

RADIOCHLORINE EXCHANGES IN
ACID CHLORIDE SOLVENTS

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1955

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Date thesis is presented May, 1954

Typed by Evelyn Kanzelmeyer

ACKNOWLEDGMENT

The author would like to express his appreciation to Professor T. H. Norris for his guidance and many helpful suggestions.

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RADIOCHLORINE EXCHANGES IN ACID CHLORIDE SOLVENTS

I. INTRODUCTION

Acid oxychloride solvents such as selenium oxy-chloride, phosgene, thionyl chloride, sulfonyl chloride, nitrosyl chloride, and phosphorus oxychloride have figured importantly in the extension of the solvent systems theory of acids, bases, and salts to non-protonic solvent systems (1, p.234). It has come to be accepted, partly on the basis of experiment and partly on the basis of assumed analogies between the different materials, that these compounds can function as solvents in which acid-base behavior may exist and can be regarded as parents for systems of acids and bases.

According to the solvent systems theory, the solvent undergoes a self-ionization similar to that of water. That is, if water ionizes to give hydronium ion and hydroxide ion, then ammonia would ionize to give ammonium ion and amide ion:

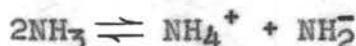
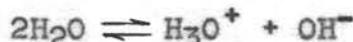
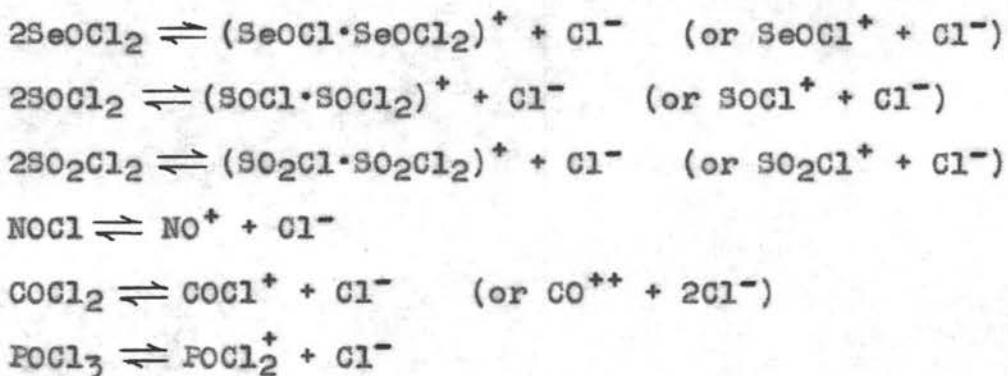


Table I shows possible self-ionizations for a number of these solvents, the equations representing either equilibria which have been specifically suggested or the existence of which is implicit in the various discussions of the subject (1, pp.234-49; 11, pp.11,53-4; 13, pp.337-68).

Although such self-ionization must ordinarily be quite small, conductance measurements clearly indicate its existence in a variety of instances. However, one cannot state with certainty the exact nature of all the ionic species present, for the ions are undoubtedly solvated to a greater or lesser extent.

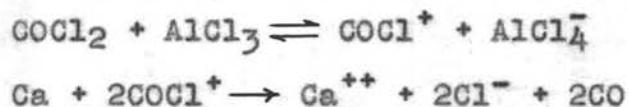
TABLE I
SELF-IONIZATION EQUILIBRIA



As a further part of the solvent systems picture, the positive fragment, in each case, is considered analogous to hydronium ion in water and the properties of hydroxide ion are ascribed to the negative fragment. Then any substance which gives the cation characteristic of the solvent is considered an acid while a base is a substance which gives the characteristic anion of the solvent.

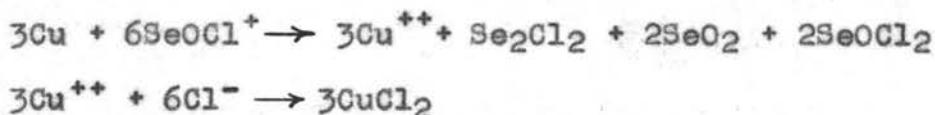
A number of specific examples will serve to illustrate the foregoing concepts. For instance, a solution of

aluminum chloride in liquid phosgene readily dissolves metals with the liberation of carbon monoxide (6, p.2470). According to the solvent systems theory, the aluminum chloride is an acid and therefore increases the concentration of the COCl^+ ion. This ion, in turn, then serves to react with and oxidize the metal. The reaction is formulated as:

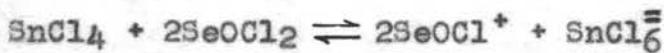


These equations are evidently consistent with the self-ionization scheme for phosgene given in Table I.

As a second example, a solution of stannic chloride in selenium(IV) oxychloride dissolves metals much more readily than does the pure solvent alone (16, p.167). Here again is "typical" acid behavior. The reaction in the pure solvent, which goes very slowly at room temperature, is formulated as:

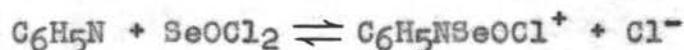


The acidic nature of the stannic chloride solution is explained by the increase of the characteristic cation on the solution of the stannic compound:



By way of contrast with the above, any substance tending to increase the concentration of the characteristic

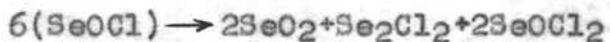
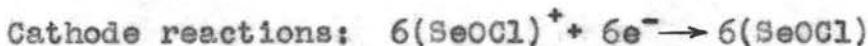
anion, Cl^- , is a base in selenium oxychloride. Thus the basic properties of pyridine in this solvent are explained in terms of the equilibrium (16, p.169):



It has been reported that sulfur monoxide can be prepared by the action of thionyl chloride on metals at elevated temperatures (15, p.113). This would seem to be an analogous reaction to that of selenium oxychloride on metals. Luder (11, p.73) has predicted that sulfur monoxide would be evolved at much lower temperatures if some acid such as stannic chloride were added to the thionyl chloride, but the actual observance of such an effect has not yet been reported.

Further evidence which lends credence to the self-ionizations proposed for selenium oxychloride and phosgene is obtained from electrolysis data. Smith (17, p.2407) has shown that the electrolysis products of pure selenium oxychloride are selenium monoxide and chlorine. Chlorine is the anode product and selenium dioxide and selenium monochloride are the cathode products in the electrolysis of either acids or bases in selenium oxychloride. Smith gives the following reasonable formulations for the electrolytic decomposition of the solvent:





The electrolysis of the acid, aluminum chloride, in phosgene solutions has been analogously formulated and yields carbon monoxide at the cathode and chlorine at the anode (7, p. 883).

Although most of the large amount of experimental work with phosgene and selenium oxychloride has been rather nicely and convincingly explained in terms of the solvent systems theory, as illustrated by the foregoing examples, recent work of Huston (9) with radioisotopes tends to show that too much emphasis may have been placed on ionic mechanisms and analogies to the water system. Thus when aluminum chloride labeled with radiochlorine was dissolved in liquid phosgene, rapid chlorine exchange was not observed. This can only be interpreted as implying that the importance of the equilibrium



has been overemphasized, since such an equilibrium would certainly lead to a rapid chlorine exchange. Huston's interpretation of his observations is that aluminum chloride is an acid in the Lewis sense rather than the solvent systems sense and reacts with basic materials directly as an electron pair acceptor without the solvent playing any direct part. Thus the phosgene is an "inert" solvent.

The present work with radiochlorine was undertaken with a view to obtaining some insight into the validity of the acid-base equilibria analogous to those discussed in the preceding paragraphs for the two acid chloride solvents thionyl chloride and phosphorus oxychloride. It is evident that this work derives special interest from Huston's recent results with liquid phosgene.

Thionyl chloride is a fair ionizing medium (1, p.234), but its usefulness as a solvent is limited by its high chemical reactivity and its inability to dissolve salts to any appreciable extent. Because of this, little actual experimental work has been done in this material.

In the course of his investigations of acid-base exchange reactions in liquid sulfur dioxide, Masters (12, pp.123-129) studied the radiochlorine exchange between the solutes tetramethylammonium chloride (TMAC) and thionyl chloride. A very rapid exchange was observed; this result provided part of the motivation for the present research.

Phosphorus oxychloride is, in general, a better solvent for inorganic substances than liquid sulfur dioxide (1,p.247). The value of the specific conductance shows that it undergoes a degree of self-ionization comparable to that of water and its dielectric constant is of the same order of magnitude as liquid sulfur dioxide. The few available data on the conductances of salts in this solvent

indicate that it is a good ionizing media for binary compounds. However, like thionyl chloride, it is highly reactive, particularly towards water, and not a great deal of work has been done with it as a solvent.

The exchange experiments done in this research consisted of the investigation of the exchange rates of (1) a basic (or ionic) chloride, tetramethylammonium chloride, with both the solvents thionyl chloride and phosphorus oxychloride, and (2) an acid chloride, antimony trichloride, with thionyl chloride. On the basis of Master's (12, p.129) and Huston's (9) results (cf. above), it was anticipated that a very rapid exchange would be observed for case (1) and that a measurably slow exchange might appear in case (2).

II. EXPERIMENTAL PROCEDURES

A. COUNTING TECHNIQUE. The tracer element used in the present work was chlorine-36, a pile-produced nuclide, available from the Oak Ridge National Laboratory of the U. S. Atomic Energy Commission. This isotope emits an electron with a maximum energy of 0.66 Mev and has a half-life of 10^6 years (5,p.305). The form of the chlorine activity on which radioassays were made was in all cases mercurous chloride.

The samples were counted as thin layers of mercurous chloride, 2-8 mgm/cm², deposited from an acetone slurry on cupped stainless steel planchets of uniform area. An empirically established curve was determined which showed that no self-absorption corrections were necessary for samples of this thickness. Except where noted, enough counts were accumulated for each sample that the statistical error was reduced to less than two per cent. The distribution of counting time between sample and background followed the square root ratio law (3,pp.60-61).

The beta activity determinations were made with an end window counter tube having a window thickness of less than 2 mgm/cm² (Tracerlab TGC-2 tubes). The pulses from this tube were scaled on a time pre-set decimal counter with a capacity of more than 3×10^4 counts per second and a dead time of 5-10 microseconds.

Whenever activities which were counted on separate days were to be intercompared, a standard sample of $Hg_2Cl_2^{36}$ was also counted and the counter efficiency standardized for the compared counts.

B. PREPARATION OF MATERIALS. 1. The chlorine-36 was received in the form of potassium chloride which contained sulfur-35 activity. The sulfur was removed from the Oak Ridge sample by adding carrier sulfate and precipitating the sulfur-35-active barium sulfate. The resulting filtrate was taken to dryness on the steam bath and the crystals were placed in a hydrogen chloride generator. Concentrated sulfuric acid was added and the hydrogen chloride generated was absorbed in dilute potassium hydroxide solution. This resulted in chlorine-36-labeled potassium chloride of moderate specific activity (up to 300 c/m/mgm counted as mercurous chloride).

2. The labeled tetramethylammonium chloride (TMAC*) was made by a heterogeneous reaction of Eastman (White Label grade) tetramethylammonium bromide solution with solid, active, silver chloride. The silver chloride was prepared by precipitation from a solution of active potassium chloride (purified above) using 1N silver nitrate.

The TMAC* was purified by washing repeatedly with chlorine water and subsequently extracting the displaced

bromine with carbon tetrachloride. Excess chlorine was removed by several further washes with carbon tetrachloride. The TMAC* was dried in the oven for twelve hours at 110°C, washed with chloroform to remove trimethylamine, redried and recrystallized from alcohol. The crystals were washed with alcohol, chloroform, absolute ether, and dried in the oven at 110°C for forty-five minutes.

This salt was always stored in a calcium chloride-dried dessicator and before each run it was thoroughly dried in the manner outlined in the description of the runs. The specific activity was 302 c/m/mgm, counted as mercurous chloride¹.

3. Thionyl chloride (Matheson, Colman, and Bell) was purified by the method of Fieser (4, pp. 381-82) which consisted essentially of a distillation; first from quinoline and second from boiled linseed oil. The process was carried out in the all-glass still described by Herber (8, p. 40). The material was first distilled from quinoline into Herber's chamber (A) which already had been charged with the linseed oil. The tube through which this had been accomplished, corresponding to sidearm (B), was then sealed off. The system was partially evacuated by means of an aspirator and a flow of barium perchlorate

¹ The author is indebted to Burton J. Masters for furnishing the TMAC* used in these experiments.

("Desicchlora")-dried air, through the capillary leak (C), was adjusted to give a steady stream of bubbles in the thionyl chloride-linseed oil mixture. Distillation occurred when the water bath surrounding (A) was brought to about 74°C, the pressure being about two centimeters of mercury as measured by a mercury-filled manometer (not shown). The condensate was allowed to flow into the collecting tube (G) which was correctly oriented by rotation of the collecting head (F) on the axis formed by the ground glass joint (E) and the ball and socket joint (H). The joints were lightly greased on the outside edge by Dow-Corning silicone stopcock grease.

After an initial quantity of about twenty per cent of the total thionyl chloride had been collected in (G), this portion was sealed off and another collector (G') was rotated into position to collect the distillate. About sixty per cent of the remaining thionyl chloride was distilled into this container.

Starting with 150 ml. of thionyl chloride, about 75 ml. were obtained, after discarding the first twenty per cent of the distillate and the residue. The density of the material so collected was 1.641 (25°C) against the published value of 1.637 (25°C) (9,p.282). It was stored in all glass break-off tip containers of about five milliliters capacity, in a dark drawer.

4. Matheson, Coleman, and Bell tetramethylammonium chloride (TMAC) was washed with chloroform until no odor of trimethylamine remained. The resulting crystals were recrystallized from 95% ethyl alcohol, the salt being collected on a "fine" frittered glass filter. The TMAC was dried in an oven at 90°C for an hour and then stored in a calcium chloride-dried dessicator.

5. C.P. antimony trichloride (Baker's Analyzed) was fractionated in an all glass apparatus under a vacuum maintained by a mechanical fore pump, a very small flame being used to effect the distillation.

The middle one-half of the distillate was caught in a receiver which was then sealed off from the apparatus. The receiver was opened in a phosphorus pentoxide-dried glove box and the antimony trichloride was scraped out into a mortar and ground to a fine powder. It was put into a container fitted with a ground glass stopper which was then stored in a calcium chloride-dried dessicator.

6. Two quantities of labeled thionyl chloride were prepared by a method based on the results of the present work. A pair of reaction bombs, which were simply six inch test tubes each fitted with a constricted sidearm, were prepared to contain TMAC*. The TMAC* was added to the bombs (about 250 mgm in each bomb in the first run, about 100 mgm in each in the second) and the tops of the

bombs were sealed. The bombs were attached to a vacuum line manifold which held a thionyl chloride storage container provided with a break-off tip. The manifold was also provided with a break-off tip container to be filled with the activated solvent. The line was evacuated to a pressure of 10^{-4} - 10^{-5} mm of mercury. The break-off tip of the thionyl chloride storage container was crushed by dropping a magnetically raised iron-mercury weight. The thionyl chloride was transferred to the first reaction bomb by cooling the bomb with a liquid nitrogen bath. When all the thionyl chloride had been transferred to the bomb, it was warmed to about 40°C by a water bath to dissolve the TMAC*. After this had all dissolved the thionyl chloride was transferred to the second reaction bomb and the process was repeated. The thionyl chloride was then transferred in the same manner to the break-off tip container provided and this container was sealed off from the line and stored in the dark.

At no time during the activation process did the thionyl chloride come into contact with stopcock grease. This was avoided because of a slight interaction which occurs between the two.

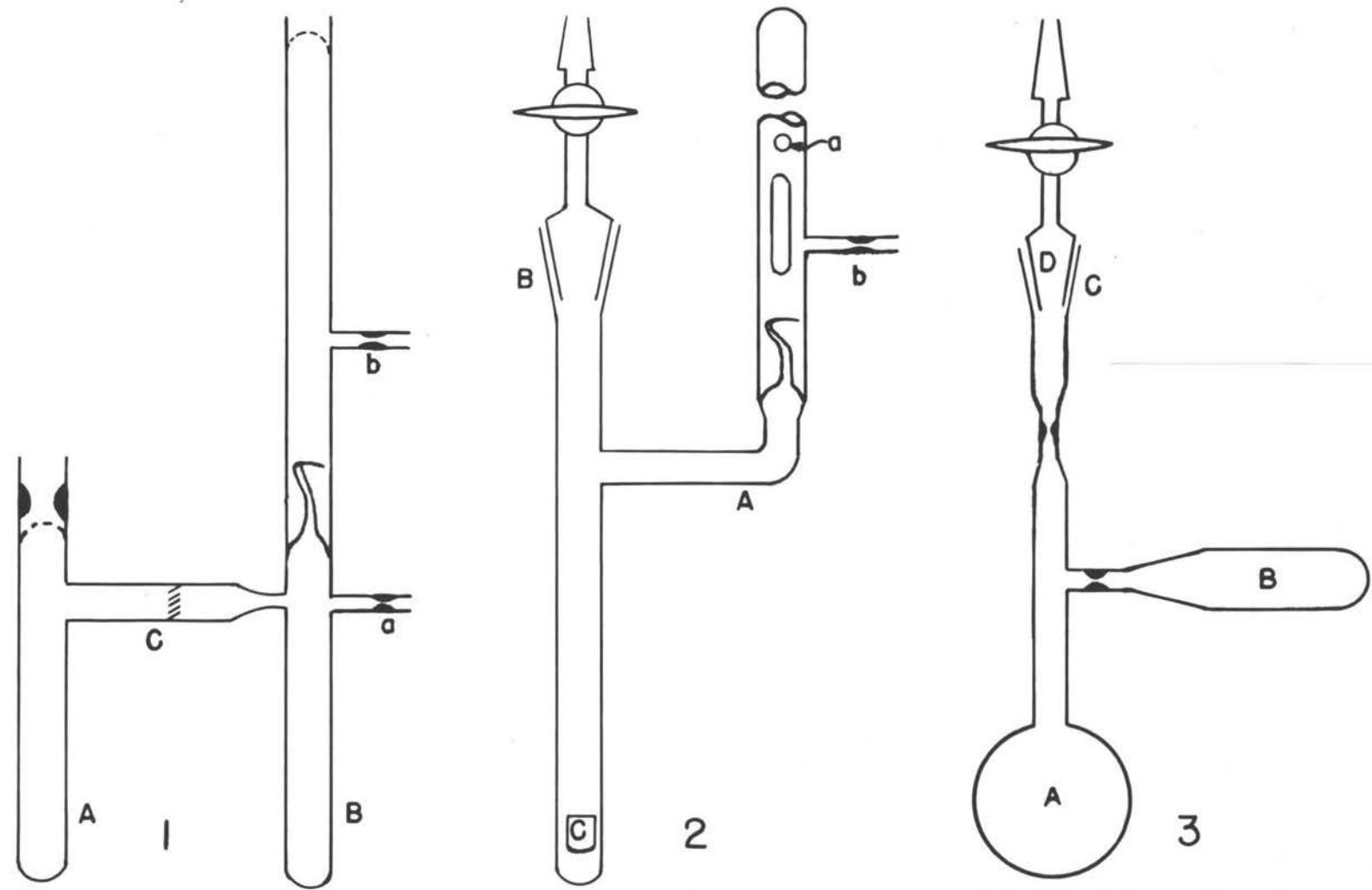
About five milliliters of thionyl chloride were activated in each run. The specific activities were: first run, 24.26 c/m/mgm; second run, 5.35 c/m/mgm.

7. Phosphorus oxychloride (Mallinckrodt, Reagent Grade) was fractionated in a reaction bomb similar to those used in the exchange runs with this solvent (see below). The fractionation was carried out in vacuo (10^{-4} - 10^{-5} mm) at room temperature, using liquid nitrogen as a condensing agent. Approximately the first and last fifteen percent was discarded, seventy percent being saved and stored in a sealed tube.

C. TETRAMETHYLLAMMONIUM CHLORIDE-THONYL CHLORIDE EXCHANGE EXPERIMENTS. The runs with TMAC in thionyl chloride were carried out in the reaction bombs of the type shown in Figure I, 1. From twelve millimeter Pyrex tubing, these bombs were glass-blown to include two legs, (A) and (B), which were separated by a ten millimeter o.d. crosspiece (C) which was provided with a sintered glass disc. The crosspiece (C) was constricted and thickened next to leg (B) to facilitate sealing it off under vacuum. Leg (A) was open at the top but had a constriction so the bomb could be easily sealed. Leg (B) was provided with a break-off tip, a glass enclosed iron-mercury weight, and two constricted sidearms (a) and (b), one above and one below the break-off tip.

The weighed TMAC[#] was introduced through the opening at the top of leg (A) which was then sealed off at the constriction. The bomb was sealed onto the vacuum system

FIG. I BOMBS USED IN EXCHANGE RUNS

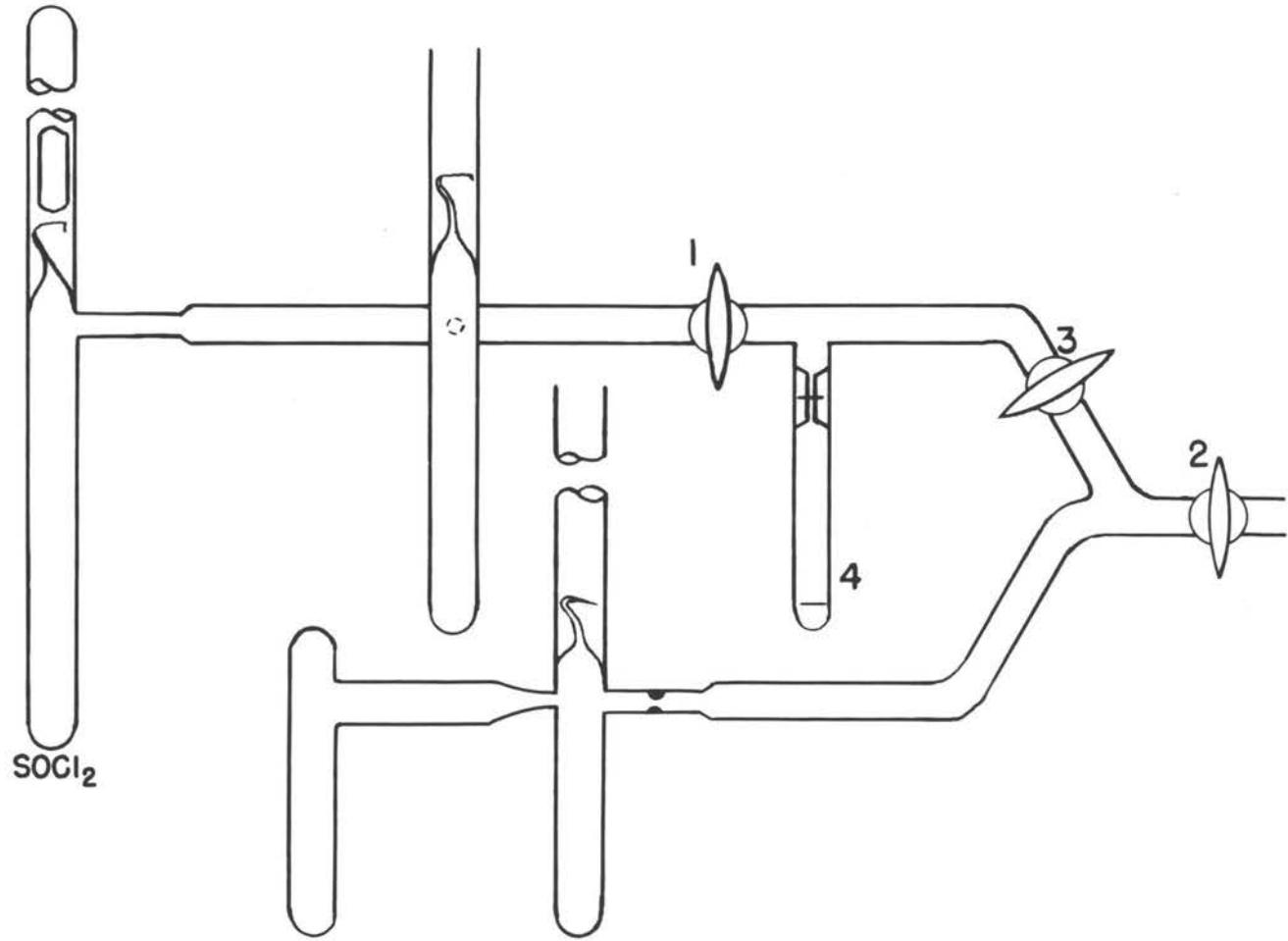


manifold which was provided with the thionyl chloride stock supply, a calibrated cold finger doser (4), and a break-off tip bomb to accommodate the excess thionyl chloride not used in the experiment. The manifold was evacuated to a pressure of 10^{-4} - 10^{-5} mm of mercury (as measured by a McCleod gauge, which is not shown). The salt was pumped on for twenty-four hours while kept at a temperature of 135°C by the wax bath surrounding leg (A).

After the salt was thoroughly dry, stopcock (2) was closed, isolating the manifold. The thionyl chloride stock supply was opened to the manifold by dropping a magnetically raised, glass enclosed, iron-mercury weight, crushing the break-off tip. With stopcock (1) open and (3) closed, the thionyl chloride was distilled into the cold finger doser (4), using a liquid nitrogen bath. This doser had previously been calibrated (by weighing when filled with mercury) to contain a known volume of thionyl chloride.

When about one third excess thionyl chloride had been distilled into the doser, it was warmed to 25°C by means of a water bath. The excess was distilled back into the stock supply bomb until the meniscus coincided with the upper calibration mark of the doser. Stopcock (1) was closed and (3) was opened. The thionyl chloride was distilled from the doser into leg (B) of the reaction bomb

FIG. II MANIFOLD FOR TMAC-SOCl₂ EXPERIMENTS



until the meniscus of the liquid in the doser coincided with the lower calibration mark. Stopcock (3) was closed and the reaction bomb was sealed off from the line at the constriction in sidearm (a).

After leg (B) had warmed to room temperature, the thionyl chloride was distilled into leg (A). Leg (A) was warmed to the temperature at which the exchange was to be run by either a $25 \pm 1^{\circ}\text{C}$ water bath or an ice-water bath. After the salt had all dissolved in the thionyl chloride (ca. 5 minutes total after removal from liquid nitrogen), the latter was distilled back into leg (A). Thirty-five to about eighty-five minutes was needed to complete this process. The residue consisted of a dry salt, a qualitative check (for sulfur) on which showed a complete absence of thionyl chloride retention. Legs (A) and (B) were sealed apart at the constriction in the crosspiece (C).

Leg (B) was sealed to a vacuum system manifold (not shown) which was provided with a tube containing five grams of sodium hydroxide in about ten milliliters of water; the sodium hydroxide solution was frozen with liquid nitrogen. The manifold was evacuated to a high vacuum and then isolated from the rest of the vacuum system by closing a stopcock. Leg (B) was opened via the break-off tip and the thionyl chloride was distilled onto the frozen sodium hydroxide. The sodium hydroxide tube

was sealed off from the manifold at a constriction and thawed in cold running tap water. The thawing effected a reaction between the thionyl chloride and the base, giving an alkaline solution containing sulfite and chloride ions.

The sodium hydroxide tube was cracked open, the contents washed into a 150 ml. beaker, and enough thirty percent hydrogen peroxide solution was added to oxidize the sulfite to sulfate. After the solution was made slightly acid with dilute nitric acid, any excess hydrogen peroxide was destroyed by boiling. Just enough 0.2N HgNO_3 (stabilized by the presence of elementary mercury) was added to precipitate about 120 mgm of mercurous chloride after the solution had cooled. The mercurous chloride was filtered through a sintered glass filter, washed several times with water and then acetone, and finally slurried in acetone and deposited on planchets for counting. In none of the precipitations of the mercurous chloride was an excess of precipitating agent added, since such a procedure, because of the presence of mercuric ion, would lead to an enhanced solubility of mercurous chloride.

Leg (A) was cracked open and the TMAC was dissolved in water and transferred to a 50 ml. beaker. The chloride was precipitated as mercurous chloride, as described above, for counting.

On the basis of the specific activities of the salt and solvent, the percent exchange (recorded in the Results and Discussion section) was calculated by a formula which is derived thus:

$$F = \frac{S_b}{S_{b\infty}} = \frac{S_b(a + b)}{S_b(b) + S_a(a)}$$

$$(1-F) = \frac{S_b(b) + S_a(a) - S_b(a + b)}{S_b(b) + S_a(a)}$$

$$(1-F) = \frac{a(S_a - S_b)}{S_b(b) + S_a(a)}$$

$$(1-F) = \frac{S_a - S_b}{\frac{S_b(b)}{S_b(a)} + S_a}$$

where: F = the fraction exchange

S_a = specific activity of salt at time t
(initially active)

S_b = specific activity of solvent at time t
(initially inactive)

$S_{b\infty}$ = specific activity of solvent at infinite time

(a) = number of moles of salt

(b) = number of moles of solvent.

The percent exchange can be found simply by multiplying F by one hundred.

D. ANTIMONY TRICHLORIDE-RADIOETHIONYL CHLORIDE EXPERIMENTS. Reaction bombs (figure I, 2) were fitted with a # joint (B), a sidearm (A) containing a break-off

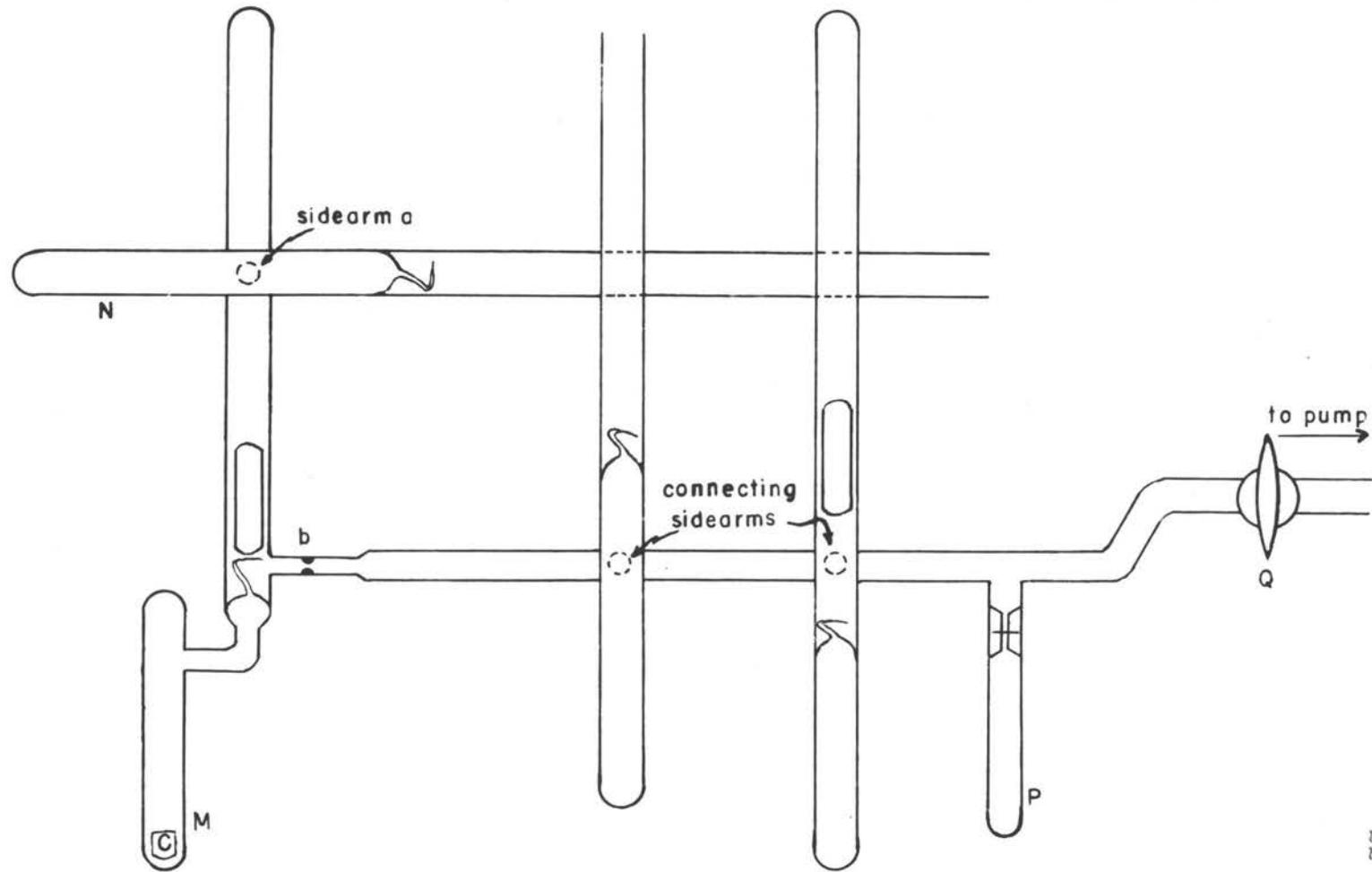
tip and a glass-enclosed iron-mercury weight. In each bomb the column above the break-off tip was fitted with two sidearms, (a) and (b), which were constricted to facilitate sealing them off under vacuum. Sidearm (a) led to an empty thionyl chloride storage container which was at right angles to the reaction bomb (figure III, M and N).

The antimony trichloride was weighed into a Pyrex glass weighing boat (C) in the phosphorus pentoxide-dried glove box. The weighing boat was dropped into the bomb through the $\frac{1}{2}$ joint (B). This joint was then fitted with a corresponding male $\frac{1}{2}$ joint which was attached to a stopcock and another male $\frac{1}{2}$ joint (2).

The bomb was removed from the dry box, attached to the vacuum line by $\frac{1}{2}$ joint (2), partially evacuated, and the $\frac{1}{2}$ joint (B) sealed off from it just above sidearm (A); the bomb was next sealed to the manifold by sidearm (b) (figure III). In addition to the reaction bomb, the manifold was provided with a cold finger doser (P), the stock supply of radiothionyl chloride in a break-off tip bomb, and an empty bomb to accommodate the excess thionyl chloride not used in the experiment.

The break-off tip of the reaction bomb was crushed and the manifold evacuated to a pressure of 10^{-4} - 10^{-5} mm of mercury; the stopcock (Q) was then closed and the

FIG. III MANIFOLD FOR $SbCl_3$ - $SOCl_2$ EXPERIMENTS



break-off tip of the thionyl chloride storage bomb was crushed. The thionyl chloride was transferred to the empty break-off tip container and the original stock supply bomb was sealed off from the manifold. Thionyl chloride was now transferred to the calibrated cold finger doser (P); when about one-third excess had been distilled into the doser, the coolant was removed and the thionyl chloride in the doser was warmed to 25°C by a water bath. The liquid was distilled back to the storage bomb until its meniscus coincided with the calibration mark on the doser. The water bath was quickly replaced by a liquid nitrogen bath and the storage bomb was sealed off from the manifold. The liquid in the doser was warmed to room temperature and the thionyl chloride was distilled onto the antimony trichloride in the reaction bomb. When the transfer was complete the reaction bomb was sealed off from the line keeping the mixture at liquid nitrogen temperature. The bomb was now turned so that the empty thionyl chloride storage bomb was vertical and the reaction bomb horizontal to facilitate rapid distillation. The liquid nitrogen bath surrounding the reaction bomb was replaced by a large ice-water bath. When the antimony trichloride had all dissolved, the thionyl chloride was quickly distilled into the storage bomb which was then sealed off at the constriction in sidearm (a). All of the above transfers were

accomplished using liquid nitrogen coolants.

The reaction bomb was cracked open and the antimony trichloride dissolved in 4N HNO₃. This solution was diluted to 0.4N HNO₃ and saturated with hydrogen sulfide. The resulting antimony pentasulfide was removed by centrifuging and, after boiling, the decantate was ready for conversion to mercurous chloride for counting.

The specific activity of the antimony trichloride was compared with the previously measured specific activity of the solvent. This was determined in the same manner as was the specific activity of the thionyl chloride in the runs with tetramethylammonium chloride.

Since in these experiments the activated solvent was present in large excess over the solute, it was assumed that its specific activity did not vary significantly in the course of a run. This being the case, the initial solvent specific activity gave a measure of the infinite time (complete exchange) specific activity of both solvent and solute. Consequently the percent exchange, 100 F, was computed from the expression

$$F = \frac{S_{\text{SbCl}_3}}{S_0 \text{SOCl}_2}$$

Because the solvent was tagged in this experiment rather than the salt, it was necessary to be certain that no solvent remained in the antimony trichloride after the

distillation. Therefore several blank runs were made and the antimony trichloride remaining after the distillation was analyzed for chlorine by titrating with 0.24*N* AgNO₃, the titration being followed on a titrimeter. The results of the blanks were as follows, reported as percent chloride: 46.54%, 46.15%, 46.51%. The average was 46.30% as against 46.34% calculated for the antimony trichloride; the percent chloride in thionyl chloride is 59.60%. Two blanks were run in which the residue after distillation was oxidized with thirty percent hydrogen peroxide, dilute barium nitrate was added and no barium sulfate resulted.

From the results of these blank runs it was concluded that the separation of the salt and solvent was complete and that no solvate is stable under experimental conditions.

E. PHOSPHORUS OXYCHLORIDE-TETRAMETHYLMONIUM CHLORIDE EXPERIMENTS. The phosphorus oxychloride-tetramethylammonium chloride runs were made in the reaction bombs of the type shown in figure I, 3. The reaction chamber (A) was constructed out of a fifty milliliter bulb, the receiver (B) was made from twenty millimeter tubing, and the bomb's manifold was made from sixteen and ten millimeter tubing. The apparatus was fitted with a female $\frac{1}{2}$ joint (C) which received an adapter (D), consisting of a stopcock sealed between two ground joints.

The adapter was in turn fitted to the vacuum system.

The empty bomb was dried for three hours in an oven at 130°C and then attached to the vacuum line and pumped on for an hour at room temperature. When it was thoroughly dry, the evacuated bomb was placed in the dry glove box, the stopcock in (D) opened, and the adapter removed from the bomb. About ten milligrams of labeled tetramethylammonium chloride was weighed out (in the dry box) and placed in the bomb through ground joint (C). Ten milliliters of phosphorus oxychloride, enough to dissolve all of the TMAC*, was pipetted into the bomb using an automatic pipetter. (It was found that TMAC was readily soluble to the extent of only about one milligram per milliliter of solution.) The stopcock in (D) was closed and the bomb was again fitted with the adapter at ground joint (C). The solution was frozen, the bomb attached to the vacuum line, evacuated to a pressure of about 10^{-4} mm, and sealed at the constriction just below joint (C).

The run was started by thawing the solvent and dissolving the salt (complete in about fifteen minutes). The phosphorus oxychloride was immediately distilled from flask (A) to receiver (B) by surrounding the latter with a liquid nitrogen bath. When all the solvent had distilled (about forty minutes), the receiver was sealed off from the bomb at the constricted neck. The receiver was

cracked open and about one milliliter of its contents were poured into a beaker containing dilute potassium hydroxide. The resulting chloride solution was made neutral with dilute nitric acid and precipitated as mercurous chloride for counting. The distillation flask (A) was cracked open and the salt residue dissolved in water making it ready for conversion to mercurous chloride for counting.

Because of the low solubility of the salt in the solvent, and the relatively low specific activity of the salt used, the final measured specific activities of the two fractions were both very low, leading to a quite large statistical error in their determinations. It was possible, however, to calculate the percentage exchange by comparing the final (very low) salt activity with its own initial (moderate) specific activity. In this way, in spite of the very low absolute accuracy of the first value, a quite accurate estimate of the actual extent of exchange could be made. The direct intercomparison of the two low solvent and solute specific activities was then used only to show that the total recovered activity checked reasonably with the starting activity.

In line with the foregoing, the fractional exchange was calculated as follows, where the symbols are consistent with those used in the section on the tetramethylammonium

chloride-thionyl chloride experiments; e.g., F is fraction exchange, (a) refers to the salt (initially active), and (b) refers to the solvent (initially inactive):

$$F = \frac{s_b}{s_{b\infty}}$$

$$s_{b\infty} = \frac{s_{a_0}(a)}{(a + b)}$$

$$s_b = \frac{(s_{a_0} - s_a)(a)}{(b)}$$

$$F = \frac{(s_{a_0} - s_a)(a + b)}{s_{a_0}(b)} = \frac{(s_{a_0} - s_a)(\frac{a}{b} + 1)}{s_{a_0}}$$

$$(1-F) = \frac{s_a - \frac{(a)}{(b)} s_{a_0} + \frac{a}{b} s_a}{s_{a_0}} = \frac{s_a(1 + \frac{(a)}{(b)}) - \frac{(a)}{(b)} s_{a_0}}{s_{a_0}}$$

Since in these experiments $\frac{(a)}{(b)} \gg 1$,

$$(1-F) = \frac{s_a - \frac{a}{b} s_{a_0}}{s_{a_0}}$$

III. RESULTS AND DISCUSSION

A. THIONYL CHLORIDE-TETRAMETHYLMONIUM CHLORIDE EXPERIMENTS. Table II gives a summary of the results for the experiments involving the "basic" solute, tetramethylammonium chloride, in thionyl chloride solution.

TABLE II

EXCHANGE BETWEEN THIONYL CHLORIDE AND TETRAMETHYLMONIUM CHLORIDE

No.	Millimoles SOCl_2	Millimoles TMAC	Time min.	Sp Act's SOCl_2	c/m/mg TMAC ^a	Temp °C	% Exch
1	20	0.431	61	6.48	6.81	25	99.8
2	20	0.235	48	3.08	2.95	25	100.5
3	20	0.326	39	4.76	4.77	25	99.9
4	20	0.336	91	4.87	5.12	0	99.9
5	20	0.341	78	4.49	4.52	0	99.9

^a Calculations showed that the recovery of the activity was well within the expected limits, based on the initial TMAC specific activity of 302 c/m/mgm.

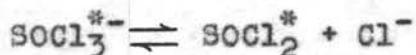
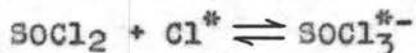
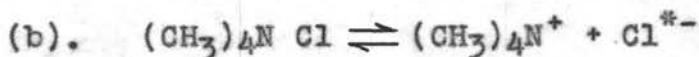
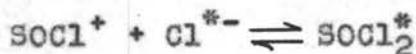
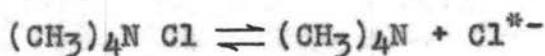
From the last column in the table it may be seen that exchange is substantially complete in all cases. It is to be noted, however, that the "time" in column four refers to the total time from the point at which the thionyl chloride-tetramethylammonium chloride mixture was removed from the liquid nitrogen, warmed to the temperature at which the experiment was to be run, solution effected by shaking, and finally, until the thionyl chloride was all distilled off from the salt. Hence it can be concluded

that one hundred percent exchange must have been accomplished in a much shorter time than this. Thus there would be little exchange from the time the mixture was removed from the liquid nitrogen until the thionyl chloride started to melt (at -104°C), or more probably, until solution was essentially complete (ca. five minutes later). Also the exchange must have been complete before a large fraction of the thionyl chloride had been distilled from the salt solution. Taking this latter time as that when a quarter of the thionyl chloride had been distilled off, one may considerably lower the estimated time for the complete exchange. Specifically this time would be about fourteen minutes for the 0°C runs and about seven minutes for the 25°C runs.

Since the specific activity of the TMAC was only moderate and its solubility in thionyl chloride was low, (in the early experiments it was found that the maximum amount of TMAC readily soluble in thionyl chloride is about 40 mgm/ml of solution), it was not feasible to shorten the time of the experiments significantly.

The conclusion seems clear that there is a rapid acid-base type interaction between solute and solvent. As in the case of Master's observations (12, pp.23-29), a certain amount of ambiguity exists as to the exact type of interactions which may be involved. There appear to be

two obvious possibilities.



Clearly, further work will be necessary to establish which of these is the more likely. For example, an isotopic sulfur exchange experiment between thionyl chloride and thionyl bromide might be illuminating in this connection. Such an exchange would presumably, in the absence of added halide, occur rapidly only if the SOX^- ion were formed.

The result of this experiment is of considerable interest in view of Huston's (9) finding, in his isotopic exchange study involving the acid solute aluminum chloride, that liquid phosgene played the role of an "inert" solvent, exchanging only slowly with the solute. Unfortunately, because of low solubility, he was not able to study an exchange involving a phosgene solution of a basic chloride; however, basic (ionic) chlorides dissolved in an aluminum chloride solution in phosgene showed no rapid exchange. Thus it seems that the behavior of thionyl chloride in the

present instance is markedly different from that of phosgene. In view of this conclusion, it seemed all the more interesting to find what the exchange behavior of a dissolved acid chloride, such as antimony trichloride, would be.

B. THIONYL CHLORIDE-ANTIMONY TRICHLORIDE EXPERIMENTS. The results of the labeled thionyl chloride-antimony trichloride experiments are summarized in Table III. It is evident that in this case, too, the exchange is substantially complete.

TABLE III
EXCHANGE BETWEEN THIONYL CHLORIDE
AND ANTIMONY TRICHLORIDE

No.	Millimoles SOCl_2	SbCl_3	Time min	Sp Act's SOCl_2^a	c/m/mg SbCl_3	Temp °C	% Exch
1	45.2	0.287	73	5.35	5.18	25	96.9
2	45.2	0.575	37	5.35	5.14	0	96.2
3	45.2	0.412	37	5.35	5.31	0	98.2

^a Initial specific activity, essentially constant because of large excess of solvent used.

A little comment is in order relative to the percent exchange figures recorded in the table, which, it will be noticed, do not approximate so closely one hundred percent as those given either in Table II or Table IV. This difference is related to the fact that in these two latter cases the salt was initially labeled, and this led to the

methods of calculation outlined in Section II, from which values of $(1-F)$ were calculated directly. Only a fair accuracy in these values leads, of course, to high accuracy in the F value when F is close to one. In the present instance, however, with the solvent initially labeled, the calculation yields F directly, with a somewhat reduced accuracy.

What was said regarding the recorded "time" in the preceding experiment can be repeated here; i.e., it is evident that the exchange must have been essentially completed between the time the thionyl chloride began to melt and the time about a fourth of the thionyl chloride was distilled off of the antimony trichloride. These times are estimated specifically as about thirty-five minutes for run 1 and about eighteen minutes for numbers 2 and 3.

It is evident that experiments of considerably shorter duration would be desirable in order to be able to obtain a better idea of just how rapid this exchange really is. The most obvious way to do this would be to use initially labeled salt rather than solvent (as was used here), and to withdraw a quick vapor sample from the solution in as short a time as possible. Although it was not done, such a procedure might possibly have been followed in the runs discussed in the preceding section; in those to be discussed in the next section, despite the use of labeled

solute, the procedure would not have been successful because of the low solubility of solute and the consequently small amount of activity introduced into the solution. In general, probably, considerably higher specific activity chlorine-36 would be necessary for a worthwhile application of such a technique than was available in these experiments. In this connection it may be mentioned that the amount of antimony trichloride readily soluble in thionyl chloride at 0°C was observed to be about 15 mgm/ml.

In view of Huston's work with aluminum chloride in phosgene (9), discussed both in the Introduction and in connection with the previous experiments, it had been anticipated that this exchange might well have a measurably slow rate. The results fail to show this, however, one hundred percent exchange being obtained even at 0°C in eighteen minutes.

This result appears to give a clue to the more likely of the two alternative exchange paths discussed in Section A above. Since acceptance of a chloride ion rather than the production of one by ionization is a much more probable process for the acid antimony trichloride, it seems likely that the thionyl chloride must itself ionize to yield the ion SOCl^+ . Thus the present exchange would proceed via the equilibrium



Equivalence of the chlorides in the $SbCl_4^-$ would then lead to rapid randomization of the chlorine-36 activity.

The present result is also of interest from another point of view. Masters (12, p. 29), in the course of his investigation of the catalyzed exchange of isotopic sulfur between sulfur dioxide and thionyl chloride, has shown that, whereas the two basic chlorides, tetramethylammonium chloride and rubidium chloride, have a pronounced catalytic effect, the two acid materials, aluminum chloride and hydrogen chloride, are essentially without effect. It seems evident, therefore, that the rapid chloride exchange observed in this work with both an acid and a basic chloride must proceed via a mechanism distinct from the rate-determining step in Masters' sulfur exchange process.

In summary, it may be said, independently of whether or not the foregoing schemes are valid, that the results of these two sets of experiments do clearly indicate that, unlike phosgene, thionyl chloride is not an "inert" solvent but enters into rapid, reversible acid-base equilibria with its solutes.

C. PHOSPHORUS OXYCHLORIDE-TETRAMETHYLAMMONIUM CHLORIDE EXPERIMENTS. The results of the experiments with the ionic salt tetramethylammonium chloride and the solvent phosphorus oxychloride are tabulated in Table IV.

TABLE IV
EXCHANGE BETWEEN PHOSPHORUS OXYCHLORIDE
AND TETRAMETHYLMONIUM CHLORIDE

No.	Millimoles POCl_3	Millimoles TMAC	Time min	Sp Act's POCl_3	c/m/mg TMAC ^a	Temp °C	% Exch
1	109	0.104	85	0.319	0.423	35	100.0
2	109	0.093	105	0.191	0.374	25	100.0

^a Initial specific activity of the TMAC was 302 c/m/mgm.

Here again it may be seen that complete exchange has occurred. With reference to the apparent lack of accordance in the recovered specific activities, it should be noted that this is related to their low absolute magnitude, which in turn results from the low solubility of solute in this solvent (only about 1 mgm/ml conveniently soluble). As indicated in the experimental section, it was necessary to calculate the percentage exchange by comparing the final with the initial salt specific activity. Consideration of the solvent and solute activities was useful in showing that in both experiments substantially complete recovery of total activity was effected, within the accuracy of these low values.

As in the previous experiments, an estimate of a time for complete exchange may be made which is considerably lower than the figures given in the table. Such a figure, again corresponding to the interval from the time of

thawing of the solvent to the time when about one quarter had been distilled off, would be about twenty minutes in either of these two experiments.

Phosphorus oxychloride, like thionyl chloride, is a potential non-aqueous ionizing solvent which as yet has not been extensively investigated, phosgene and selenium oxychloride being the only two acid chloride materials so studied. However, Audrieth and Kleinberg (1, p. 234) suggest that the phosphorus compound would be of real interest for further investigation in view of its general properties. As was indicated in the Introduction, for example, it is reported to be a relatively good solvent for inorganic substances, although only qualitative data are available. (In view of this report, it is presumably coincidental that the one salt chosen to investigate in the present work showed a very low solubility.)

It was because of the potentialities of this solvent that the two exploratory experiments here reported were done. Again it is found that the solvent is, unlike phosgene, not inert, but enters into a rapid ionic interaction with a basic chloride solute. Further isotopic experiments would clearly be of interest; in particular, exchange experiments involving acid chlorides would be illuminating. Such work would perhaps be helpful in showing whether the exchange here observed goes via loss

or gain of a chloride ion; that is, whether the ion POCl_2^+ or possibly POCl_4^- is involved. In any case it seems apparent that, as suggested by Audrieth and Kleinberg (1, p. 234), a more extensive general investigation of this solvent would be fruitful.

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