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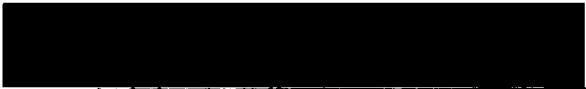
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(Name)   (Degree)   (Major)

Date thesis is presented ___December 11, 1963___

Title _____RADIOCHLORINE EXCHANGE REACTIONS_____

_____WITH SULFURYL CHLORIDE_____

Abstract approved ████████████████████_____
                      (Major professor)

As part of a continuing study of sulfur containing non-aqueous solvents, the present investigation was undertaken in an effort to obtain a better understanding of the solvent sulfuryl chloride. The primary object of the investigation involved a study of the rate of radiochlorine exchange between sulfuryl and thionyl chloride in mixtures of the two, the radioisotopic tracer chlorine-36 being used. The principal motivation for such experiments rested in the hope of being able to find some evidence relative to the possible significance of an ionic dissociation process for sulfuryl chloride. The system was of particular interest in presenting analogies to at least two related types of systems previously studied, namely the thionyl chloride-thionyl bromide system (where rapid radiosulfur exchange was observed) and the thionyl chloride-sulfur monochloride system (where negligible radiochlorine exchange occurred). The system

was further of interest in the light of the previous observation of a rapid chlorine exchange between sulfuryl chloride and the solute pyridinium chloride (in chloroform solution). Another point of some pertinence related to the fact that earlier research had shown that, between these two substances, little if any radiosulfur exchange occurred, and the suggestion had been made that a rapid radiochlorine exchange might result if the two substances interacted in an acid-base type of ionization equilibrium, thionyl chloride acting as a basic, chloride ion donor.

It was found in this work that radiochlorine exchange between thionyl chloride and sulfuryl chloride was, at best, very slow, with an exchange half time, t 1/2, of at least 35 days or more. The rate of the exchange did not appear to vary greatly, at least in apparent order of magnitude, over the concentration range from a five fold excess of sulfuryl chloride to a two fold excess of thionyl chloride, the value of the order of magnitude at 25°C being 10^{-1} g-atoms 1^{-1}day^{-1}. The obtaining of precise rate data was, however, hampered both by the extreme slowness of the reaction and by the considerable difficulty in a clean cut reactant separation at the end of each experiment, a factor which resulted in a large and rather irreproducible apparent zero time exchange.

A single experiment was done investigating the radiochloride exchange between sulfuryl chloride and the initially labeled solute

tetramethylammonium chloride. Despite incomplete solution of the salt in the solvent, 84% exchange occurred in the time of the experiment (14.75 hours). It appears most likely that, if solution had been complete, exchange would also have been complete within the period of the experiment, and in all probability in a far shorter time, probably less than an hour.

The results are taken to imply that sulfuryl chloride neither undergoes any significant chloride ion dissociation, nor any acid-base ionic interaction with thionyl chloride. They further suggest that exchange of the solvent with ionic chloride solutes probably occurs via either a rapid association equilibrium or a bimolecular equilibrium. The results demonstrate the hazard of a too indiscriminate application of the solvent systems interpretation of chemical phenomena in non-aqueous systems. Many processes can be better understood in less restricted terms, Lewis acid-base concepts, for example, being particularly useful. Further investigations of sulfuryl chloride exchange reactions, particularly with other basic and some acidic solutes appear most inviting.

RADIOCHLORINE EXCHANGE REACTIONS
WITH SULFURYL CHLORIDE
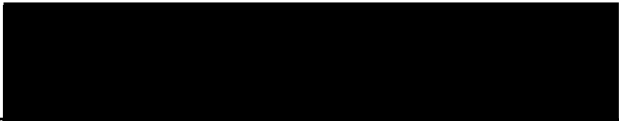
by

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in partial fulfillment of
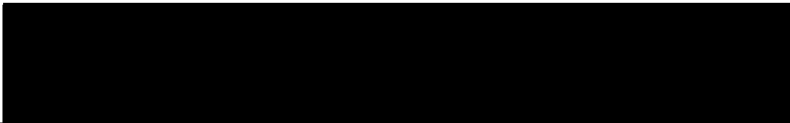the requirements for the
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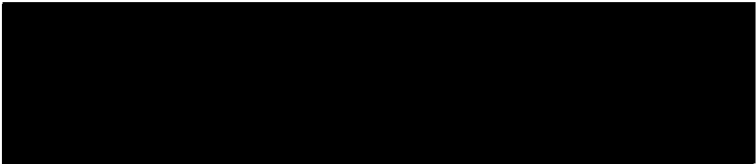
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ACKNOWLEDGMENT

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RADIOCHLORINE EXCHANGE REACTIONS
WITH SULFURYL CHLORIDE

I. INTRODUCTION

The field of non-aqueous solvent systems and their reactions
has seen much activity in recent years. Especially in reference to
non-protonic solvents attempts have been made to extend the concepts
of the Solvent Systems theory of acids, bases and salts to cover reac-
tions in such solvents as selenium oxychloride, dinitrogen tetroxide,
nitrosyl chloride, phosphorus oxychloride, sulfur dioxide, thionyl
chloride and sulfuryl chloride (1, 7, 11, 12, 15, 16, 17, 33, 34).

In this Laboratory and others, investigations with isotopic
tracers have been continued over a number of years to try to elucidate
some of the reactions occurring in liquid sulfur dioxide and related
sulfur containing solvents.

It has been found (20, 21) that the sulfur exchange rate between
thionyl halides and sulfur dioxide is negligibly slow. However,
Masters (26, p. 23-29, 28) found that thionyl chloride exchanges
radiochlorine rapidly with the basic solute tetramethylammonium
chloride in solvent sulfur dioxide. Masters, et al. and Potter (28, 31)
found this exchange also to be rapid in the absence of sulfur dioxide.
They further found that the radiochlorine exchange was rapid between
the acidic solute antimony trichloride and solvent thionyl chloride.
Subsequently Johnson (18, 19) found that thionyl chloride and thionyl

bromide exchange sulfur very rapidly in solvent sulfur dioxide and

rapidly though slightly less so, dissolved in each other in the absence

of sulfur dioxide. These experiments would seem to indicate that the

thionyl halides either pure or dissolved in liquid sulfur dioxide, ionize

according to the equation

$$SOX_2 \rightleftharpoons SOX^+ + X^- \qquad (X = Cl \text{ or } Br) \qquad (1)$$
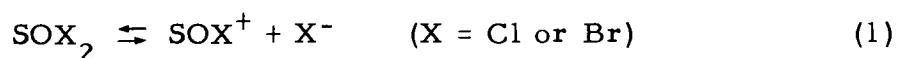
However, the ionization of thionyl halides in sulfur dioxide according

to

$$SOX_2 \rightleftharpoons SO^{++} + 2X^- \qquad (X = Cl \text{ or } Br) \qquad (2)$$
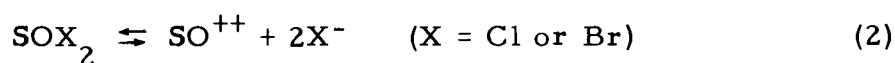
as proposed by Jander (15, p. 210; 17) seems very unlikely.

It might be noted here that further work has also shown that

a rapid sulfur exchange between sulfur dioxide and thionyl halides

can be initiated by addition of certain halide catalysts. Herber (13)

observed this in the thionyl bromide-sulfur dioxide system with the

basic, ionic halides, tetramethylammonium bromide, cesium brom-

ide, rubidium bromide or rubidium chloride. In the thionyl chloride-

sulfur dioxide system, Masters (26, 27) investigated the kinetics of

the tetramethylammonium chloride catalyzed sulfur exchange. Others

studied the acid catalyzed sulfur exchange between sulfur dioxide and

thionyl chloride (4, 26, 27), the mixed acid-base catalyzed exchange

(5) and the nonionic base catalyzed exchange (30).

In his research Johnson (18,19) also showed that the sulfur

exchange between thionyl chloride and sulfuryl chloride was almost

immeasurably slow. He suggested this to be further support for the

probable occurrence of an ionization mechanism instead of a bimole-

cular mechanism for sulfur exchange in the thionyl chloride-thionyl

bromide system. He further postulated that a chloride exchange

between sulfuryl chloride and thionyl chloride might well be rapid

due to acid-base interaction between the two species, with thionyl

chloride, as a base, donating a chloride ion to sulfuryl chloride in

a rapid acid-base equilibrium. One of the main objects in the initia-

tion of the present experiments was the testing of this hypothesis.

Despite the interpretation of the foregoing exchange experi-

ments as indicating the probable ionization of thionyl halides in

accordance with equation (1), it must be pointed out that an inherent

difficulty exists with such experiments so that their interpretation

is not completely unambiguous. Thus, a rapid radiochlorine (or

radiosulfur) exchange in systems of the type here involved does not

definitely indicate an ionic dissociation of the solvent, since exchange

can also occur via association of the solvent with either the solute or

ions from the solute. In a related system, for instance, Lewis and

Sowerby (24) found that radiochlorine exchange between phosphorus

oxychloride and tetraethylammonium chloride probably proceeds via

the formation and dissociation of the $POCl_4^-$ ion.

In further relationship to this point, Wiggle (37) found that the solvent sulfur monochloride exchanges radiochlorine rapidly with the acid solutes antimony tri- and penta-chlorides, as well as with the ionic, basic tetraethylammonium chloride. He infers that the acidic solutes are strong chloride acceptors and promote ionization of the solvent. On the other hand he believes that exchange with the ionic tetraethylammonium chloride goes via a bimolecular or association equilibrium. Supporting this thesis is the lack of radiochlorine exchange observed between the sulfur monochloride and the solute thionyl chloride. Wiggle considered this to be due to the fact that thionyl chloride is neither a strong chloride ion acceptor nor donor and therefore does not promote ionization of the sulfur monochloride. This latter effect is in line with the explanation (involving $POCl_4^-$ formation) proposed by Lewis and Sowerby (23) for the slow radiochlorine exchange between the solvent nitrosyl chloride and solute phosphorus oxychloride, on the basis of which these workers estimated the ion product for nitrosyl chloride to be 10^{-16} g-ion^{2}l^{-2}. This is despite the fact that both nitrosyl chloride and phosphorus oxychloride exchange radiochlorine rapidly with certain other solutes (23, 24).

As one may see, the results of research of the type described tends to show that, while the concept certainly has some merit, the Solvent Systems interpretation of phenomena occurring in non-aqueous, non-protonic solvents must be applied with considerable reservation. To distinguish between an association or a dissociation ionic process, for example, is quite difficult and considerable data must be accumulated about the reactions in a given system before a decision can be made.

The present work was undertaken in order to better understand the reactions in the solvent, sulfuryl chloride, a solvent system related to others investigated previously in this Laboratory (4, 5, 13, 18, 17, 19, 20, 21, 23, 24, 25, 26, 27, 28, 29, 30, 31, 34, 37).

Previous radioisotopic exchanges involving sulfuryl chloride are not numerous. Johnson (18, 19) found little if any radiosulfur exchange between thionyl chloride and sulfuryl chloride. Frazer (8) found that both thionyl chloride and sulfuryl chloride exchanged rapidly with the basic pyridinium chloride in the inactive solvent chloroform. The present research involved an investigation of the radiochlorine exchange between sulfuryl chloride and thionyl chloride in four concentration ranges. These ranges were: (1) five-fold mole ratio excess sulfuryl chloride, (2) equimolar sulfuryl and thionyl chlorides and (3), (4) excess thionyl chloride, both at a

five-fold and at a two-fold mole ratio excess. A survey experiment

was also done to investigate the possible radiochlorine exchange

between sulfuryl chloride and tetramethylammonium chloride.

II. EXPERIMENTAL

A. GENERAL

The work was in general carried out in a vacuum system of standard design, utilizing a mercury diffusion pump with a liquid nitrogen cold trap, and a mechanical backing pump. Pressures were measured with a mercury manometer or a McLeod gauge. Pressures of 10^{-5} mm Hg or less could be obtained.

The exposure of both the sulfuryl chloride and thionyl chloride to mercury was minimized. Stopcocks were lubricated with Halocarbon[1] regular or high temperature, and Apiezon "N" or "T" greases, the Halocarbon high temperature and Apiezon "T" being used in hot weather. The Halocarbon greases were used in the dosing system and other places where contact with sulfuryl or thionyl chlorides could occur. These greases tended to be displaced somewhat through the system by both solvent vapors, but no reaction appeared to take place. The Apiezon greases were used on all other greased joints and stopcocks.

The system was evacuated to 10^{-5} mm Hg and then pumped on for at least four hours before any dosing operations. This minimized

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[1] Halocarbon is the trade-name for a lubricant consisting of a mixture of chloro- and fluorocarbons. It is available from Halocarbon Products Corp., Hackensack, N.J.

amounts of water vapor left in the system.

The reaction temperatures were maintained by immersion of the reaction bombs in thermostatted water baths, a large Dewar flask being employed for most of the experiments, using a mercury regulator and electronic relay capable of regulating the water temperature to ±0.05°C. The controller temperature was originally set with a National Bureau of Standards calibrated thermometer and then continuously checked with a similar uncalibrated thermometer, graduated to 0.1°C. All reaction bombs were kept frozen in liquid nitrogen after dosing, until reaction initiation was desired.

B. RADIOACTIVITY ASSAY

The tracer isotope used in this work was chlorine-36, obtained from the Oak Ridge National Laboratory in the form of labeled hydrochloric acid solution. This isotope has a half-life of 3.2×10^5 years. It emits a negative beta particle with a maximum energy of 0.714 Mev. (35). All specific activities were calculated as cpm/mg (counts per minute per milligram) of mercurous chloride.

The samples were counted as thin layers of mercurous chloride, approximately 2-8 mg/cm^2, deposited on stainless steel planchets from an absolute ethanol slurry and dried under an infrared lamp. Self-absorbtion corrections were made when necessary from

an empirically determined curve[1]. Counting time was long enough to collect sufficient counts to minimize statistical error, giving in most cases a calculated standard deviation of less than 2% (9, Chap. 9), and duplicate planchets were prepared from all samples.

The counting equipment consisted of a thin end window Geiger counter tube (Tracerlab TGC-2, window thickness less than 2 mg/cm^2). The pulses were fed to a pre-set time decimal scaler (Berkeley Model 1000 B). All sample rates were corrected for background and, when necessary in one case, for a small coincidence loss[2].

C. CHEMICAL ANALYSIS

Since the selective hydrolysis reactant separation procedure used in this research gave only rather incomplete separation, it was desirable to have a means of checking on the completeness of the process. This was achieved by carrying out chloride analyses of the two separated fractions, viz. the "thionyl chloride" and the "sulfuryl chloride" fraction. In each case an exactly known portion of the chloride in that fraction was precipitated for radioassay and the residual chloride in the filtrate from the fraction was then analytically deter-mined. The total chloride in the fraction was then taken as the sum of that precipated plus that found by analysis. The results of these

[1] Prepared by B. J. Masters in this Laboratory.

[2] Correction was made on the basis of counter resolving time measurements previously made in this Laboratory.

analyses are presented in the tabulations of the exchange data. They were used both for assessing the effectiveness of the separation procedure in a particular case as well as for monitoring the completeness of recovery of radioactivity in each experiment. They were not, however, employed in the actual calculation of the fraction exchange values, F, recorded in the data tabulations.

The analysis for chloride was done by means of a potentiometric titration with silver nitrate. The indicator electrode was silver-silver chloride and the reference electrode was mercury-mercurous sulfate, used in conjunction with a Beckman Model H pH meter. Analysis of standards treated the same as the samples showed the endpoint to occur at 150 mv with this system.

Prior to the potentiometric analysis of the "sulfuryl chloride" and "thionyl chloride" fractions after an exchange experiment, and separation by selective hydrolysis, .505 millimoles of standardized mercurous nitrate were added to each fraction to precipitate mercurous chloride for radioassay. The solution was then filtered through a sintered glass crucible and washed with a minimum amount of water. The precipitate was then prepared for counting as described in section B, above.

The total filtrate, plus washings, was then analyzed potentiometrically for contained chloride. The analyses values were reported

as the sum of the chloride value determined potentiometrically plus

the 0.505 millimole removed as mercurous chloride, divided by two

to obtain millimoles of "sulfuryl" or "thionyl chloride".

The sulfur analysis was done only to check the purity of sul-

furyl chloride. After hydrolysis of a known weight of this material

in dilute sodium hydroxide, barium sulfate was precipitated from

the slightly acidified solution. This was then determined gravimetri-

cally after digestion and filtering onto a tared sintered glass crucible.

D. PREPARATION OF MATERIALS

1. THIONYL CHLORIDE, $SOCl_2$. The commerically avail-

able material (British Drug House, iodometric assay 97-103%), was

purified by a method essentially that of Cottel (6, 27, p. 21), using

a modified apparatus. A sample, approximately 150 milliliters, of

the impure thionyl chloride was sealed into the still bottom of a

glass-packed fractionation column about 38 inches long, along with

five grams flowers of sulfur. This mixture was agitated with a mag-

netic stirring bar and refluxed for five hours at atmospheric pres-

sure, the lower end of the column being cooled with water circulated

through a water jacket. Before being filled, the apparatus had been

flushed for twelve hours with thoroughly dried air, and was again

briefly flushed with dry air after filling. During reflux and both

subsequent distillations, the only contact from the interior of the column to the atmosphere was through a tube containing both Ascarite and calcium chloride. The reflux heat was provided by an oil bath held at 84° C. by means of a mercury regulator. (The b. p. of thionyl chloride is 75. 4°C.) (22, p. 101). About two thirds of the thionyl chloride was then distilled rapidly, at atmospheric pressure, through the glass-packed column into a second still pot by raising the bath temperature to about 89°C. and circulating warm water through the water jacket surrounding the lower end of the column. About 100 milliliters of product (slightly yellow) were collected, the residue remaining behind. This product was then carefully fractionated, still at atmospheric pressure, through a second glass packed column (length, 33 inches) using a 9:1 reflux ratio, 20 milliliters of slightly yellow forerun being discarded. Then 70 milliliters of water-clear product was distilled into two storage ampoules fitted with break-tips, at a 3:1 reflux ratio, about 10 milliliters residue being left behind. The product in one of the ampoules was frozen with a dry ice-chloroform bath and the receiver sealed off (the other ampoule being lost through breakage in an attempt at a similar operation). The storage ampoule was stored in a dark cupboard until time for fractionation of the contents in vacuo.

This fractionation was done by sealing the ampoule onto the vacuum system, freezing the contents with liquid nitrogen, breaking the break-tip, and pumping to a high vacuum. The contents were allowed to thaw and then distilled into a second receiver, refrozen and reevacuated. This procedure eliminated permanent gases. The vacuum fractionation then done involved discarding the first one fourth of the distillate and collecting two thirds of the remainder in four small, sealed break-tip ampoules. The product in the first three of these was water-clear and remained so (the ampoules being stored in the dark) until used in the experiments, a period lasting up to about two months. The fourth and last ampoule, containing much less product than any of the other three, was reserved for analysis for impurities by gas chromatography (30, p. 23 and 52). The contents of this ampoule showed a faint yellow tinge initially, which became slightly more pronounced by the time it was analyzed, about two weeks following purification. (This ampoule may have been exposed to more light than the three used in the actual experiments). Nevertheless gas chromatographic analysis showed less than 5% sulfur dioxide and less than 0.5% other undetermined impurities.[1]

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[1] Analyzed by N. D. Potter of this Laboratory.

2. LABELED TETRAMETHYLAMMONIUM CHLORIDE,

$(CH_3)_4NCl^*$. The method of preparation was essentially that of

Masters (26, p. 20) modified to use labeled hydrochloric acid instead

of the lower specific activity potassium chloride previously employed.

The hydrochloric acid solution was diluted from 0.4 $\underline{N}$ (as received

from Oak Ridge National Laboratory) to 0.1 $\underline{N}$ and treated with a

slight excess of 0.1 $\underline{N}$ silver nitrate, the labeled silver chloride

formed being digested on a hot plate, collected on a sintered glass

crucible and washed with water. This fresh silver chloride was then

shaken with a slight stochiometric deficiency of tetramethylammonium

bromide (Eastman White Label) in a Corning "Low Actinic" flask and

then left to metathesize for several days with periodic shaking. The

silver bromide and excess silver chloride were then removed by suc-

tion filtration and washed with water. The filtrate and washings were

then shaken, in a separatory funnel, with successive portions of chlo-

rine water and carbon tetrachloride until no further traces of bromine

coloration appeared and then evaporated to dryness on a steam bath.

Primarily the labeled tetramethylammonium chloride was

prepared for the purpose of subsequently preparing labeled thionyl

chloride, and highly pure tetramethylammonium chloride was not

needed for this purpose. Hence the crystals were finally simply

washed with acetone, dried at 110°C. and stored in an opaque

dessicator. This sample of tetramethylammonium chloride had a specific activity of about 19,000 cpm/mg as mercurous chloride, calculated on the basis of the original amount of labeled hydrochloric acid employed.

For the sulfuryl chloride-tetramethylammonium chloride exchange experiment, a sample of labeled hydrochloric acid was diluted with inactive hydrochloric acid, tetramethylammonium chloride was prepared as above, washed with acetone, recrystallized from absolute ethanol and washed with chloroform. The dried product was then dissolved in sufficient distilled water to give 100 milliliters of solution. Radioassay showed the specific activity to be 424 cpm/mg as mercurous chloride, and a potentiometric titration showed the solution to be 0.1975 $\underline{N}$ Cl⁻ or 21.63 mg tetramethylammonium chloride per milliliter. This solution made possible the precise measurement of a desired quantity of the salt for the exchange experiment, the dry salt then being obtained by evaporation of the water as described below.

3. LABELED THIONYL CHLORIDE, $SOCl_2$*. Labeled thionyl chloride was prepared through the rapid exchange between labeled tetramethylammonium chloride and thionyl chloride (28, 29, 31, p. 12). A convenient quantity of labeled tetramethylammonium chloride (above) was placed in a ground-joint equipped, test-tube-like

apparatus and, in this apparatus, thoroughly dried in an oven at

110°C. This apparatus was then quickly attached to the vacuum sys-

tem and evacuated. An ampoule of unlabeled thionyl chloride was

also sealed to the vacuum system. After the salt had been pumped

on at high vacuum for some time, the break-tip on the thionyl chlo-

ride ampoule was crushed and thirty millimoles were dosed onto the

tetramethylammonium chloride (see III B. Dosing). After the mix-

ture had been sealed off, it was allowed to thaw and then the solution

(the salt dissolved completely) was agitated for about 20 minutes at

room temperature. All of the now labeled thionyl chloride was then

distilled into a break-tip equipped storage ampoule, sealed and stored

in a dark cupboard until used. This labeled thionyl chloride appeared

absolutely colorless. Radiochemical assay of a subsequent thionyl

chloride-sulfuryl chloride exchange experiment indicated an apparent

initial thionyl chloride specific activity of about 104. 1 cpm/mg. This

figure was used as the basis for fraction exchange calculations in

about the first half of the experiments. About half way through the

experiments this stock was diluted with inactive thionyl chloride to

give material with a specific activity of 45. 4 cpm/mg as mercurous

chloride, as directly determined by radiochemical assay. This

diluted preparation was then used throughout the remaining experi-

ments.

4. SULFURYL CHLORIDE, SO_2Cl_2. The purification of sulfuryl chloride involved a simple fractionation in vacuo (10^{-5} mm Hg), without application of heat, of commercial (Eastman White Label) sulfuryl chloride. The first one fourth of the distillate was discarded and two thirds of the remainder was distilled into four break-tip equipped storage ampoules which were then sealed off from the vacuum system. In the first two of these ampoules the product was a slight yellow but in the last two it was water-clear. Unfortunately, because of breakage, it was necessary to use one of the discolored samples. However the colored material was found to be quite volatile, and was removed prior to dosing an experiment by evaporating and discarding a small portion of the sample. In all cases the material dosed into an exchange bomb was water-clear. Analysis of an ampoule whose contents were water-clear gave the results presented below.

Analysis showed: S, 24.19%; Cl, 48.46%; $d^{23.5}$, 1.695

Expected: S, 23.75%; Cl, 52.53%; $d^{23.5}$, 1.667

(36, p. 22).

III. RUN PROCEDURES

A. GENERAL

The bulk of the experiments involved in this research involved a study of the exchange between thionyl chloride and sulfuryl chloride. These experiments were all done in an identical manner. The desired amounts of the reactants were dosed into the reaction bombs, using procedures described in the following section. The bombs were made from about ten mm. o. d. Pyrex tubing fitted with short necks made from about six mm tubing. The bombs were frozen with liquid nitrogen and sealed off from the vacuum system. They were then stored in liquid nitrogen until initiation of exchange was desired. When an exchange experiment was to be started, the reaction bomb was thawed in cool water and placed in the thermostatically controlled bath (held at the desired temperature). When the predetermined exchange time had elapsed, the bomb was placed in a small amount of water in a small beaker and broken at a scored line near its tip. The two liquid layers were then separated for radioassay as described below.

A single experiment was done to investigate the exchange between sulfuryl chloride and dissolved tetramethylammonium chloride. Execution of this experiment was complicated by the quite limited solubility of the salt. Details of the procedure followed are given in the following section.

B. DOSING

In general, measured amounts of the reactants were condensed, in vacuo, into the reaction bombs by cooling the container with liquid nitrogen (32, 38).

Thionyl chloride was dosed as the liquid from a cold finger doser calibrated with mercury to contain a known volume. After filling the doser to approximately one third excess from the storage ampoule, the excess was distilled back to storage until the liquid level reached the desired calibration mark, the doser being kept at 0°C. with an ice-water bath. The material in the doser was then distilled into the reaction bomb. This procedure tended to remove any excessively volatile or non-volatile contaminants from the thionyl chloride.

Sulfuryl chloride was dosed in much the same manner, but instead of using a liquid nitrogen bath for freezing the storage ampoules as was done with thionyl chloride, a carbon disulfide slush (-110°C.) was used. This was done because several sulfuryl chloride storage ampoules were broken when frozen by liquid nitrogen. The reason for this breakage is not known, but is possibly due to an expansion of the sulfuryl chloride caused by a crystal phase change at very low temperatures. An alternative possibility could be a

contraction of sulfuryl chloride adhering to the walls of the ampoule.

Some small loss upon high vacuum pumping (10^{-5} mm Hg) occurred

at -110°C., but this loss was not of sufficient magnitude to lead to

any important depleting of the stock supply.

Tetramethylammonium chloride was added as the weighed

salt during the thionyl chloride activation experiment, and a known

volume of the stock solution of known concentration was quantitatively

pipetted into the reaction bomb and dried in an oven at 110°C. for use

in the sulfuryl chloride-tetramethylammonium chloride exchange

experiment.

C. SEPARATION

In the thionyl chloride-sulfuryl chloride exchange experiments,

reactant separation proved to be one of the most difficult procedures

involved. Since the vapor pressures of thionyl chloride and sul-

furyl chloride are quite close together (2, 3, 22, p. 113, 32, p. 148),

separation by fractional distillation in the vacuum system, a proce-

dure often employed in this type of work, was not feasible, so that

an alternative method was necessary. The procedure actually

employed involved a chemical separation utilizing the slower rate of

hydrolysis of sulfuryl as compared to thionyl chloride in water (18,

p. 34).

The tip of the reaction bomb was broken in a small beaker containing a few milliliters of water. After a few minutes the hydrolyzed aqueous thionyl chloride layer was removed from the heavier immiscible sulfuryl chloride layer with a medicine dropper. Each fraction was then dissolved in 1 $\underline{N}$ sodium hydroxide (the sulfuryl chloride hydrolyzing in this medium). These solutions were then made slightly acid with nitric acid, a portion of the chloride precipitated by addition of a known amount of mercurous nitrate, and the precipitated mercurous chloride filtered on sintered glass filters. The mercurous chloride was then counted in duplicate on stainless steel planchets as previously described. The excess chloride in the filtrate was subsequently determined potentiometrically as described elsewhere in this thesis.

It was found that this procedure left some thionyl chloride in the "sulfuryl chloride" fraction due to incomplete removal, and also often gave some of the chloride from sulfuryl chloride to the "thionyl chloride" fraction due to the slow but definite hydrolysis of the former. This gave an appreciable and not too reproducible apparent exchange at zero time, and led, in consequence, to a rather large scatter in the experimental data, an effect probably primarily responsible for limiting the precision of the results of this work. An indication of the extent of the irreproducibility here involved is to be

found in the analytical data for the separated reactant fractions recorded in the data tabulations in the presentation of exchange results.

In the case of the tetramethylammonium chloride-sulfuryl chloride exchange experiment, separation of sulfuryl chloride from the tetramethylammonium chloride was much simpler, with far less risk of cross contamination of the two fractions. The exchange was carried out in an H shaped apparatus as indicated below. After the exchange experiment, the sulfuryl chloride was distilled completely away from the leg containing the non-volatile salt through a fritted glass disc into the other leg which was cooled with liquid nitrogen. The connecting tube was then heated with a torch, sealed off and the two legs were separated from each other. Each tube was then broken open, its contents hydrolyzed and acidified, mercurous chloride was precipitated and planchets were prepared for counting.

D. SULFURYL CHLORIDE-TETRAMETHYLAMMONIUM CHLORIDE EXPERIMENT

The solubility of tetramethylammonium chloride (less than about .066 millimoles per 40 millimoles of sulfuryl chloride as determined by a preliminary experiment) is so low that in this experiment all of the dosed amount (0.395 millimoles) would not dissolve in the 40 millimoles of sulfuryl chloride used. The relatively low specific

activity of the tetramethylammonium chloride dictated that no greater

dilution would be practical if complete exchange were to occur and

the reactants then still to show a measurable activity. Because of

this difficulty the following procedure was used.

A special H-shaped bomb, fabricated from 10 mm glass tub-

ing, with the two legs separated by a sintered glass disc, was pre-

pared. The solution of tetramethylammonium chloride (labeled) was

quantitatively pipetted into one leg, A, evaporated to dryness and A

was sealed off at the top. The bomb was then attached to the vacuum

system and evacuated to a high vacuum $(10^{-5}$ mm Hg) and pumped on

overnight. Sulfuryl chloride was then dosed into the other leg, B,

and the bomb sealed off from the vacuum line. The sulfuryl chloride

was then distilled through the sintered glass disc onto the tetramethyl-

ammonium chloride by cooling leg A with liquid nitrogen.

On being warmed to room temperature, the sulfuryl chloride

would dissolve only part of the tetramethylammonium chloride.

After about 15 minutes agitation, the supernatant solution was

decanted into a small dogleg on A and then the sulfuryl chloride

distilled back to A by a slight warming of the dogleg (approximately

10°C. differential) a process taking somewhat less than an hour.

This procedure was repeated many times. Although all the tetra-

methylammonium chloride was never dissolved and transported to

to the small dogleg, after about 14 hours the experiment was terminated.

The sulfuryl chloride was distilled back through the fritted glass disc into leg B and the two legs sealed off and separated from each other. Solution had been indicated by the distinctly yellow color of the sulfuryl chloride after contact with the tetramethylammonium chloride.

After separation, leg A was broken and the tetramethylammonium chloride was washed out with distilled water and mercurous chloride was precipitated for radioassay. Leg B was broken and the contents were washed out and hydrolyzed with dilute sodium hydroxide, acidified and mercurous chloride was precipitated for radioassay.

IV. RESULTS

A. GENERAL

1. SULFURYL CHLORIDE-THIONYL CHLORIDE EXPERI-

MENTS. The exchange experiments between sulfuryl chloride and

thionyl chloride were divided into three groups. These were:

1. Experiments in excess sulfuryl chloride

2. Experiments in equimolar sulfuryl chloride-thionyl

   chloride mixtures

3. Experiments in excess thionyl chloride

All reactions were carried out at a temperature of 25.3 ±0.05°C.

except for some experiment in group 1 which was carried out at 39.8

±0.05°C. in an effort to determine any possible temperature effects.

Thionyl chloride was the initially labeled species in all these experi-

ments. Early experiments utilized short reaction periods, but when

results appeared somewhat erratic and ambiguous, much longer

exchange time experiments were initiated.

Calculations of the fraction exchange that occurred assumed

a simple two component system with complete separation of the two

fractions during hydrolysis. Since, in fact, the separation procedure

did not actually yield such a complete separation, some initially

active thionyl chloride being left in the initially inactive sulfuryl

chloride fraction, and vice versa, the fraction exchange thus calcu-
lated represents a maximum, and the true exchange would actually
be significantly lower in a particular case.

The fraction exchange, F, was determined by observing the
increase in the specific activity of the separated "sulfuryl chloride"
fraction compared to the specific activity expected if total exchange
had occurred:

$$F = \frac{A_b}{A_\infty}$$

where

$$A_\infty = \frac{(A_{oa})(a) + (A_{ob})(b)}{a + b}$$

but $A_{ob} = 0$, therefore

$$A_\infty = \frac{(A_{oa})(a)}{a + b}$$

The symbols are defined as follows:

A_{oa} = specific activity of the $SOCl_2$ at beginning of the
experiment

A_{ob} = specific activity of the SO_2Cl_2 at beginning of the
experiment

A_∞ = specific activity of both fractions if complete exchange
had occurred

A_b = specific activity at end of exchange time t, of SO_2Cl_2
fraction taken for radioassay

a = millimoles of $SOCl_2$ dosed

b = millimoles of SO_2Cl_2 dosed

2. SULFURYL CHLORIDE-TETRAMETHYLAMMONIUM

CHLORIDE EXPERIMENT. The single exchange experiment between

sulfuryl chloride and solute tetramethylammonium chloride was car-

ried out over a period of about 14 hours at room temperature. For

this experiment a slightly different method of calculation was used,

the exchange being followed by observation of the decrease in activity

of the initially active salt, instead of the increase in activity of the

initially inactive sulfuryl chloride. The symbols used are similar to

those above, (b) referring to the sulfuryl chloride (initially inactive),

but (a) referring to the tetramethylammonium chloride (initially

active). Also

A_a = specific activity at end of exchange time, t, of the tetramethylammonium chloride taken for radioassay

$$F = \frac{A_b}{A_\infty}$$

where

$$A_\infty = \frac{(A_{oa})(a)}{(a + b)}$$

and

$$A_b = \frac{(A_{oa} - A_a)(a)}{b}$$

Combining the equations above gives the equation actually used in

calculating the fraction exchange

$$F = \frac{(A_{oa} - A_a)(a/b + 1)}{A_{oa}}$$

B. DATA

1. EXCESS SULFURYL CHLORIDE-THIONYL CHLORIDE

EXPERIMENTS. In these experiments a five fold excess of inactive

sulfuryl chloride was dosed into an exchange bomb along with the

labeled thionyl chloride. Initial experiments were done with exchange

times of 15 minutes and 30 minutes. The results appeared to suggest

a fairly rapid but measurable rate of exchange, so exchanges of more

extended lengths of time were done, as were two zero time exchanges.

It was then found that the exchange rate was in fact far slower than

had originally appeared, poor separation of the sulfuryl chloride and

thionyl chloride fractions having led to appreciable apparent zero

time exchanges. Also included in this group was the one experiment

done at 39. 8 ± 0. 05°C. in an attempt to determine the dependence of

exchange rate upon temperature. It turned out, however, that the

temperature differential and general experimental accuracy of the

data were too low to find any significant effect in this case.

The results of these experiments are presented in Table I.

Also included in this table are the analytical data previously described

for the total apparent millimole content of each of the separated reac-

tant fractions, data based on the total chloride content of each of the

fractions. The data are important in giving an indication of the

reactant separation success in a particular case, an indication of value in the weighing of the significance of a particular exchange result. The fraction exchange, F, is shown for each experiment in the next to the last column in the table. It may be seen that the data show a good deal of scatter, but do allow of some definite conclusions. In no case, even in 480 hours, does anything even approaching complete exchange appear. On the contrary the evidence, in a rough way, is that a more or less comparable amount of apparent exchange is to be observed, irrespective of the exchange time. Clearly a very large separation error occurred in all cases, but the actual exchange rate, if in evidence at all, was exceedingly slow.

Examination of the results of the individual experiments tabulated in Table I shows that, in general, the apparent exchange is more or less in the vicinity of 30%, the 0.5, 240 and 480 hour experiments showing the greatest deviation from this figure. The 0.5 hour experiment was done early in this work, and the fact that manipulative technique was poor may explain the high results. However, in both of the longer term experiments the separations seemed to proceed quite smoothly. The results for the 240 hour experiment show the smallest apparent exchange in the group, an observation probably to be traced to a significantly smaller separation error in this case, a conclusion supported by the recorded analytical results which show

that, in this case, the hydrolysis proceeded the furthest of that in any of these experiments. In contrast, the 480 hour experiment shows an exchange that is at least 15% higher than would be expected on the basis of the 240 hour experiment, even if the observed result in that case had represented a true exchange with no separation error at all (which can scarcely be the case). This result may possibly be explained by the observation that, in the 480 hour experiment, the sulfuryl chloride fraction gave an unusually high analysis, with the thionyl chloride fraction, conversely, showing a low analysis. Such results, indicating very likely some contamination of the former reactant in its separated fraction by the latter, due to insufficient hydrolysis, would appear consistent with an unduly high apparent exchange in this instance.

It is well known that an isotopic exchange reaction in a stable system follows a first order rate law in accordance with the McKay relationship

$$R = - \frac{2.303 \, ab}{(a + b)} \frac{d \log (1-F)}{dt} \tag{3}$$

where a and b represent the concentrations (active plus inactive atoms) of the element undergoing exchange (chlorine, in this case) in each of the two reactants, respectively. R is the exchange rate, constant in a given stable system. F is the fraction exchange observed at time, t, counting from zero time. It may be shown that

this equation remains valid whether F represents a true exchange, or an apparent exchange, inflated through a separation error, so long as this separation error remains reproducible over a series of experiments. Thus, even though there may be a significant apparent zero time exchange, a plot of log (1-F) versus time should give a straight line, from the slope of which one should be able to calculate the exchange rate according to the foregoing equation.

As an alternative device for expressing the exchange rate, one may employ the exchange half-time, the time for (1-F), whatever its initial value, to decrease by one half. This quantity may be obtained from the relationship

$$t_{1/2} = - \frac{.3010}{d \log (1-F)/dt} \tag{4}$$

The data of Table I have been treated in accordance with equation (3) in an effort to arrive at some possible quantitative indication either of the actual exchange rate, or some maximum value for it. A plot of the data as log (1-F) versus time shows a good deal of scatter (presumably mainly related to a variable separation error), but does suggest a slight progressing exchange. The data have been subjected to a least squares treatment which yields an apparent slope, d log (1-F)/dt, of $-(2.10 \pm 6.73) \times 10^{-4}$ hour^{-1}. From the densities at 25°C. of sulfuryl and the thionyl chlorides, respectively, of 1.6645 and 1.628 g/ml (36, p. 22) one may calculate average concentrations

of chlorine in the two respective reactants in the Table I experiments

of 21.1 and 3.91 g-atoms l^{-1}. Combination of these concentrations,

together with the observed slope, leads to calculated exchange rate

of $(3.93 \pm 12.58) \times 10^{-2}$ g-atom l^{-1} day^{-1}, corresponding to an exchange

half time of 59.7 days.

The quoted uncertainties in the above figures represent com-

puted standard deviations derived from the least squares treatment.

Clearly they suggest a very significant uncertainty in the data, and

suggest that on the one hand, the results give no very certain indica-

tion that any definite exchange rate at all has been observed, and on

the other, that the rate may possibly be significantly greater than

the recorded value. In either case, however, the data do clearly

demonstrate that, at best, the exchange is exceedingly slow.

An alternative device for arriving at least at an upper limit

for the exchange rate is available in that one may concentrate on a

long term experiment showing minimum exchange, the minimum

exchange presumably reflecting a minimum separation error and

hence a maximum approach to a true exchange representation. An

exchange rate calculated from such an experiment, assuming no sep-

aration error to have occurred, and therefore F at zero time to

have been zero (i.e. a rate calculated from the log (1-F) versus time

slope defined by the origin and the F value for that experiment) will

lead to an estimate of the maximum value for the exchange rate consistent with the data. In the Table I data, the 240 hour experiment provides the basis for this type of treatment and the resulting indicated maximum rate is 6.5×10^{-2} g-atom l^{-1} day^{-1}, corresponding to a minimum half time of 36 days. These figures are generally consistent with those recorded above and serve, once more, to confirm the exceeding slowness of the exchange.

2. EQUIMOLAR SULFURYL CHLORIDE-THIONYL CHLORIDE

EXPERIMENT. In these experiments, recorded in Table II, the apparent exchange appeared quite low in the initial pair of short reaction time experiments (15 minutes and 30 minutes), suggesting a much smaller separation error than in the first group of experiments. A second pair of experiments, with significantly longer reaction periods confirmed this view and further showed that, here, as in excess sulfuryl chloride, no rapid exchange was occurring. As can be seen in Table II, in all the first four experiments, the apparent exchange is at a low and consistent level in the vicinity of 13%. Only in the two long term experiments does a clear suggestion appear of a progressing exchange. In this connection, it may be noted that, in contrast to the situation with the analogous long term experiment in Table I, the 35% apparent exchange in the 480 hour experiment cannot be rationalized as being high due to any unduly poor separation in this particular

case, as the analytical results for this experiment are quite similar

to these for the other experiments in the series.

A good deal less manipulative difficulty was experienced in the

carrying out of the separation procedure in these equimolar experi-

ments than in either those of group 1 or group 3. This fact finds its

reflection in the greater consistency of the analytical results recorded

in Table II as contrasted with those for either of the other two groups.

On the basis of this circumstance, a good deal more confidence may

be placed in the quantitative significance of the exchange results in

this group and it seems likely that the apparent trend of increasing

exchange with time is probably valid. The data have been treated in

accordance with the same procedure as that described above for group

1. The least squares treatment of the log (1-F) versus time data

yield a slope, d log (1-F)/dt, of $-(2.76 \pm .36) \times 10^{-4} hr.^{-1}$. The cal-

culated average concentrations of chlorine in sulfuryl and thionyl chlo-

rides are, respectively, 13.36 and 12.54 g-atoms 1^{-1}, and the result-

ing calculated apparent exchange rate is $(9.84 \pm 1.30) \times 10^{-2}$ g-atoms

$1^{-1} day^{-1}$, corresponding to an exchange half-time of 45.5 days.

The quoted calculated standard deviations are evidently a good

deal less than was the case in the first group of experiments, a point

consistent with the above suggested greater reliability of the present

set of data, and suggestive that the rate and half-time here recorded

are deserving of a reasonable measure of confidence in a quantitative sense. It is therefore of particular interest to find the indicated rate again very slow and not too greatly different from that indicated in the first group of experiments.

As in the first group, an estimate has also been made of the maximum indicated exchange rate on the basis of the most limiting experiments, in this case the two long term ones, assuming that, as a limit, no separation error occurred in these cases. The maximum rate so calculated was 13.15×10^{-2} g-atoms l^{-1}day^{-1}, corresponding to a minimum half-time of 34 days. Such data are again consistent with the picture of an exceedingly slow exchange.

3. SULFURYL CHLORIDE-EXCESS THIONYL CHLORIDE EXPERIMENTS. The experiments in excess thionyl chloride are given in Table III. In this group of experiments in the early, short reaction time exchanges (15 and 30 minutes), thionyl chloride was in a five-fold excess. However, due to a shortage of labeled thionyl chloride, in the later, extended exchange period experiments only a two-fold excess of thionyl chloride was used. While the first experiment appeared to show essentially complete exchange in 15 minutes, this result was not supported by the remaining experiments and must be discounted as due to experimental error.

Overall, the experiments again show, as in the other two groups, an exchange at best exceedingly slow, the smallest apparent exchange actually being displayed by the longest time experiment (32.7% exchange in 480 hours). The obviously large zero time exchange certainly relates to a large separation error, an error evidently greater than that in either of the first two groups. In this connection, it may be noted that the second of the five-fold excess experiments shows an apparent short time exchange essentially comparable to that shown by the two-fold excess zero time exchange, and one is tempted to believe that, at five-fold excess, as at two-fold excess, the apparent exchange represents simply separation error and that the actual exchange rate must be very slight.

The high zero time exchanges in these experiments are readily explicible in terms of the consistent experimental difficulty found in separating the sulfuryl and thionyl chloride fractions for radio-assay. The small amount of sulfuryl chloride seemed to tend to hydrolyze along with the thionyl chloride and, to prevent this, the hydrolysis time was sharply limited. It appears that this limitation was such as to lead to insufficient separation, with the resulting high separation error.

Clearly the two-fold excess experiments show no significant progressing exchange. An attempt to treat the data in terms of a

McKay plot of log (1-F) versus time, as was done with the first two

groups of experiments leads, on least squares calculation, to a posi-

tive slope, rather than any negative slope which might be associated

with any real exchange rate. This represents a physically impossible

situation, and one may only conclude that the data clearly show the

exchange to be at best exceedingly slow. In order to gain an estimate

of the maximum exchange rate consistent with the observations, one

may employ the apparent exchange at 480 hours. Assuming, as with

the previous data, that, in the limit, this might represent a true

exchange, with no separation error, the calculated maximum rate is

found to be 10.94×10^{-2} g-atoms 1^{-1} day^{-1}, corresponding to a mini-

mum half-time of 36 days. It is of some interest to find these figures

roughly comparable to those obtained in the first two groups of experi-

ments, although it seems quite likely that the exchange is significantly

slower than the indicated limits. In any case, as for the other condi-

tions, one may conclude that the exchange in excess thionyl chloride

is again exceedingly slow.

4. SULFURYL CHLORIDE-TETRAMETHYLAMMONIUM

CHLORIDE EXPERIMENT. The result of the single experiment done

on the exchange between sulfuryl chloride and solute tetramethyl-

ammonium chloride is presented in Table IV. Since the separation

procedure used here was, unlike that in the previously discussed

experiments, such as to lead in all probability to essentially complete

reactant separation, it seems quite reasonable to accept any apparent

exchange in this instance as genuine. It may be seen that the record-

ed exchange, while not complete, is quite large. As indicated in the

description of the run procedure for this experiment, complete dis-

solution of the salt was never quite achieved, and it seems quite prob-

able that the apparent incomplete exchange is to be traced to this

incomplete dissolution. If such is the case, it then may be concluded

that the exchange, as far as the material which dissolved is concerned,

was quite likely complete within the time of contact. Despite the

14.75 hours listed as time of exchange, the actual residence time

for the portions of salt actually in solution was of the order of a few

minutes to an hour. In any case, it is evident that one is dealing

here with a fast exchange, a situation in marked contrast to that ob-

served in the sulfuryl chloride-thionyl chloride system where the rate

was exceedingly slow.

TABLE I

RADIOCHLORINE EXCHANGE IN EXCESS SULFURYL CHLORIDE
Conditions: 25.3 ± 0.05°C. (except Exp. VE); Thionyl Chloride Initially Labeled

EXP. [a] NO.	REACTANTS (DOSED)		$A_{SO_2Cl_2}$	A_{SOCl_2}	A_o	A_∞	ANALYSIS OF FRACTIONS[b] SO_2Cl_2	$SOCl_2$	F	EXCHANGE TIME
	(millimoles)		(cpm/mg)		(cpm/mg)		(millimoles)			hours
II B	SO_2Cl_2	5.29	4.83	55.90	104.1	16.43	3.563	1.403	.294	.25
A	$SOCl_2$	0.99	6.74	52.89	104.1	16.43	3.688	1.203	.410	.50
V D			4.37	56.77	104.1	16.43			.266	0^c
C	SO_2Cl	5.29	5.75	59.45	104.1	16.43			.350	0^d
B	$SOCl_2$	0.97	4.71	54.37	104.1	16.43			.287	1
A			4.47	51.14	104.1	16.43			.272	5
E^e			4.86	50.66	104.1	16.43			.296	5
VI A			2.10	20.16	45.4	7.03	3.890	1.418	.298	24
B	SO_2Cl_2	5.29	1.60	25.02	45.4	7.03	3.378	1.463	.227	120
C	$SOCl_2$	0.97	1.26	26.72	45.4	7.03	3.106	2.063	.179	240
D			3.44	28.36	45.4	7.03	4.290	0.938	.489	480

[a]The Roman numerals designate bombs dosed at the same time, the letters designating different bombs within a group. The chronolgical order of performance of the experiments corresponded essentially to the Roman numerals.

[b]Used for checking on recovery of activity, but not in calculation of F. Analyses were not done on Exp. V. For checking on activity recovery in this experiment, average analyses of Exp. II A and B were used.

[c]Maximum separation time was 35 seconds.

[d]Maximum separation time was 20 seconds.

[e]Experiment was done at 39.8 ± 0.05 C.

TABLE II

RADIOCHLORINE EXCHANGE IN EQUIMOLAR SULFURYL CHLORIDE

Conditions: 25.3 ± 0.05°C. ; Thionyl Chloride Initially Labeled

EXP. [a] NO.	REACTANTS (DOSED)		$A_{SO_2Cl_2}$	A_{SOCl_2}	A_o	A_∞	ANALYSIS OF FRACTIONS[b] SO_2Cl_2	$SOCl_2$	F	EXCHANGE TIME
	(millimoles)		(cpm/mg)		(cpm/mg)		(millimoles)			hours
IV A	SO_2Cl_2	2.24	6.55	76.55	104.1	50.8	1.008	2.203	.129	.25
B	$SOCl_2$	2.13	6.24	77.20	104.1	50.8	1.183	2.013	.123	.50
VII A			1.80	34.76	45.4	21.9	1.168	2.528	.082	24
B	SO_2Cl_2	2.24	2.94	33.62	45.4	21.9	1.021	2.436	.134	120
C	$SOCl_2$	2.08	4.02	32.56	45.4	21.9	0.748	2.638	.184	240
D			7.73	32.34	45.4	21.9	1.093	2.153	.353	480

[a]See footnote a Table I.

[b]See footnote b Table I.

TABLE III

RADIOCHLORINE EXCHANGE IN EXCESS THIONYL CHLORIDE
Conditions: 25.3 ±0.05 °C. ; Thionyl Chloride Initially Labeled

EXP. [a] NO.	REACTANTS (DOSED)		$A_{SO_2Cl_2}$	A_{SOCl_2}	A_o	A_∞	ANALYSIS OF FRACTIONS[b] SO$_2$Cl$_2$	SOCl$_2$	F	EXCHANGE TIME
	(millimoles)		(cpm/mg)		(cpm/mg)		(millimoles)			(hours)
III A	SO$_2$Cl$_2$	0.96	85.66	85.65	104.1	85.7	.483	4.408	1.000	.25
B	SOCl$_2$	4.45	39.38	8.45	104.1	85.7	.423	4.372	.460	.50
VIII A	SO$_2$Cl$_2$	0.94	13.42	34.28	45.4	31.3	.523	1.696	.428	0[c]
B	SOCl$_2$	2.08	15.57	34.28	45.4	31.3	.17 [d] .25	2.400	.497	120
C			10.25	38.60	45.4	31.3	.353	1.835	.327	480

[a]See footnote a Table I.

[b]See footnote b Table I.

[c]Maximum separation time was 20 seconds

[d]After Hg$_2$Cl$_2$ precipitation, an attempted potentiometric titration showed negligible excess chloride. However, 0.17 millimoles of Hg$_2$Cl$_2$ were weighed and counted, enough precipitant having been added to precipitate 0.25 millimoles.

TABLE IV

SULFURYL CHLORIDE-TETRAMETHYLAMMONIUM CHLORIDE EXCHANGE
Conditions: Ca. 25°C   Tetramethylammonium Chloride Initially Labeled

SO$_2$Cl$_2$	Me$_4$NCl	$A_{SO_2Cl_2}$	A_{Me_4NCl}	A_o	F	EXCHANGE TIME
(millimoles)		(cpm/mg)		(cpm/mg)		(hours)
40.17	0.395	1.846	73.87	424.3	.835	14.75 (max)

C. CONCLUSIONS

A series of radiochlorine exchange experiments with sulfuryl chloride has been done in order to try and obtain a better understanding of some of the reactions in a solvent system of previous interest in this Laboratory (18, 19, 29). A number of experiments were done between sulfuryl chloride and thionyl chloride and one experiment was done between the basic, ionic solute tetramethylammonium chloride and sulfuryl chloride.

Although considerable difficulty was encountered in separating the sulfuryl chloride from the thionyl chloride for radioassay after an exchange experiment, certain conclusions can be drawn from the data. The most significant of these is that, in this system, the occurrence of a rapid exchange can definitely be excluded, the exchange rate being exceedingly slow. On the other hand, the evidence does appear to suggest that it is not negligible and that though slow, the rate is, in fact, probably observable. The reaction rate appears to be of the order of magnitude (at 25°C) of 10^{-1} g-atom 1^{-1} day^{-1}, irrespective of relative reactant concentrations. This corresponds to reaction half times of at least about 35 days if computed on the basis of minimum exchange experiments, or half times of 46-60 days if calculated on the basis of McKay plots involving least squares treatment of the data.

More specifically, on the basis of the least squares treatment, the equimolar sulfuryl chloride-thionyl chloride experiments showed the highest exchange rate, $9.84 \pm 1.30 \times 10^{-2}$ g-atoms 1^{-1}day^{-1}. The excess sulfuryl chloride experiments appear to show a slower exchange, $3.93 \pm 12.58 \times 10^{-2}$ g-atom 1^{-1}day^{-1}, but the standard deviation is so large as to make this number very ambiguous. The excess thionyl chloride data had much scatter and a high apparent zero time exchange, so as to give a McKay plot with a positive slope, thus making impossible a calculation of the reaction rate by this method.

All of the calculations based on the minimum exchange experiment at each reactant mole ratio studied showed a similar reaction half time, 35 ± 1 days. This is, however, only a limiting value, and the actual half time could well be much longer.

All experiments of consequence in this research were done at 25°C. A single experiment was done at a somewhat higher temperature in an abortive attempt to arrive at a temperature coefficient for the reaction rate, but failed to show any effect. More extensive experiments at other temperatures would be necessary in order to arrive, as would be desirable, at some estimate for the activation energy for the exchange rate.

One of the principal motivating factors for doing the present experiments was the desirability of obtaining evidence relative to the importance of chloride ion dissociation equilibria on the part of sulfuryl and thionyl chloride in the presence of each other, i. e. dissociation equilibria of the type envisioned in the solvent systems treatment of solvents of this type. Such experiments seemed particularly pertinent in view of the earlier work, as discussed in the Introduction, which appeared to support the validity of the occurrence of a significant chloride ion dissociation on the part of thionyl chloride, the rapid thionyl chloride-thionyl bromide radiosulfur exchange observed by Johnson (18, 19) being particularly pertinent in this regard. A further relevant point had been the observation by Frazer (8) of a rapid radiochlorine exchange of pyridinium chloride with sulfuryl chloride (as well as with thionyl chloride) in chloroform; such a result suggested the possible occurrence of rapid chloride ion dissociation equilibria for both of these substances in this medium, though it did not necessarily prove it, a rapid association equilibrium or bimolecular process also being possible.

The results of the present work are of real interest in the contrast they present to the rapid radiosulfur exchange observed between thionyl chloride and thionyl bromide. Clearly in mixtures of thionyl chloride and sulfuryl chloride a different situation prevails.

If important dissociation equilibria (presumably rapid) operated for both of these compounds in the presence of each other, a rapid radio-chlorine exchange would certainly be observed. Such is far from the case, however. Since any dissociation tendency on the part of thionyl chloride in mixtures with thionyl bromide would, one might imagine, probably still tend to operate in mixtures with sulfuryl chloride, one is led to the conclusion that the present slow exchange probably implies that chloride ion dissociation is not an important process for sulfuryl chloride, the material contrasting, then, significantly in this respect with thionyl chloride. Such a result implies, of course, that the rapid exchange observed by Frazer probably should, in fact, be explained by either a rapid association equilibrium or a bimolecular process.

While the results here obtained present, as indicated, an interesting contrast to the rapidity of the thionyl chloride-thionyl bromide exchange system, they are of equal interest in the parallel they present to the radiochloride exchange system investigated by Wiggle (37). Here rapid chloride exchange was observed between the solvent sulfur monochloride and either the acidic, strong chloride acceptor solutes antimony tri- and pentachloride or the basic, ionic chloride donor solute tetraethylammonium chloride; in contrast, however, the more "neutral" solute thionyl chloride exchanges at best

only slowly with sulfur monochloride. Wiggle deduced that sulfur monochloride in the absence of a strong acid, chloride ion acceptor has little tendency to dissociate chloride ions. The parallel with the implication of but little ionization on the part of sulfuryl chloride in the presence of thionyl chloride, as inferred from the observed slow chloride exchange in that system, is self-evident.

The present results are of further significance relative to another point discussed in the Introduction. As there indicated, Johnson, in his research on radiosulfur exchange between thionyl and sulfuryl chlorides (18, 19) (in which he observed at best an exceedingly slow exchange) suggested that possibly an acid-base type of interaction between these two species might occur, the thionyl chloride, as a base, donating a chloride ion to the sulfuryl chloride in an acid-base ionization equilibrium. Johnson's suggestion was that such an interaction should, in contrast to the slow sulfur exchange situation, lead to a rapid radiochlorine exchange between the two species, an alternative pathway for such a process thus being provided if it did not occur via dissociation of both species. It was one of the important objects of the present research to try to obtain evidence relative to this postulate. It is apparent that the results obtained give no support to the hypothesis. Johnson observed a minimum aulfur exchange half-time (at 0°C) of 70 days. Clearly the chlorine exchange

rates here observed are roughly of comparable slowness, suggesting that, quite possibly, related exchange mechanisms may be involved. The data certainly rule out the simple, rapid type of acid-base exchange equilibrium between the two solvents postulated by Johnson. It seems most probable that the exchange which, though slow, does appear to be real, must involve some definitely more complex type of interaction.

As suggested by the foregoing discussion, Frazer's observation of a rapid exchange between the ionic solute pyridinium hydrochloride and thionyl chloride in the inert solvent chloroform (8) is of some interest relative to the slow exchange here observed between thionyl and sulfuryl chlorides. The use of chloroform as a solvent, however, to a degree lessens the applicability of Frazer's observations so far as direct comparison with the present results are concerned, where the primary focus of attention is on sulfuryl chloride itself as a solvent. For this reason it seemed desirable to do an experiment comparable to Frazer's but not involving any foreign solvent. The present experiment dealing with exchange between tetramethylammonium chloride and sulfuryl chloride was done to this end.

Unfortunately, the very low solubility of the tetramethyl-ammonium chloride in the solvent led to the necessity for carrying

out this experiment in the rather elaborate manner described in the Run Procedures section, a method yielding not altogether satisfactory results, the procedure making necessary, for example, a long contact time between portions of the solvent and the salt. As already indicated, however, the results do seem to indicate a rapid exchange, one probably complete within a few minutes at 25°C and requiring at the very most something like 20 hours for completion.

Plainly the result with tetramethylammonium chloride is consistent with Frazer's observation with pyridinium c h l o r i d e , and presumably is to be interpreted in the same manner. Since, as already indicated, it would appear that chloride ion dissociation by sulfuryl chloride is probably inconsequential, one probably must conclude that the rapid exchange here observed involves direct solvent-chloride ion interaction. As already indicated relative to pyridinium c h l o r i d e , t h i s could be either a bimolecular process such as Lewis and Sowerby postulated for the analogous exchange of chloride ion with phosphorus oxychloride (23) or, alternatively, an association equilibrium.

The results presented in this thesis would appear to make a significant contribution towards a deeper understanding of an interesting non-aqueous solvent and to provide information of some value in its relation to associated pieces of research that have previously been

carried out with related solvents either in this Laboratory or elsewhere. On the basis of the work so far done, a number of inviting further lines of investigation also present themselves. It might prove very illuminating, for example, if the exchange between sulfuryl and thionyl chlorides were to be studied at a higher temperature, where a more significant rate might be anticipated. Such experiments would be particularly aided if a better separation procedure than that here used could be devised. This system might also be investigated by use of labeled (heavy) oxygen to determine if the mechanism of exchange is via a binuclear oxide bridge structure. Also, further experiments clarifying the rate of exchange between sulfuryl chloride and tetramethylammonium chloride should be done. These might lead to an estimate of the ionization product of thionyl chloride much in the same manner as Lewis and Sowerby obtained an estimate for the ionization product of nitrosyl chloride (23). Finally, chloride exchange experiments between sulfuryl chloride and acidic solutes such as antimony tri- and pentachlorides would be of value. Experiments of the indicated sort should give a better insight into details of the nature of sulfuryl chloride as a solvent and, in so doing, serve significantly to broaden the scope of the information relative to this solvent provided by the present thesis. Some further work along the suggested lines has already been commenced in this Laboratory and the results, when complete, should be of real value.

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