of catalysis by all the tetramethylammonium chloride present, calculated from the data previously observed in this Laboratory,[3] and assuming the presence of anti-