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

Anal. Calcd. for $SbCl_5$: 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.

Acknowledgment.—This research has been supported by the U. S. Atomic Energy Commission under Contract AT(45-1)-244.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. VI. Mixed Acidic and Basic Catalysts and the S^{35}-Exchange between Thionyl Chloride and Sulfur Dioxide[1]

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RECEIVED SEPTEMBER 23, 1958

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 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 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-

TABLE I

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

Me_4NCl, mole/l.	$SbCl_5$, mole/l.	Rate × 10^3, mole/l.-hr.[b] Cbsd.	Exptd.	$k^c \times 10^3$, 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] $SOCl_2$ (labeled 1.05–1.14 molar, SO_2 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 $SbCl_5$ present in excess of that required for formation of $(Me_4N)SbCl_6$.

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(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)

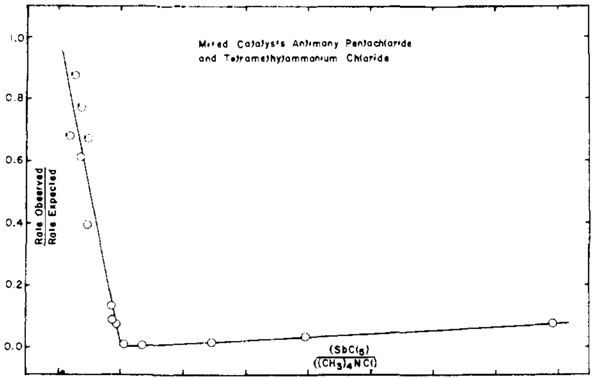

Fig. 1.—Plot of exchange rate ratio *versus* acid–base concentration ratio.

mony pentachloride to be without effect on the catalysis. The latter rates are consistently higher than those observed, clearly indicating catalysis inhibition by antimony pentachloride. This point is more specifically illustrated by Fig. 1 in which the ratio of the rate figures in the two columns is plotted against the mole ratio of the two catalysts. It may be seen that the rate falls off linearly with the amount of antimony pentachloride added, approximating zero at a $SbCl_5$:Me_4NCl ratio of unity.

The plot in Fig. 1 shows a most satisfactory correlation with and hence corroboration of the reality of stable hexachloroantimonate complex formation at the 1:1 mole ratio, the complex itself evidently having negligible catalytic activity. By the same token, the plot also serves to support the previously deduced interpretation of the tetramethylammonium chloride catalysis as due specifically to chloride ion. The linearity of the plot, running from a rate ratio of unity at zero antimony pentachloride to zero at complete complex formation, shows the catalysis to depend simply on chloride ion present in excess of that needed for complex formation, this evidently exhibiting the same catalytic effect as when present alone in the absence of complex.

Beyond a 1:1 mole ratio, Fig. 1 shows a slowly and again linearly increasing rate ratio, evidently now due to a weak catalysis by the excess antimony pentachloride, the slope of the line corresponding quantitatively to the approximate hundred-fold smaller catalytic effectiveness expected for this material as compared to tetramethylammonium chloride. A check on this interpretation is provided by the rate constants given in the last column of Table I. These have been calculated on the basis of the rate law already deduced for antimony pentachloride catalysis,[4] using the equilibrium constant $K = 0.8$ for $SOCl_2 \cdot SbCl_5$ complex formation, and assuming catalysis due to the stoichiometric excess antimony pentachloride. In all four cases where this substance is clearly in excess, the values agree well among themselves, serving to support the applicability of the rate law used. It is further to be noted that the absolute magnitude of the observed constants is almost the same as the value 1.48×10^{-3} l. mole^{-1}hr.$^{-1}$ found when antimony pentachloride alone is used.[9] On both counts, therefore, it is clear that catalysis in excess antimony pentachloride mixtures is to be ascribed specifically to the stoichiometric excess of this material, exerting substantially the same catalytic effect in the "mixed" solutions as when present alone.

This last conclusion is of particular interest in the support it lends to the mechanism deduced for the antimony pentachloride catalysis. In that case it was concluded that the undissociated material itself was the catalytic agent and not some small concentration of chloride ion derived from a slight ionic dissociation. By virtue of the hexachloroantimonate complex dissociation constant it may

$$\frac{(SbCl_5)(Cl^-)}{(SbCl_6^-)} = K \qquad (1)$$

be seen that chloride ion concentration would be governed by the ratio $(SbCl_5)/(SbCl_6^-)$ and would therefore be very different at the same net $SbCl_5$ concentration in the "mixed" as compared to the pure antimony pentachloride catalysis experiments. The similarity in the observed rates in the two cases clearly shows $SbCl_5$ itself and not chloride ion (or some other ionic deviative such as $SbCl_4^+$) to be the catalyst.

In the tenth listed experiment in Table I the indicated *k* value is excessively high. The most obvious explanation for this effect is that, in this solution where the indicated antimony pentachloride excess is very slight, chloride ion concentration is not negligible and therefore gives a pronounced catalysis, overshadowing the acid chloride catalysis. This could occur from either one of two causes. It is possible that the recorded antimony pentachloride concentration, determined by antimony analysis at the end of the experiments, is slightly in error, perhaps enough so as not actually to be in excess. Alternatively it is possible that the high *k* value is to be ascribed to a slight dissociation of the complex at this mole ratio. In connection with this point, it is interesting to estimate an upper limit for the dissociation constant of the complex (equation 1). On the basis of the work of Masters and Norris,[3] the figure $k = 30$ corresponds to a chloride ion concentration of 5.6×10^{-4} molar. An estimate of the maximum concentration of the uncomplexed $SbCl_5$ on the basis of a reasonable estimate of the error in antimony analysis, together with the value 0.086 for complex concentration, leads to an estimated upper limit for the equation 1 constant of 5×10^{-5}, a figure which supports the already assumed considerable stability of the hexachloroantimonate complex.

Aluminum Chloride–Tetramethylammonium Chloride Mixtures.—Jander and Immig[10] have reported aluminum chloride to increase markedly the solubility of potassium chloride in liquid sulfur dioxide, an observation suggesting complex formation in line with the recognized tendency for tetrachloroaluminate complex formation under non-

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[9] The self-consistency among the *k* values in Table I suggests that the difference from 1.48×10^{-3} may possibly be real and due to some undetected systematic effect. The difference does not, however, seem large enough to affect the argument presented.

[10] G. Jander and H. Immig, *Z. anorg. Chem.*, **233**, 295 (1937).

aqueous conditions.[11] On the other hand, Seel and Bauer,[7] while indicating that with benzoyl chloride a crystalline tetrachloroaluminate complex tended to be formed, found that in sulfur dioxide solutions conductances indicated very little formation of the ionically dissociated complex, in contrast to the situation with antimony pentachloride.

In the light of these observations it has been of interest to study the catalytic behavior of mixtures of aluminum chloride, itself a quite weak catalyst, with tetramethylammonium chloride. The results of five experiments are recorded in Table II in the same form as in Table I. Unfortunately these experiments were marred by the appearance of a precipitate of uncertain composition in three instances, possibly due to a slight hydrolysis of aluminum chloride by a small residue of moisture, as discussed in the Experimental section. The self-consistency of four out of five experiments, in only two of which the precipitate appeared, suggests, however, that, for present purposes, the presence of the precipitate may be disregarded. Were we interested in more quantitative results, additional "clean" experiments would certainly be required. For the present they do not seem necessary.

TABLE II

RADIOSULFUR EXCHANGE RATES WITH ALUMINUM CHLORIDE–TETRAMETHYLAMMONIUM CHLORIDE MIXTURES[a]

Me_4NCl, mole/l.	$AlCl_3$, mole/l.	Rate × 10^3, mole-l.-hr.	
		Obsd.	Exptd.[b]
0.112[c]	0.053	70.0	165
.111[c]	.062	220	162
.050[c]	.041	5.2	73
.081	.079	2.0	119
.048	.108	0.28	70

[a] $SOCl_2$ (labeled) 1.14 molar, SO_2 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 aluminum chloride and using data of Masters and Norris.[3] [c] Precipitate present in these solutions during exchange.

The results clearly show, except in the second experiment, a marked inhibition of catalysis by aluminum chloride, the ratio of the rates in column three to those in column four becoming progressively smaller as the $AlCl_3$:Me_4NCl ratio increases, more or less in accordance with the expected amount of catalysis by tetramethylammonium chloride remaining in excess of that necessary for a 1:1 complex formation. Only when the $AlCl_3$:Me_4NCl ratio exceeds 1:1 does the catalysis rate fall to a value of the order of magnitude of that expected for aluminum chloride alone. This last result is of interest in that it shows there to be no significant formation of any complex other than the 1:1, such for example as a possibly conceivable hexachloroaluminate.

The data display, then, a situation parallel to that found with antimony pentachloride and appear definitely to indicate the probable formation of at least a reasonably stable and non-catalytically active tetrachloroaluminate complex in these solutions.

Hydrogen Chloride–Tetramethylammonium Chloride Mixtures.—The foregoing experiments have shown acid chlorides to inhibit strongly the basic chloride catalysis through complex formation. A similar effect might possibly be expected of hydrogen chloride through formation of bichloride ion, HCl_2^-, reported both by Herbrandson, *et al.*,[12] and by West.[13]

Two experiments were done with hydrogen chloride–tetramethylammonium chloride mixtures. Thionyl chloride (labeled) and sulfur dioxide concentrations as well as temperature were the same as in the aluminum chloride experiments. With 0.105 M Me_4NCl and 0.095 M HCl, the observed rate was 0.123 to be compared to an "expected" rate (assuming no Me_4NCl–HCl interaction) of 0.157 moles $l.^{-1}$ $hr.^{-1}$. This result might be taken to suggest a small amount of interaction. However, with 0.107 M Me_4NCl and 0.274 M HCl, the observed rate was 0.139 to be compared to an "expected" rate of 0.159 mole $l.^{-1}$ $hr.^{-1}$. Despite the use of a clear excess of hydrogen chloride, the apparent catalysis inhibition was actually less, suggesting it probably to be without significance in either case. Thus it appears that the presence of hydrogen chloride has no effect on the catalytic activity of tetramethylammonium chloride, and it seems probable that any tendency toward bichloride formation in these solutions must be quite slight. The alternative explanation that bichloride is equally effective catalytically as chloride itself seems unlikely in view of the fact that even the cation associated with chloride ion has a marked effect on its catalytic activity.[3] Furthermore, Herbrandson, *et al.*, found, in epimerization studies, that bichloride ion was only about one twentieth as effective, catalytically, as chloride ion itself.

Hydrogen Chloride–Antimony Pentachloride Mixtures.—In the course of studying the basic chloride catalysis,[3] hydrogen chloride was shown to be without catalytic effect, *i.e.*, it does not behave as a base in these solutions. However, the very strong acidic properties found for antimony pentachloride by Seel and Bauer[7] suggest that it might possibly form a complex with hydrogen chloride in spite of this substance's weak basicity. A single experiment accordingly was done under similar conditions to those already described, with the solution containing 0.59 M HCl and 0.42 M $SbCl_5$. The observed rate was 6.25×10^{-3} to be compared to an "expected" rate of 5.2×10^{-3} mole $l.^{-1}$ $hr.^{-1}$, calculated for catalysis by antimony pentachloride, assuming no interaction with hydrogen chloride.

The indication of this experiment is that, in fact, no interaction does occur, the presence of hydrogen chloride clearly having no tendency to lower the rate. Any complex formation would surely interfere with formation of the thionyl chloride–antimony pentachloride complex postulated as an intermediate in the catalysis mechanism. Apparently hydrogen chloride behaves, in this system, as a weaker base than thionyl chloride.

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[11] J. C. Bailar, Jr., "The Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 6.

[12] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, THIS JOURNAL, **76**, 4046 (1954).

[13] R. West, *ibid.*, **79**, 4568 (1957).

Experimental

The experimental procedure and calculation methods were the same as or involved obvious modifications of those previously described.[3,4] The solutions contained 18.0 millimoles of sulfur dioxide and 1.0 millimoles of S^{35}-labeled thionyl chloride in every case, together with various added amounts of mixed catalysts. Exchange was followed by withdrawing periodic vapor samples, predominantly sulfur dioxide, from the solutions, contained in pressure stopcock-equipped bombs. Although this procedure may quite possibly have resulted in a significant progressive drain on hydrogen chloride concentration from the solutions involving this material, the non-observance of evidence for any effect on the exchange rates of the presence of this component did not make modification of the procedure seem worthwhile. It may be noted that the effect looked for, namely, the occurrence of any interaction between the catalyst and hydrogen chloride, would presumably have tended to minimize loss of the material.

In three of the aluminum chloride–tetramethylammonium chloride experiments a white flocculent precipitate appeared whose composition we did not succeed in establishing. It did not appear to be simply the complex itself precipitating out, however. Possibly traces of moisture left on the glass in these experiments, done early in the research, may have caused a slight hydrolysis of aluminum chloride to insoluble hydroxide. It seems unlikely that any hydrogen chloride so produced would affect the exchange rates, considering the results of the experiments involving this material. The effect of aluminum hydroxide is uncertain. In any case, it is to be observed that, except in one instance, the results of these precipitate-containing experiments are in general conformity with those anticipated and are in accord with those where no precipitate appeared. In subsequent experiments, however, considerably greater pains were taken to ensure the absence of moisture.

Acknowledgment.—This research has been supported by the U. S. Atomic Energy Commission under Contract AT(45-1)-244.

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[Contribution from the Chemistry Division, Oak Ridge National Laboratory]

The Enrichment of Lithium Isotopes by Ion-exchange Chromatography. I. The Influence of the Degree of Crosslinking on the Separation Factor

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Received September 18, 1958

Single stage separation factors have been determined for Li^6 and Li^7 between aqueous lithium ions and lithium ions on sulfonated polystyrene-divinylbenzene copolymers of various degrees of crosslinking. A band elution technique on an ion-exchange column was used. The single stage separation factor, α, (Li^6/Li^7)resin/(Li^6/Li^7)aqueous, was determined according to the method of Glueckauf from the elution curve and isotopic assays. Variations in α (1.0006 to 1.0038) with the degree of crosslinking can be explained by a simple concept of partial "dehydration" of lithium ions in the resin phase. Assuming a model for the lithium ion species in the two phases, the magnitude of α can be estimated quantum mechanically.

The enrichment of lithium isotopes on ion-exchange media has been reported by several workers. Taylor and Urey[1] were first to demonstrate the separation of lithium isotopes on a hydrated sodium aluminum silicate ion exchanger called "Decalso." Using the Rayleigh distillation formula, they calculated α, defined in this paper as (Li^6/Li^7)resin/(Li^6/Li^7) aqueous, to be 1.022 for a multiple extraction of lithium from a LiCl solution using successive small quantities of the zeolite. Sessions, Kibbey, Roberts and Blanco[2] repeated Taylor and Urey's experiments but were unable to reproduce their results. For the batch-type multiple extraction experiment using LiCl solution *vs.* Na^+-Decalso, no significant enrichment was found. For Li^+-Decalso *vs.* NaCl solution, α was estimated to be 1.0058 ± 0.0098. In two column experiments α was determined to be 1.0055 in one and 1.0038 in the other. Glueckauf, Barker and Kitt[3] used Zeo Karb H.I. in an ion-exchange column to obtain a partial separation of lithium isotopes. They concluded that the enrichment factor for this system was considerably smaller, perhaps tenfold less, than 1.022 as obtained by Taylor and Urey. Gross[4] separated lithium isotopes on a 10% cross-linked Dowex 50 column. From Gross' data Jury[5] calculated α to be 1.0065. Blanco, Kibbey, Land and Roberts[6] made fifteen successive batch equilibrations of lithium form Dowex 50W with an aqueous solution of LiCl. The separation factor was determined to be 1.0027 with a 95% confidence range of 1.0015 to 1.005. Studier, Brody and Mech[7] from their column elution data obtained an α of 1.0025 using Dowex 50. Menes, Saito and Roth[8] obtained an α of 1.002 also using Dowex 50. Bregman[9] discussed the effect of several variables on the selectivity of cation exchange resins for monovalent ions. These variables were: structure of the resin, nature of the acidic functional group, mole fraction of the exchange cations in the resin phase, resin capacity, external ionic strength and temperature. Whether these variables have any effect on the separation of isotopes is unknown. The purpose of this work was to establish the magnitude of α for lithium isotopes on ion-exchange materials with various degrees of crosslinking. Some of the other variables will be reported in subsequent papers.

Experimental

The ion-exchange columns used for these studies were generally from 50 to 150 cm. long and 1.5 to 3.5 cm. i.d. The ion-exchange materials were usually 50 mesh or finer. A band elution technique was used in all of the experiments. For each experiment, the resin column was saturated with

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(1) T. I. Taylor and H. C. Urey, *J. Chem. Phys.*, **5**, 597 (1937); **6**, 429 (1938).

(2) R. I. Sessions, A. H. Kibbey, J. T. Roberts, R. E. Blanco, Oak Ridge National Laboratory Report CF-53-6-241 (June 1, 1953).

(3) E. Glueckauf, K. H. Barker and G. P. Kitt, *Disc. Faraday Soc.*, **7**, 199 (1949).

(4) J. H. Gross, AECD-2952 (Nov. 29, 1950).

(5) S. H. Jury, Oak Ridge National Laboratory Report CF-52-8-218 (Aug. 15, 1952).

(6) R. E. Blanco, A. H. Kibbey, J. I. Land and J. T. Roberts, Oak Ridge National Laboratory Report CF-53-11-47 (Nov. 4, 1953).

(7) M. H. Studier, J. K. Brody and J. I. Mech, "Summary Report of Chemistry Division," July 1, 1953–March 31, 1955, ANL-5450, p. 23.

(8) F. Menes, E. Saito and E. Roth, "Proceedings of the International Symposium on Isotope Separation," North-Holland Publishing Co., Amsterdam, Netherlands, 1958, p. 227.

(9) J. I. Bregman, *Ann. N. Y. Acad. Sci.*, **57**, 125 (1953).