

THE CATALYSIS BY NONIONIC BASES
OF RADIOSULFUR EXCHANGE BETWEEN
LIQUID SULFUR DIOXIDE AND THIONYL CHLORIDE

by

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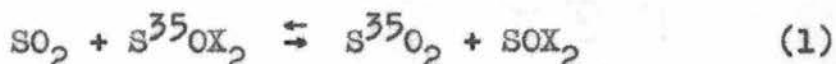
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THE CATALYSIS BY NONIONIC BASES
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I. INTRODUCTION

Over the past several years the kinetics of radiosulfur exchange between liquid sulfur dioxide and thionyl halides



has been the object of intensive study (7, 14, 16, 24, 25). Johnson, Norris and Huston (16), in a study of the possible contribution of ionization processes to the acid nature of solutions of thionyl halides in liquid sulfur dioxide,¹ showed that the sulfur exchange between such solutes and liquid sulfur dioxide is almost immeasurably slow. It was observed, however, that in the presence of potassium bromide, sulfur dioxide and thionyl chloride undergo a rapid exchange of sulfur.

A kinetic study of the sulfur exchange in the system $\text{S}^*\text{O}_2\text{-SOBr}_2\text{-MX}$ ($\text{MX} = \text{Me}_4\text{NBr}$, CsBr , RbBr or RbCl) was carried out by Herber, Norris and Huston (14). Their results showed the sulfur exchange to be first order in halide salt and zero order in thionyl bromide.

¹For a general review of this work see reference 25.

The order with respect to sulfur dioxide concentration was not investigated. They assumed a rate law of the form

$$\text{Rate} = k(\text{catalyst}) \quad (2)$$

$$k = 4.17 \times 10^6 e^{-13,200/RT} \text{ sec}^{-1} \text{ for} \\ \text{tetramethylammonium bromide catalyst}$$

and presented a possible mechanism involving basic catalysis by the ionic halides.

Following the above work, Masters and Norris (24) undertook a detailed kinetic study of the ionic chloride-catalyzed sulfur exchange between dissolved thionyl chloride and liquid sulfur dioxide. Like the thionyl bromide-sulfur dioxide exchange, this was interpreted as a case of base catalysis by ionic halide, but in this instance the rate law was shown to be

$$\text{Rate} = k_3(\text{catalyst})(\text{SOCl}_2)(\text{SO}_2) \quad (3)$$

$$k_3 = 1.08 \times 10^7 e^{-14,700/RT} \text{ liter}^2 \text{ mole}^{-2} \text{ sec}^{-1} \\ \text{for catalyst tetramethylammonium chloride} \\ \text{in excess sulfur dioxide.}$$

Although this rate law was found valid both in excess sulfur dioxide and in excess thionyl chloride solutions, k_3 is about three times as great in the latter case as

in the former. Further, the value of k_3 is dependent on the catalyst, being about twice as great for tetramethylammonium as for rubidium chloride. A brief study of this same thionyl chloride-sulfur dioxide exchange reaction (with tetramethylammonium chloride as catalyst) in which the reactants were dissolved in the inert solvent, acetonitrile, was carried out by Norris and Cooper². Here again, the rate law, equation (3), was found to hold. The activation energy is the same, but the pre-exponential term is higher, 2.22×10^7 , as compared to 1.08×10^7 liter²mole⁻²sec⁻¹ in the absence of the solvent.

The catalysis of the thionyl chloride exchange by the acids, hydrogen chloride, hydrogen chloride and water, and aluminum chloride was shown by Masters and Norris (24) to be at best slight in comparison to the catalysis by ionic chlorides. This brief investigation of acid catalysis was followed by a detailed study by Burge and Norris (6) of the catalysis by the acid, antimony pentachloride. Here, the most fitting rate law is

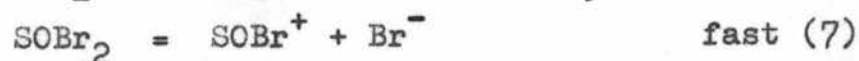
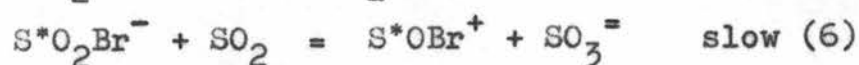
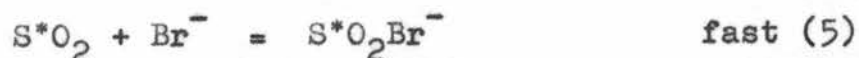
$$\text{Rate} = k_2(\text{SO}_2)(\text{SOCl}_2 \cdot \text{SbCl}_5) \quad (4)$$

The rates observed were, again, much lower than those

²Private communication from T. H. Norris and T. Cooper.

observed with the ionic chloride (basic) catalysts.

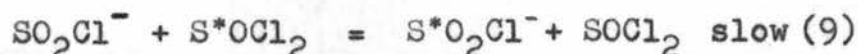
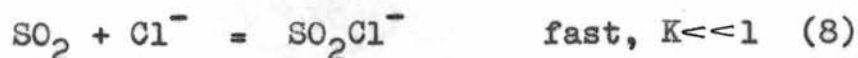
The mechanism for the thionyl bromide exchange (studied only in excess sulfur dioxide) was inferred (14) to involve, in a preliminary equilibrium, addition of ionic bromide to sulfur dioxide, this process serving to promote oxide ion transfer to another sulfur dioxide molecule in the rate-determining step:



In this mechanism the reactant shown as bromide ion actually represents total ionic bromide, presumably largely ion pairs, no indication being found for any catalytic distinction between these and free ions³.

The mechanism of the thionyl chloride exchange was interpreted as involving rapid solvation of the chloride to form the species SO_2Cl^- , followed by the slow, simultaneous exchange of an oxide and chloride between the solvated chloride and a thionyl chloride (24).

³Bartlett and Herbandson (1) observed similarly that there is no kinetic distinction between free ions and associated species in the chloride catalysis of the thionyl chloride-dibutyl sulfite reaction. A distinction between free ions and ion pairs has, however, recently been demonstrated in the exchange of bromide between alkali bromides and p-nitrobenzyl bromide dissolved in liquid sulfur dioxide (19).



The variation of k_3 with change in solvent, referred to above, was believed due to a shift in equilibrium (8), since the value of the equilibrium constant is included in k_3 . As in the thionyl bromide case, "chloride ion" in (8) and (9) represents total chloride, no catalytic distinction having been apparent between free ions and ion pairs. The higher value of k_3 for tetramethylammonium chloride as compared to rubidium chloride (6.25 versus $3.02 \times 10^{-2} \text{ liter}^2 \text{ mole}^2 \text{ hr}^{-1}$ at 0° , both in excess sulfur dioxide) was taken to indicate that ion pairs are the major kinetic species in solution. A similar effect on k was observed with the corresponding bromide catalysts in the thionyl bromide system ($k = 0.37$ versus 0.21 hr^{-1} at 0°C). It seemed reasonable that the larger quaternary ammonium ion would favor the transfer of halide ions to sulfur dioxide, the rate differences thus being due to shifts in equilibria (5) and (8). The constancy of the activation energy but difference in frequency factors with the two catalysts (in the thionyl chloride case) also appeared to point toward this conclusion.

The chloride-catalyzed thionyl chloride exchange

proceeds at a rate about seven times greater than the rate of bromide-catalyzed thionyl bromide exchange at comparable reactant and catalyst concentrations. Calculation of rate constants on the basis of (2),

$$\text{Rate} = k_1(\text{catalyst})$$

(catalyst here is the appropriate
tetramethylammonium halide)

yields values of 4.63 versus $4.17 \times 10^6 \text{ sec}^{-1}$ for the pre-exponential terms and apparent activation energies of 14.7 versus 13.2 Kcal/mole for the chloride and bromide systems, respectively. It seemed to the investigators reasonable that the greater basicity for chloride than bromide ion would shift equilibrium (8) relative to (5), but this did not explain the difference in mechanism. It did not seem reasonable that an oxide transfer process would be strongly favored for the bromide over the chloride. It was felt that it might well be that the formation of the activated complex, assumed for the thionyl chloride exchange to involve a binuclear, double oxide-halide bridge, is less favored with bromide as one of the bridging species. In such a case, exchange by this pathway would be favored for chloride, leading to the observed change in mechanism.

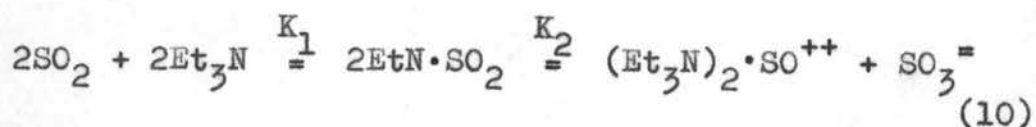
The rate law observed for the antimony

pentachloride-catalyzed exchange in the thionyl chloride system clearly implies a prior rapid equilibrium step to form a complex between thionyl chloride and the acid, followed by the slow sulfur exchange of this species with sulfur dioxide molecules. The complex proposed by the investigators of this system involves the formation of hexachloroantimonate by coordination to the antimony of one chloride from the thionyl chloride. They then suggested for the activated complex a binuclear structure involving a double chloride-oxide bridge between the sulfurs of the complex and of sulfur dioxide, an additional chloride then being coordinated by the hexachloroantimonate to the sulfur of sulfur dioxide to complete a symmetrical structure. It may be seen that this is essentially just the sort of activated complex postulated for the base-catalyzed exchange.

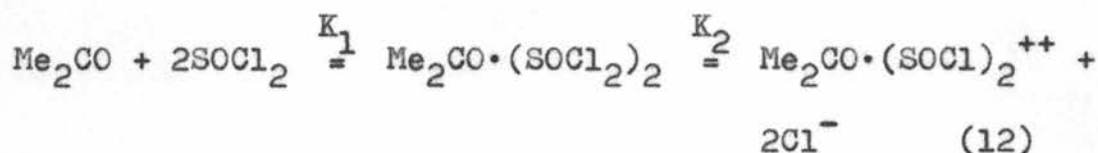
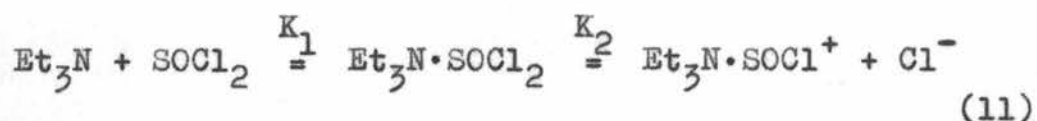
The observations of both acid and basic catalysis of exchange between sulfur dioxide and thionyl chloride led Burge and Norris (7) to investigate the catalytic effectiveness of mixtures of acids and bases. Rather detailed experiments carried out on mixtures of tetramethylammonium chloride and antimony pentachloride showed a minimum catalytic activity at a 1:1 mole ratio of acid to base. This observation confirms the formation of a hexachloroantimonate complex as has previously been

reported (15, p. 300; 29; 30). This complex is evidently but little dissociated and possesses, itself, but little catalytic activity.

It has appeared that considerable light could be thrown on the mechanism of base catalysis in these exchange systems by a detailed kinetic study of the possible catalytic effectiveness of non-halide bases, especially ones which might possibly be more strongly solvated in sulfur dioxide than ionic halides. The present research consists of a study directed to this end. Jander and co-workers (15, p. 287-293) and Spandau and Brunneck (32, 33) have studied acid-base relationships in liquid sulfur dioxide and thionyl chloride, respectively. The interpretation of the experimental observations, in either solvent, was that triethylamine is a weak base. Further, the observations with acetone (33) were also interpreted as showing this substance to be a very weak base in thionyl chloride. Though weak, it seems certain that of these two substances, triethylamine, at least, would be a significantly stronger Lewis base than are ionic halides. Jander (15, p. 289, 290) pictures the basicity of triethylamine as being due to the interaction



While the precise ionization process postulated here has been effectively shown to be incorrect (2, 13), there is no denying the fact that triethylamine shows basic properties in sulfur dioxide. According to the views of Spandau and Brunneck (32, 33) triethylamine and acetone interact with thionyl chloride as solvent to yield chloride ions and the appropriate cations by such equilibria as



Since, in their views (oriented as they are towards the "solvent systems" interpretation of acid-base phenomena), sulfite and chloride ions, respectively, represent the "anion characteristic of the solvent", they thus explain the behavior of these materials as bases. In (11) and (12) K_1 and K_2 are equilibrium constants for the association and the ionization, respectively. (We might identify the associated species in (11), for example, as an ion pair, $(\text{Et}_3\text{N} \cdot \text{SOCl})^+\text{Cl}^-$, or simply as a molecular addition complex which can ionize rather readily.)

Assuming the validity of Spandau and Brunneck's

postulated equilibria, it would seem reasonable to expect that any exchange catalysis by triethylamine which might occur in a thionyl chloride-sulfur dioxide system would bear some relationship to the chloride ions formed in (11). The rate law should depend on the values of K_1 and K_2 and on the relative extent of the formation of molecular complexes between triethylamine and sulfur dioxide or thionyl chloride, respectively. The association constant (K_1) in (10) is evidently large since the triethylamine-sulfur dioxide addition compound is easily isolated (2; 13; 15, p. 291-292) and has only a modest vapor pressure compared to the vapor pressure of sulfur dioxide (approximately 10^{-2} atm versus more than 3 atm at 25°) (12, p. 18). Presumably a compound such as thionyl chloride, which, dissolved in liquid sulfur dioxide, forms weakly acid solutions, would tend to form in this solvent, similarly, reasonably stable addition compounds with bases such as triethylamine, i.e., K_1 in equation (11) should be large. The rate law for the exchange catalyzed by triethylamine might well reflect the influence of free chloride ion as a catalyst since there should be a wide variation of chloride ion concentration in going from a solution rich in sulfur dioxide to a solution rich in thionyl chloride at a fixed amount of triethylamine.

Any catalysis of the reaction by acetone might be

expected to be similar to that by the amine except that acetone has not been shown to interact with sulfur dioxide and it forms only very weakly conducting solutions with thionyl chloride; thus it appears to be a weaker base. Further, if (12) is correct, acetone acts as a di-functional base, and this fact should be reflected in the rate law.

The investigation here reported consists primarily of a detailed kinetic study of the basic catalysis by triethylamine of the thionyl chloride-sulfur dioxide exchange, along with some experiments on the exchange as catalyzed by acetone. Spandau and Brunneck (33) have reported that triethylamine dissolved in thionyl chloride solutions can be titrated conductimetrically with antimony pentachloride to yield a break on the conductance curve at a one to one mole ratio of acid to base, presumably reflecting complex formation. Consequently, a brief study of the effectiveness of mixtures of triethylamine and antimony pentachloride as catalysts has also been carried out in an attempt to elucidate further the nature and properties of this one to one complex.

II. EXPERIMENTAL

A. General

All moisture sensitive compounds, after rigorous drying, were handled either in a dry box or in a vacuum system. The dry box was of conventional design. So as to not allow moisture to enter the main box, materials were introduced into the box through a lock which could be readily dried. The box was first dried by sweeping it out for at least 24 hours with compressed air which had been dried by bubbling through concentrated sulfuric acid and then passed, in turn, through anhydrous calcium sulfate, through anhydrous magnesium perchlorate, and finally over phosphorus pentoxide. At the end of the preliminary drying, the compressed air was turned off and the air in the box was circulated, by means of a small pump, through barium oxide. A positive pressure was maintained in the box by means of the slow evaporation of liquid nitrogen.

The vacuum system was of standard design. It was evacuated through a liquid nitrogen (or air) cooled trap by means of a mercury diffusion pump backed by a mechanical pump. Pressures were measured by a thermocouple gauge, an ionization gauge (a McLeod gauge in the earlier work) or a mercury manometer, whichever was appropriate. Pressures in the range of 10^{-5} mm of Hg were readily

attained.

Thionyl chloride and antimony pentachloride were not exposed to mercury, but acetone, triethylamine and sulfur dioxide pressures were measured on mercury manometers. Stopcocks were lubricated with Spectro-vac I¹, Halocarbon², or Apiezon "N" or "T" greases, the latter being used during hot summer weather. Antimony pentachloride was passed through stopcocks lubricated only with the Halocarbon material. Even this grease was attacked slowly, but it was by far the best material found for use with this compound. On the dosing section of the vacuum system, the stopcocks through which triethylamine passed were lubricated with Spectro-vac I, since this grease was found to dissolve only small amounts of the amine in sharp contrast to all other greases tried which interacted with triethylamine to an alarming extent. The stopcocks through which thionyl chloride passed were lubricated with Halocarbon grease, which was attacked only slightly in the time required to dose a set of ampoules. All other stopcocks were lubricated with Apiezon "N" or "T".

¹Spectro-vac is the trade-name for a crepe-rubber-based lubricant available from Robert Austin, Ph.D., Pasadena, California.

²Halocarbon 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.

To minimize contamination by water, all ampoules into which exchange solutions were to be dosed or volatile compounds were to be stored, after being attached to the vacuum system and evacuated, were heated with a luminescent flame until the system pressure dropped to approximately 10^{-5} mm of Hg. Usually the system was pumped on overnight -- at least 6 hours -- before the ampoules were filled, thus making doubly certain that moisture was excluded.

Considerable use was made of the technique of vacuum fractionation (see, for instance, 28, p. 86-93). Samples to be separated, for instance sulfur dioxide-thionyl chloride mixtures, were frozen with liquid nitrogen. The cooling bath was removed, thus allowing the mixture to vaporize slowly. The vapors were passed through a chilled "U" trap and into a cold finger. The "U" trap was maintained at such a temperature so as to condense the vapor of the less volatile component and not the more volatile. The cold finger was maintained at a low enough temperature to condense the vapors of the more volatile component. For the latter purpose liquid nitrogen was usually employed. If only the less volatile component or a middle cut was to be saved, as in the case of the purification of antimony pentachloride, triethylamine, acetone and so forth, the "U" trap temperature was

maintained at a high enough temperature so that perhaps ten percent of this component was not retained in the trap but passed through to the cold finger. The trap condensate was then roughly fractionated, about the middle one-half portion being retained. In cases where it was not desirable to discard a large portion of the less volatile component, as, for example, in the instance of removing sulfur dioxide from labeled thionyl chloride preparations, the "U" trap was maintained at a temperature such that only a very small portion of the less volatile material was not condensed but, with careful manipulation (as, for example, by working with only small portions at a time), little of the more volatile fraction was condensed. The fractionation through the trap (or through a second trap) was repeated until it appeared that no further material was being collected in the cold finger. Gas chromatographic analysis showed repeatedly that by this procedure one could remove quantitatively ($< 1\%$) all of the sulfur dioxide from samples of thionyl chloride. Further details of this procedure are given in the Run Procedure section.

Reaction temperatures at 0°C were maintained, in all cases, by crushed ice, packed in a Dewar flask. Control at other temperatures was achieved with regulated constant temperature baths of conventional design in

which the temperature could be controlled to $\pm 0.1^{\circ}\text{C}$. Bath temperatures were occasionally checked with National Bureau of Standards-calibrated thermometers and were routinely monitored by similar, uncalibrated thermometers which were subdivided in tenths of degrees.

B. Radioactive Assay

The isotope used in this study, sulfur-35, emits negative beta particles of maximum energy 0.167 Mev and has a half-life of 86.35 days (9). It was obtained from the Oak Ridge National Laboratory either in the form of neutron irradiated potassium chloride or as carrier-free sulfate in dilute hydrochloric acid solution.

Radiosulfur samples were assayed as barium sulfate. For this purpose, labeled compounds were dissolved in potassium hydroxide solution, oxidized with bromine water or 30% hydrogen peroxide solution, brought to approximately pH 1 with hydrochloric acid (or nitric acid when a chloride analysis was to be made), heated to boiling and treated with 1M barium chloride (or nitrate). After digestion for an hour at boiling temperature, the precipitate was collected on a sintered-glass filter, washed with distilled water and acetone and slurried with acetone. Appropriate amounts of the slurry were transferred to cupped, nickel-plated planchets and dried under

an infrared lamp. Duplicate planchets of samples were made in most cases. Sample thicknesses ranged from about 2 to 20 mg/cm².

The counting procedure was essentially that of Norris (26, p. 1221). The pulses from an end-window Geiger tube (Tracerlab TCG-2, equivalent window thickness less than 2 mg/cm² Al) were counted with a conventional scaler. The sample holder was provided with shelves at various distances from the Geiger tube. Samples of high specific activity were counted a greater distance from the tube to obviate large coincidence corrections, and shelf corrections, empirically determined, were used in order to compare directly the samples counted on different shelves. The coincidence loss was experimentally determined and this correction applied when it was one percent or greater. In order to compare samples counted on different days, a "standard" sample of barium sulfate was counted each day, thus taking care of both the half-life correction and any possible variation in counter sensitivity. Self-absorption corrections were empirically determined and applied to all sample measurements. The total number of sample counts and background counts were, in each case, sufficient to insure a standard deviation of not more than, and usually less than, 3%. Experience tells us that this is well within the overall error in

specific activity determinations made on solid samples of barium sulfate.

C. Chemical Analysis

1. Chloride. Analysis for chloride was carried out by potentiometric titrations with silver nitrate. A Beckman Model H pH meter with silver-silver chloride indicator electrode and mercury-mercurous sulfate reference electrode³ was used to detect the endpoint. Preliminary experiments with standards, similar in nature to the samples to be analyzed, showed the endpoint occurred at a meter reading of 125 mv with this particular indicating system. This value was used to mark the endpoint in the actual determination of unknowns.

2. Sulfur. Two very similar methods were used here. In the first, the sulfur-containing solutions were oxidized with bromine water, acidified with 4N HCl, brought to a boil and treated with 1M BaCl₂. The barium sulfate thus formed was collected on weighed, sintered-glass filters after digestion for an hour at boiling temperature, washed successively with water and then acetone prior to drying for at least 3 hours at 180°C, and finally weighed. The second method, used where it

³Available from Beckman Instrument Co., Fullerton, Calif.

was desirable to carry out an analysis for sulfur and chloride on the same sample, employed 30% hydrogen peroxide in place of bromine water, dilute nitric acid in place of dilute hydrochloric acid, and saturated barium nitrate in place of barium chloride solution. Otherwise the procedure was the same.

D. Preparation of Materials

1. Sulfur dioxide was obtained from three sources: (1) The Ohio Chemical and Manufacturing Company in a steel cylinder, (2) The Matheson Company, Inc., in a steel cylinder and (3) The American Potash and Chemical Corp. in sealed one-pound cans. In any instance, the gas was introduced into the vacuum system, passed through two bubblers which contained concentrated sulfuric acid, passed over phosphorus pentoxide or through anhydrous magnesium perchlorate and condensed into a Dry Ice-acetone cooled trap. The sulfur dioxide in the trap was allowed to vaporize, the first and last one-third portions being discarded and the middle portion being stored, either as a gas in a large bulb on the vacuum system or as a liquid in a sealed ampoule fitted with a break-tip. Before use, the gas was condensed, frozen and pumped on to insure removal of any possible permanent gases.

2. Labeled sulfuric acid (or S^{35} -labeled solutions of $Ba(HSO_4)_2$ in H_2SO_4), $H_2S^{35}O_4$, was prepared by two methods. When the source of the sulfur-35 was neutron irradiated potassium chloride, the method of Norris and Masters (23) was used. Here, the salt was dissolved in 0.002N H_2SO_4 . The resulting solution was boiled and an excess of 1M $BaCl_2$ added. After digestion, the material was centrifuged and the centrifugate decanted. The precipitate was washed with water, then acetone, and finally dried. The dry barium sulfate was dissolved in a small amount of concentrated sulfuric acid to yield an S^{35} -labeled solution of $Ba(HSO_4)_2$ in sulfuric acid.

The preparation of $H_2S^{35}O_4$ from solutions of carrier-free sulfate in dilute hydrochloric acid was carried out by adding measured amounts of this solution to concentrated sulfuric acid and evaporating the resulting solution, with the aid of an infrared lamp, to approximately 12M H_2SO_4 concentration.

3. Labeled sulfur dioxide, $S^{35}O_2$, was prepared from $H_2S^{35}O_4$ (or $Ba(HS^{35}O_4)_2$ in H_2SO_4) and purified sulfur dioxide by the method of Norris and Masters (23). About 2 mc of labeled sulfuric acid (approximately 0.3 ml) and 10 mmoles of purified sulfur dioxide were sealed in a 500 ml flask and heated to $325^\circ C$ for about

two weeks to insure reasonably complete randomization of the sulfur-35 between the sulfur dioxide and the sulfuric acid solution. The product, $S^{35}O_2$, of high specific activity, was transferred from the reaction flask to the vacuum system through a break-tip, bubbled through concentrated sulfuric acid and passed through anhydrous magnesium perchlorate. To the reaction flask was added 1 mmole of unlabeled sulfur dioxide. This material was then also passed through the bubbler and the drying tube. This "washing" step was repeated twice more and the original labeled sulfur dioxide plus the "wash" sulfur dioxide were collected together. If the labeled sulfur dioxide was to be used in the preparation of labeled thionyl chloride (see below) it was dissolved, at this point, in a solution of tetramethylammonium chloride in thionyl chloride. If the labeled sulfur dioxide was to be used as such, it was transferred to a large storage bulb on the vacuum line.

4. Thionyl chloride, $SOCl_2$. The commercially available material (Matheson, Coleman and Bell, b.p. 75-76°C or British Drug House, iodometric assay, 97-103%) was purified by one of two methods. The one less used (Method I) was essentially that of Cottel (8). Typically a flask containing one gram of flowers of sulfur and

100 milliliters of impure thionyl chloride were sealed onto the bottom of a fractionating column packed with glass helices and refluxed for 12 hours, then distilled at atmospheric pressure through the column. The fraction boiling at 75.4° (uncorr.), about 90 milliliters, was collected. This fraction, light yellow in color, was then fractionated through the same column at a reflux ratio of 5:1. A heart fraction of about 40 milliliters (b.p. 75.4° , uncorr.) was collected in an ampoule and sealed to the vacuum system. The ampoule was frozen and evacuated through a break-tip. The solution was freed of permanent gases by thawing, freezing, and pumping repeatedly. When the thionyl chloride no longer bubbled on thawing, it was vacuum fractionated to remove dissolved hydrogen chloride and sulfur dioxide, as described under General Procedures, the coolants for the "U" trap and cold finger being Dry Ice-acetone and liquid nitrogen, respectively. The material collected in the "U" trap was transferred to small ampoules fitted with break-tips, sealed and stored in subdued light.

The second method (Method II) for the purification was similar to that used by Burge (5, p. 18). A stirred, degassed solution of raw linseed oil and thionyl chloride was allowed to react for five to six hours at room temperature. The volatile material was then fractionated

in vacuo as above. The most volatile and least volatile one-quarter portions of the material collected in the "U" trap were discarded and the middle portion was stored in sealed ampoules under subdued light.

Either of these two methods leads to crystal clear thionyl chloride preparations. In several cases, however, thionyl chloride prepared by the first method turned yellow on standing. The material, freshly prepared by either method, gave no indications of impurities when analyzed by vapor phase chromatography (see below). The samples which had yellowed on storage did, however, show indications of small amounts of an impurity (as much as 2% in one case) with a retention time just less than that of thionyl chloride. These yellow solutions were discarded, and no obviously discolored solutions were used in any of the work. The material, freshly prepared by the first method, was used extensively in the present experiments but the possible presence of impurities did not appear to be reflected in the kinetics data. Table I shows typical analytical data for samples prepared by each method.

5. Labeled thionyl chloride, $S^{35}OCl_2$, was prepared from purified thionyl chloride and S^{35} -labeled sulfur dioxide by means of the base-catalyzed exchange

TABLE I

Typical Analytical Data for Thionyl Chloride Samples

Sample of	Density (g/ml)		Sulfur (%)		Chloride (%)	
	Expected	Found	Expected	Found	Expected	Found
Method I	1.696	1.706	26.96	27.20	59.60	59.98
Method II	1.696	1.709	26.96	27.02	59.60	59.40

between labeled sulfur dioxide and thionyl chloride (24, p. 1346-1352). Typically, 100-150 mmoles of purified thionyl chloride and 10-15 mmoles of labeled sulfur dioxide were distilled onto about 4 mmoles of tetramethylammonium chloride in a glass ampoule. The ampoule was sealed and the reaction was allowed to run several days at room temperature. The ampoule was then sealed to the vacuum line and the thionyl chloride freed of sulfur dioxide by fractionation as described previously. About 1 mmole of inactive sulfur dioxide was added to the condensate in the "U" trap -- mostly labeled thionyl chloride -- and the solution was refractionated. This last step was repeated twice more, thus making certain no labeled sulfur dioxide remained in the labeled thionyl chloride. The most volatile and least volatile one-tenth portions of the condensate in the "U" trap were discarded and the vapor over the remaining condensate was checked for the presence of sulfur dioxide by means of gas chromatography. In no case was sulfur dioxide found to be present. The labeled thionyl chloride preparation was stored in sealed ampoules in subdued light.

6. Antimony pentachloride, SbCl_5 , Baker and Adamson, Reagent Grade, was fractionated in vacuo, the most volatile and least volatile one-quarter portions of the

condensate collected in a "U" trap cooled to -20°C were discarded, and the middle portion was stored in sealed ampoules.

7. Tetramethylammonium chloride, Me_4NCl , obtained from Matheson, Coleman and Bell, Inc., was washed with chloroform, recrystallized from absolute alcohol, dried at 130°C and stored in a desiccator containing phosphorus pentoxide. Before use, the material was "washed" in the reaction vessel on the vacuum line, with two successive portions of thionyl chloride for absolute drying, the products being distilled off completely after each "washing".

8. Triethylamine, Et_3N , obtained from Matheson, Coleman and Bell, Inc., was refluxed two hours over freshly cut sodium and then distilled. The middle fraction, boiling range $89-90^{\circ}\text{C}$ (uncorr.), was thoroughly degassed under vacuum, dried by passing over phosphorus pentoxide or through anhydrous magnesium perchlorate, and vacuum fractionated, the heart fraction of the condensate in a -30°C trap being retained for use. It was stored in sealed ampoules.

9. Acetone, Me_2CO , was distilled through a column packed with glass helices, the middle

three-quarters of the fraction boiling at 56°C being retained. This was degassed under high vacuum, passed over phosphorus pentoxide and vacuum fractionated, the heart fraction being stored in sealed ampoules for further use.

III. RUN PROCEDURES

A. General

Three similar procedures were employed in studying the exchange. In the first (Procedure I), used in the vast majority of experiments, replicate samples were dosed, on the vacuum system, into several, usually five, glass ampoules. The ampoules were sealed and placed in a thermostatted bath to react. Periodically, an ampoule was removed from the bath, the reaction quenched by cooling the bomb in liquid nitrogen, and the reactants separated for radioactive analysis. The results of these experiments are given in Tables IIa, IIIa and IV.

In a few of the experiments employing acetone to catalyze the exchange in excess thionyl chloride (and having sulfur dioxide the initially active species -- as was the reactant present in minor concentration throughout this research) a second procedure (Procedure II) was used. Here the reactants were dosed into one ampoule fitted with a pressure stopcock. After dosing, the ampoule was transferred to an ice bath. Periodically, small samples of thionyl chloride (approximately 0.3 mmoles) were removed from the ampoule as vapors through the stopcock for assay. The results of these experiments are given in Table IIb. Procedure III was used in two

TABLE IIa

Radiosulfur Exchange Experiments with Acetone (Procedure I)

Exp. No.	Amount of Reactants	A_{SOCl_2}	A_{SO_2}	A_{O}	$1\text{-F}_{\text{SOCl}_2}$	$1\text{-F}_{\text{SO}_2}^{\text{a)}$	Time
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hrs)
Temperature 25°C							
IV ^{b)} 1	$\left\{ \begin{array}{ll} \text{SO}_2 & 11.8 \\ \text{SOCl}_2 & 0.742 \\ \text{Me}_2\text{CO} & 0.661 \end{array} \right\}$	1090	2.68	1173	0.923	0.962	0
2		1110	19.4	1173	0.944	0.723	3.00
3		371	37.1	1173	0.274	0.470	15.0
4		181	39.3	1173	0.102	0.439	27.0
5		104	39.9	1173	0.031	0.430	39.0
6		37.0	36.4	1173	-0.03	0.480	75.0
7		39.7	31.9	1173	-0.03	0.544	350
V ^c 1	$\left\{ \begin{array}{ll} \text{SO}_2 & 1.29 \\ \text{SOCl}_2 & 8.28 \\ \text{Me}_2\text{CO} & 0.100 \end{array} \right\}$	0.617	4360	4360	0	0	0
2		0.570*	2834*	4360			4.00
3		48.5	1585*	4360	0.915		17.0
5		12.3*	3503	4360		0.774	31.4
6		48.5*	564*	4360			71.0
7		352	1702	4360	0.468	0.299	570

*Chemical and radiochemical balance unsatisfactory, these points not used.

(Continued on next page)

TABLE IIa (Cont'd.)

Exp. No.	Amount of Reactants	A_{SOCl_2}	A_{SO_2}	A_{O}	$1-F_{\text{SOCl}_2}$	$1-F_{\text{SO}_2}^{\text{a)}$	Time			
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hrs)			
Temperature 0°C										
XI ^{c)} -A	1	SO ₂ 4.63	5.30	1216	1308	0.988	0.879	26.1		
	2	SOCl ₂ 14.1	14.9	1120	1308	0.966	0.766	84.1		
	3	Me ₂ CO 0.677	93.0	840	1277	0.793	0.583	324		
XI ^{c)} -B	1	SO ₂ 4.63	9.09	741	0.954	0.912	96.0			
	2	SOCl ₂ 14.1								
	3	Me ₂ CO 0.624						20.2	741	0.912
XII ^{c)} -A	1	SO ₂ 14.1	1.61	530	0.994	0.979	74.0			
	2	SO ₂ 14.1	5.67					530	0.979	144
	3	SOCl ₂ 14.1	3.64					530	0.987	250
	4	Me ₂ CO 0.204	7.02					530	0.973	559
XII ^{b)} -B	1	SO ₂ 14.1	286	287	0.993	0.980	85.0			
	2	SO ₂ 14.1	284					287	0.980	300
	3	SOCl ₂ 14.1	279					287	0.950	401
	4	Me ₂ CO 0.204	279					287	0.915	999

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TABLE IIa (Cont'd.)

Exp. No.	Amount of Reactants		A_{SOCl_2}	A_{SO_2}	A_{O}	$1-F_{\text{SOCl}_2}$	$1-F_{\text{SO}_2}^{\text{a)}$	Time
	(millimoles)		(cpm/mg)	(cpm/mg)	(cpm/mg)			(hrs)
Temperature 0°C								
XVI ^{b)}	1	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 4.00 \\ \text{Me}_2\text{CO} & 2.70 \end{array} \right\}$	646	15.0	669	0.0428	0.877	1.00
	2		638	27.3	669	0.0572	0.776	3.00
	3		639	34.4	669	0.0558	0.717	5.00
	4		606		669	0.876		7.00
	5		517	53.4	669	0.814	0.514	23.1
XVII ^{b)}	1	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 4.00 \\ \text{Me}_2\text{CO} & 1.35 \end{array} \right\}$	518	23.6	566	0.896	0.771	24.2
	2		485	40.4	566	0.824	0.608	49.0
	3		489	39.4	566	0.820	0.606	75.0
	4		455	48.2	561	0.770	0.527	95.9
	5		453	49.0	561	0.765	0.519	123
XVIII ^{b)}	5	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 4.00 \\ \text{Me}_2\text{CO} & 4.05 \end{array} \right\}$	582	45.5	594	0.977	0.588	5.00
	1		544	53.8	603	0.848	0.509	9.60
	2		358	67.2	603	0.512	0.387	15.0
	3		373	67.1	600	0.540	0.386	20.0
	4		162	69.8	600	0.113	0.361	24.4
	6		112	67.1	594	0.009	0.378	35.0

(Continued on next page)

TABLE IIa (Cont'd.)

Exp. No.	Amount of Reactants	A_{SOCl_2}	A_{SO_2}	A_{O}	$1-F_{\text{SOCl}_2}$	$1-F_{\text{SO}_2}^{\text{a)}$	Time	
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hrs)	
Temperature 0°C								
XIX ^{b)}	1	$\left\{ \begin{array}{l} \text{SO}_2 \quad 6.93 \\ \text{SOCl}_2 \quad 0.742 \\ \text{Me}_2\text{CO} \quad 0.516 \end{array} \right\}$	426	22.3	428	0.995	0.456	16.0
	2		357	19.8	429	0.806	0.518	35.0
	3		342		417	0.801		48.0
	4		323	28.2	429	0.726	0.313	64.5
	5		259	23.4	417	0.580	0.415	86.0
XX ^{b,d)}	1	$\left\{ \begin{array}{l} \text{SO}_2 \quad 6.90 \\ \text{SOCl}_2 \quad 0.742 \\ \text{Me}_2\text{CO} \quad 0.482 \end{array} \right\}$	381	14.8	401	0.947	0.07**	16.0
	*2				401			
	3		277	42.2	391	0.695	-1.72**	66.5
	4		231	22.1	382	0.600	-0.46**	94.0
	*5				382			

*Ampoules 2 and 5 exploded during separation.

**The SO_2 fraction in this instance was freed of SOCl_2 , the most volatile tenth discarded and the remainder treated in the usual way. The result, very high activity in the SO_2 fraction, is a result of concentrating MeS^{35}H which arises from the reaction of $\text{S}^{35}\text{OCl}_2$ and Me_2CO .

a) Calculated from specific activity of SO_2 fraction. This fraction was apparently contaminated with MeS^{35}H or COS^{35} or both.

b) SOCl_2 initially active.

c) SO_2 initially active.

d) Run in absence of light.

TABLE IIb

Radiosulfur Exchange Experiments with Acetone at 0° (Procedure II)

Experiment Number	Reactants	A_{SOCl_2}	$A_{\infty}^{\text{a)}}$	$1-F^{\text{b)}}$	Time
	(millimoles)	(cpm/mg)	(cpm/mg)		(hrs)
VII-A 1	S^*O_2 4.45	4.28	60.5	0.929	51.7
2	SOCl_2 70.6	7.31	60.5	0.879	140
3	Me_2CO 4.10	10.9	60.5	0.820	245
VII-B 1	S^*O_2 4.56	8.60	86.0	0.900	108
2	SOCl_2 70.6	23.5	86.0	0.727	344
3	SOCl_2 70.6	32.1	86.0	0.627	487
4	Me_2CO 4.15	42.2	86.0	0.501	665
VIII-A 1	S^*O_2 6.42				
	SOCl_2 56.4	30.5	138	0.779	166
	Me_2CO 4.26				
VIII-B 2	S^*O_2 6.34	51.8	121	0.573	340
3	SOCl_2 56.4	67.7	115	0.410	494
4	Me_2CO 4.28	94.3	135	0.307	688

(Continued on next page)

TABLE IIb (Cont'd.)

Experiment Number	Reactants	A_{SOCl_2}	A_{∞} ^{a)}	$1-F$ ^{b)}	Time
	(millimoles)	(cpm/mg)	(cpm/mg)		(hrs)
IX ^{c)} 1	$\left\{ \begin{array}{ll} \text{S}^*\text{O}_2 & 6.50 \end{array} \right\}$	9.94	128	0.920	64.8
2	$\left\{ \begin{array}{ll} \text{SOCl}_2 & 56.4 \end{array} \right\}$	55.1	128	0.568	266
3	$\left\{ \begin{array}{ll} \text{Me}_2\text{CO} & 4.26 \end{array} \right\}$	74.8	128	0.409	468

a) A_{∞} is calculated from known initial specific activity of the S^*O_2 and the reactant concentrations.

$$\text{b) } 1-F = \frac{A_{\text{SOCl}_2} - A_{\infty}}{A_{\infty}} .$$

c) Me_2CO and SOCl_2 allowed to react about 60 hours at room temperature before SO_2 was dosed in and exchange reaction started.

TABLE III_a

Radiosulfur Exchange Experiments
with Antimony Pentachloride-Triethylamine Mixtures
(Procedure I)

Conditions: 0°C, 18.0 mmoles SO₂, 4.00 mmoles S*OCl₂

Exp. No.	SbCl ₅	Et ₃ N	A _S OCl ₂	A _{SO₂}	A _O	1-F	Exchange Time
	(mmoles)	(mmoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)		(hours)
1a ^{a)} 1	2.4	0.00	1740	75.3	2204	0.775 ^{b)}	25.8
2			1610	140		0.663 ^{b)}	49.8
3			1431	151		0.601 ^{b)}	60.4
4			1291	216		0.470 ^{b)}	80.2
5			1253	263		0.407 ^{b)}	93.9
3a ^{a)} 1	2.4	3.1	363	300	2039	0.034 ^{b)}	43.0
2	2.4 ^{c)}	3.6	301	303	2039	0.00	47.1
3	2.4	1.8	2016	43.8	2039	0.892 ^{b)}	38.3
4	2.4	1.3	1976	19.6	2039	0.948 ^{b)}	48.3
5a 2	0.854	0.714	846	7.54	860	0.966 ^{d)}	10.1
3			827		860	0.953 ^{d)}	19.9
4			908	7.36	912	0.930 ^{d)}	58.3
5			830		912	0.891 ^{d)}	131

(Continued on next page)

TABLE III - (Cont'd.)

Exp. No.		SbCl_5	Et_3N	A_{SOCl_2}	A_{SO_2}	A_{O}	1-F	Exchange Time
		(mmoles)	(mmoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)		(hours)
7a-A	1	0.854	0.0514	687	14.1	721	0.917 ^{b)}	17.8
	2			544	44.8	714	0.697 ^{b)}	71.0
	3			523	52.7	714	0.634 ^{b)}	94.1
-B	4	0.854	0.096	653	23.2	707	0.855 ^{b)}	35.6
	5			480	58.9	707	0.585 ^{b)}	108
8a	1	0.854	0.830	242		244	0.991 ^{d)}	37.4
	2			253		244	-0.042 ^{d)}	64.0
	3			227	3.68	243	0.917 ^{d)}	121
	4			227		249	0.893 ^{d)}	180
	5			224	6.89	255	0.851 ^{d)}	288
9a-A	1	0.854	0.0	220		252	0.845 ^{d)}	20.0
	2			203		252	0.763 ^{d)}	40.0
	3			193		252	0.714 ^{d)}	60.0
	4			178		252	0.643 ^{d)}	80.0

(Continued on next page)

TABLE III - (Cont'd.)

Exp. No.	SbCl_5	Et_3N	A_{SOCl_2}	A_{SO_2}	A_o	1-F	Exchange Time
	(mmoles)	(mmoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)		(hours)
9a-B 5	0.854	0.913	234		252	0.911 ^{d)}	5.00
6			217		252	0.831 ^{d)}	10.0
7			183		252	0.683 ^{d)}	20.0
8			110		252	0.311 ^{d)}	25.0
-C 9	0.854	1.854	217		252	0.829 ^{d)}	0.50
10			195		252	0.721 ^{d)}	1.00
11			158		252	0.546 ^{d)}	2.00
12			120		252	0.361 ^{d)}	3.00
-D 13	0.854	4.854	197		248	0.751 ^{d)}	0.333
14			166		248	0.595 ^{d)}	0.667
15			145		248	0.494 ^{d)}	1.00
16			117		248	0.353 ^{d)}	1.50

a) Inaccuracy in SbCl_5 concentration about 30%.

b) Average of (1-F) calculated from 1) A_o and A_{SOCl_2} and 2) A_o and A_{SO_2} .

c) Complete exchange within the sampling time.

d) Calculated from A_o and A_{SOCl_2} .

TABLE IIIb

Radiosulfur Exchange Experiments
with Antimony Pentachloride-Triethylamine Mixtures
(Procedure III)

Conditions: 0°C, 18.0 mmoles SO₂, 4.00 mmoles S*OCl₂

Exp. No.		SbCl ₂	Et ₃ N	Exchange Time	A _{SO₂}	A _∞ ^{a)}	Sample Size	R _c ^o x t
		(mmoles)	(mmoles)	(hours)	(cpm/mg)	(cpm/mg)	(mmoles)	(moles/l)
2a ^{b)}	a	0.64	0.224	15.4	57.2	396	0.153	0.0192
	b			41.6	128	403	0.220	0.0480
	c			58.2	175	412	0.164	0.0696
	d			∞	418	418	6.644	
6a	a	0.854	0.357	4.00	5.82	164	0.248	0.00510
	b			14.6	11.0	166	0.237	0.00980
	c			47.4	26.1	169	0.216	0.0244
	d			68.9	34.8	170	0.240	0.0336
	e			103	57.3	172	0.278	0.0602
	f			126	73.8	173	0.040	0.0839
	g			∞	174	174	18.03	

a) Calculated from A_∞ from final sample and known change in concentration of sulfur and sulfur-35.

b) 1.4 mmoles S*OCl₂ and 6.29 mmoles SO₂ in this run.

TABLE IV
Radiosulfur Exchange Experiments with Triethylamine
(Procedure I)

Exp. No.	Reactants		A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{SO_2}^{a)}$	$1-F_{SOCl_2}^{b)}$	Exchange Time
	(millimoles)		(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)
Temperature 0°C								
13 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 4.00 \\ Et_3N & 0.0593 \end{array} \right\}$	213	1547	2479	0.528	0.544	24.1
	2		323	1035	2479	0.283	0.294	40.8
	3		340	991	2479	0.247	0.272	50.8
	4		377	870	2479	0.164	0.216	55.8
	5		393	795	2479	0.129	0.174	65.2
14 ^{c)}	2	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 4.00 \\ Et_3N & 1.00 \end{array} \right\}$	4.44	832	866	0.972	0.955	0
	1		17.7	769	866	0.885	0.863	0.500
	3		52.7	667	866	0.665	0.718	1.27
	4		121	306	881	0.216	0.208	4.00
	5		154	186	881	0.038	0.036	8.10
15 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 4.00 \\ Et_3N & 3.96 \end{array} \right\}$	29.9	708	828	0.800	0.823	0.252
	3		619	619	828	0.692	0.692	0.500
	2		86.8	446	828	0.421	0.437	0.750
	4		90.5	402	828	0.397	0.372	1.00
	5		106	346	828	0.293	0.289	1.25

(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A _{SO₂}	A _{SOCl₂}	A _O	1-F _{SO₂} ^{a)}	1-F _{SOCl₂} ^{b)}	Exchange Time	
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)	
Temperature 0°C								
21 ^{c)}	1	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 0.742 \\ \text{Et}_3\text{N} & 0.0505 \end{array} \right\}$	2.97	355	377	0.801	0.940	2.00
	2			248	377		0.645	15.4
	3		10.1	194	377	0.322	0.505	24.0
	4		11.2	141	368	0.235	0.357	36.0
	5		14.0	96.0	368	0.044	-0.002	48.0
22 ^{c)}	1	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 0.742 \\ \text{Et}_3\text{N} & 0.146 \end{array} \right\}$	7.3	227	356	0.480	0.623	7.40
	2		7.7	208	356	0.453	0.567	10.5
	3		12.5	71.8	350	0.099	0.172	19.3
	4		12.4	67.7	344	0.105	0.164	23.1
	5		14.2	34.8	344	-0.04	0.064	32.3
23 ^{c)}	1	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 0.742 \\ \text{Et}_3\text{N} & 0.641 \end{array} \right\}$	2.70		346	0.802		0.500
	2		3.26		346	0.762		1.00
	3		6.10		343	0.550		1.50
	4		4.77		343	0.648		2.00
	5		6.64		342	0.497		2.52
24 ^{c)}	1	$\left\{ \begin{array}{ll} \text{SO}_2 & 28.3 \\ \text{SOCl}_2 & 0.522 \\ \text{Et}_3\text{N} & 0.0782 \end{array} \right\}$	7.24	2166	2533	0.842	0.853	5.00
	2		14.9	2101	2533	0.676	0.826	10.0
	3		23.2	1656	2533	0.494	0.648	18.2
	4		31.5	1237	2526	0.312	0.520	24.0
	5		30.9		2526	0.324		30.0
			957	2483		0.374	30.0	

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(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{SO_2}^{a)}$	$1-F_{SOCl_2}^{b)}$	Exchange Time	
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)	
Temperature 25°C								
25 ^{c)}	2	{ SO ₂ 28.5 SOCl ₂ 0.522 Et ₃ N 0.0782 }	24.2	1277	2427	0.446	0.517	2.50
	3 ^{d)}		33.0	700	2427	0.244	0.276	5.00
	4		37.4	334	2328	0.107	0.128	8.00
	1 ^{d)}		41.3	215	2427	0.055	0.072	10.3
	5		39.5	143	2328	0.058	0.044	12.6
26 ^{c)}	1	{ SO ₂ 52.2 SOCl ₂ 0.522 Et ₃ N 0.0513 }	8.4	1913	2317		0.824	2.30
	2		10.0	1521	2317		0.653	4.00
	3		1124	2351		0.473	7.00	
	4		1074	2351		0.452	8.00	
	5		814	2351		0.340	10.0	
27 ^{c)}	1	{ SO ₂ 18.0 SOCl ₂ 0.992 Et ₃ N 0.0503 }	24.3	2044	2351	0.811	0.862	0.500
	2		37.3	1706	2210	0.676	0.759	1.00
	3		59.4	1262	2210	0.484	0.547	2.00
	4		81.6	794	2210	0.291	0.324	4.00
	5		95.2	449	2210	0.173	0.159	6.00

(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{SO_2}^{a)}$	$1-F_{SOCl_2}^{b)}$	Exchange Time
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)
Temperature 25°C							
28 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 3.98 \\ Et_3N & 0.0634 \end{array} \right\}$	9.4	575	618 ^{e)}	0.917	0.200
	2		16.1	549	621 ^{e)}	0.857	0.403
	3		24.0	496	614 ^{e)}	0.766	0.800
	4		43.3	397	592 ^{e)}	0.597	1.60
	5		59.5	313	584 ^{e)}	0.434	2.60
29 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 4.01 \\ SOCl_2 & 3.98 \\ Et_3N & 0.0203 \end{array} \right\}$	20.7	556	577 ^{e)}	0.928	0.200
	2		38.8	548	587 ^{e)}	0.868	0.420
	3		48.5	532	581 ^{e)}	0.832	0.600
	4		66.5	495	562 ^{e)}	0.763	0.800
	5		70.6	480	550 ^{e)}	0.743	1.00
30 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 3.98 \\ Et_3N & 0.00547 \end{array} \right\}$		537	573 ^{e)}	0.923	2.00
	2		13.3	518	579 ^{e)}	0.873	4.00
	3		20.0	480	571 ^{e)}	0.807	6.00
	4		21.6	479	577 ^{e)}	0.793	8.00
	5		33.0	418	567 ^{e)}	0.679	12.4

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TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{SO_2}^{a)}$	$1-F_{SOCl_2}^{b)}$	Exchange Time	
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)	
Temperature 25°C								
31 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 3.98 \\ Et_3N & 0.0173 \end{array} \right\}$	12.1	524	578 ^{e)}	0.884	0.884	0.75
	2		15.9	481	553 ^{e)}	0.841	0.841	1.50
	3		29.7	660	0.752			2.25
	4		48.0	461	660	0.599	0.632	3.00
	5		53.6	439	660	0.552	0.594	3.75
Temperature 35°C								
32 ^{c)}	1	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 0.522 \\ Et_3N & 0.0497 \end{array} \right\}$	15.6	107	644	0.139	0.142	3.25
	2		17.0	34.7	644	0.0628	0.0264	6.00
	3		27.1	19.9	631	-0.523	0.0034	9.50
	4		18.3	18.2	631	-0.026	0.0006	11.5
	5		16.0		598	0.054		14.0
Temperature 15°C								
33 ^{c,f)}	2	$\left\{ \begin{array}{ll} SO_2 & 18.0 \\ SOCl_2 & 0.522 \\ Et_3N & 0.0189 \end{array} \right\}$		353	598		0.578	0
	1			150	598		0.229	12.6
	3			49.3	598		0.056	24.0
	4			44.5	566		0.052	36.0
	5			52.8	566		0.067	48.0

(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_O	$1-F_{SO_2}^{a)}$	$1-F_{SOCl_2}^{b)}$	Exchange Time
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)
Temperature 25°C							
34 ^{g)}	1 { SO ₂ 0.291		87.8	5801		0.028	5.00
	2 { SO ₂ 0.291		88.4	5762		0.022	10.0
	3 { SOCl ₂ 18.33		83.4	5762		0.071	15.0
	4 { Et ₃ N 0.0186		86.7	5762		0.034	20.0
	5 { Et ₃ N 0.0186		90.1	5762		-0.040	25.2
35 ^{g)}	1 { SO ₂ 0.870	4655	88.1	5762	0.788	0.839	1.00
	2 { SO ₂ 0.870	4230	161	5762	0.706	0.706	2.00
	3 { SOCl ₂ 8.28	3694	213	5762	0.605	0.610	3.00
	4 { Et ₃ N 0.0088	2453	338	5846	0.359	0.392	6.00
	5 { Et ₃ N 0.0088	1978	412	5846	0.269	0.259	7.00
36 ^{g)}	1 { SO ₂ 0.870	1011	26.5	1272	0.771	0.803	2.00
	2 { SO ₂ 0.870	877	45.6	1272	0.653	0.662	4.00
	3 { SOCl ₂ 8.28	700	61.3	1262	0.508	0.489	6.00
	4 { Et ₃ N 0.0055	596	71.9	1262	0.416	0.398	8.00
	5 { Et ₃ N 0.0055	416	88.8	1260	0.260	0.260	12.0
37 ^{g)}	1 { SO ₂ 0.870	999	22.8	1243	0.783	0.807	0.500
	2 { SO ₂ 0.870	620	67.6	1243	0.446	0.429	1.00
	3 { SOCl ₂ 8.28	327	96.2	1233	0.187	0.180	1.50
	4 { Et ₃ N 0.0460	258	104	1233	0.126	0.118	2.50
	5 { Et ₃ N 0.0460	169	117	1233	0.042	0.042	3.50

(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{SO_2}^{a)}$	$1-F_{SOCl_2}^{b)}$	Exchange Time	
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)	
Temperature 25°C								
38 ^{g)}	1	SO ₂ 2.30	1136	23.1	1239	0.894	0.914	1.00
	3	SOCl ₂ 8.28	730 ^{h)}	46.2	1239	0.475	0.829	2.00
	4	Et ₃ N 0.0061	1017	52.3	1209	0.771	0.801	2.50
	5		938	77.2	1209	0.714	0.706	3.50
39 ^{g)}	3	SO ₂ 0.288	1245		1250	0.997		0
	1		644	18.8	1250	0.498	0.522	4.00
	2	SOCl ₂ 8.28	425	26.9	1250	0.317	0.360	7.00
	4	Et ₃ N 0.0060	303	34.4	1250	0.216	0.181	10.0
	5		186	35.6	1250	0.119	0.152	14.0
40 ^{g)}	1	SO ₂ 0.288	666	7.94	1211	0.543	0.576	3.00
	2		474	11.4	1211	0.383	0.394	6.00
	3	SOCl ₂ 18.33	343	13.4	1211	0.273	0.287	8.00
	4	Et ₃ N 0.0119	258	14.9	1211	0.201	0.206	10.0
	5		152	16.1	1211	0.112	0.143	14.0

(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{\text{SO}_2}^{\text{a)}$	$1-F_{\text{SOCl}_2}^{\text{b)}$	Exchange Time
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)
Temperature 0°C							
41 ^{g)}	$\left\{ \begin{array}{ll} \text{SO}_2 & 0.863 \\ \text{SOCl}_2 & 8.28 \\ \text{Et}_3\text{N} & 0.00602 \end{array} \right\}$	878	17.1	1127	0.841	0.756	12.0
2		725	34.2	1127	0.679	0.606	25.0
3		622	47.0	1127	0.558	0.505	36.0
4		525	57.0	1111	0.457	0.418	48.0
5		420	71.0	1111	0.323	0.313	68.0
Temperature 35°C							
42 ^{g)}	$\left\{ \begin{array}{ll} \text{SO}_2 & 0.866 \\ \text{SOCl}_2 & 8.28 \\ \text{Et}_3\text{N} & 0.00599 \end{array} \right\}$	867	15.9	1088	0.844	0.776	0.750
2		783	30.0	1088	0.703	0.691	1.50
3		641	42.1	1088	0.545	0.547	2.62
4		510	63.2	1088	0.377	0.414	4.00
5		298	83.8	1088	0.173	0.199	7.00
Temperature 0°C							
43 ^{c)}	$\left\{ \begin{array}{ll} \text{SO}_2 & 18.0 \\ \text{SOCl}_2 & 0.711 \\ \text{Et}_3\text{N} & 0.765 \end{array} \right\}$	2.77		440	0.835		0.500
2		4.68		440	0.720		1.05
3		6.61		440	0.604		2.00
4		10.5		440	0.371		4.00
5		13.6		440	0.186		6.01

(Continued on next page)

TABLE IV - (Cont'd.)

Exp. No.	Reactants	A_{SO_2}	A_{SOCl_2}	A_o	$1-F_{SO_2}$ ^{a)}	$1-F_{SOCl_2}$ ^{b)}	Exchange Time
	(millimoles)	(cpm/mg)	(cpm/mg)	(cpm/mg)			(hours)
Temperature 0°C							
44 ^{c)}	1	$\left\{ \begin{array}{l} SO_2 \quad 18.0 \\ SOCl_2 \quad 0.711 \\ Et_3N \quad 1.53 \end{array} \right\}$	1.59	425	0.901		0.300
	2		2.70	425	0.833		0.496
	3		6.23	425	0.614		1.00
	4		11.2	425	0.383		2.00
	5		11.5	434	0.302		3.50
45 ^{c,i)}	2	$\left\{ \begin{array}{l} SO_2 \quad 17.8 \\ SOCl_2 \quad 0.711 \\ Et_3N \quad 0.66 \\ \quad \pm 0.06 \end{array} \right\}$	2.75	307	0.764		0.500
	3		4.33	307	0.628		1.50
	4		9.12	307	0.217		3.50
	5		9.81	307	0.158		4.50
46 ^{c,j)}	1	$\left\{ \begin{array}{l} SO_2 \quad 18.0 \\ SOCl_2 \quad 1.33 \\ \quad \pm 0.08 \\ Et_3N \quad 0.765 \end{array} \right\}$	6.90	307	0.628		1.00
	2		10.7	307	0.425		2.00
	3		12.4	307	0.332		3.00

a) Calculated from A_o and A_{SO_2} .

b) Calculated from A_o and A_{SOCl_2} .

c) $SOCl_2$ initially active.

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TABLE IV - (Cont'd.)

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- d) The SOCl_2 and Et_3N were allowed to react briefly at -10° before SO_2 was added.
 - e) A_0 calculated from A_{SO_2} and A_{SOCl_2} .
 - f) Bad run. Bath relay stuck for a time before initial sample taken. Hence first sample shown was taken arbitrarily as zero time and gave high zero time exchange. Thus calculated rate was of but low precision.
 - g) SO_2 initially active.
 - h) Poor counting sample.
 - i) $\text{SO}_2 + \text{Et}_3\text{N}$ allowed to interact 30 minutes at 0°C and excess SO_2 evaporated before S^*OCl_2 dosed in and exchange started. Uncertainty in Et_3N concentration approximately $\pm 10\%$.
 - j) $\text{S}^*\text{OCl}_2 + \text{Et}_3\text{N}$ allowed to interact 30 minutes at 0°C and volatile material evaporated before SO_2 and additional S^*OCl_2 dosed in and exchange started.

experiments employing a mixture of triethylamine and antimony pentachloride as catalysts, thionyl chloride as the initially active component and sulfur dioxide as the solvent. The reactants were dosed into an ampoule fitted with a pressure stopcock as in the second method. Here, sulfur dioxide samples (approximately 0.25 mmoles each) were withdrawn periodically by evaporation to observe the exchange rate. Table IIIb contains the data from these experiments.

The major difference in Procedure II and Procedure III was in the amounts of material withdrawn for sampling relative to the amounts in solution. In Procedure II, the total thionyl chloride amounted to 50 to 70 mmoles and the amount of thionyl chloride removed for assay prior to the termination of the reaction was less than 1 mmole, whereas in the last procedure only 18.0 mmoles of sulfur dioxide were initially present, and prior to the termination of the run as much as 1.3 mmoles of sulfur dioxide had been removed from the solution. In this last case then, it was necessary to correct the calculated rates for the resulting change in concentration throughout the course of the run.

B. Dosing

In most cases, measured amounts of the reactants

were condensed into the reaction ampoules by cooling these containers with liquid nitrogen. Alternatively, part of the reactants could be pipetted into the ampoules in the dry box, the contents frozen and the stoppered containers attached to the vacuum line and evacuated, whereupon, the remaining reactants were condensed onto those previously pipetted.

Sulfur dioxide was dosed as a gas, a known volume at a known temperature and pressure being condensed into the reaction tube.

In most cases, thionyl chloride was dosed as a liquid from a cold finger doser, calibrated at 0°C to contain a known volume of thionyl chloride between two scratch marks. After filling this doser from the storage ampoule, thionyl chloride was distilled back to storage until the liquid level in the doser, which was cooled with ice-water mixture, dropped to the upper calibration mark. The contents of the doser were distilled into the reaction ampoule until the liquid level dropped to the lower calibration mark. Finally, the remaining contents of the doser were transferred to the all-glass storage container. This procedure tended to remove any volatile or relatively non-volatile impurities from the thionyl chloride. Triethylamine and acetone were dosed either as liquids from calibrated cold fingers, in the same manner

as the thionyl chloride, or as vapors from calibrated volumes at known temperature and at the vapor pressure of the liquid at a known temperature. Stock solutions of antimony pentachloride in thionyl chloride were made up in the dry box and these solutions were pipetted into reaction ampoules. In a few instances, it was convenient to dose triethylamine and acetone also by pipetting the pure liquids into the bombs in the dry box.

C. Separation

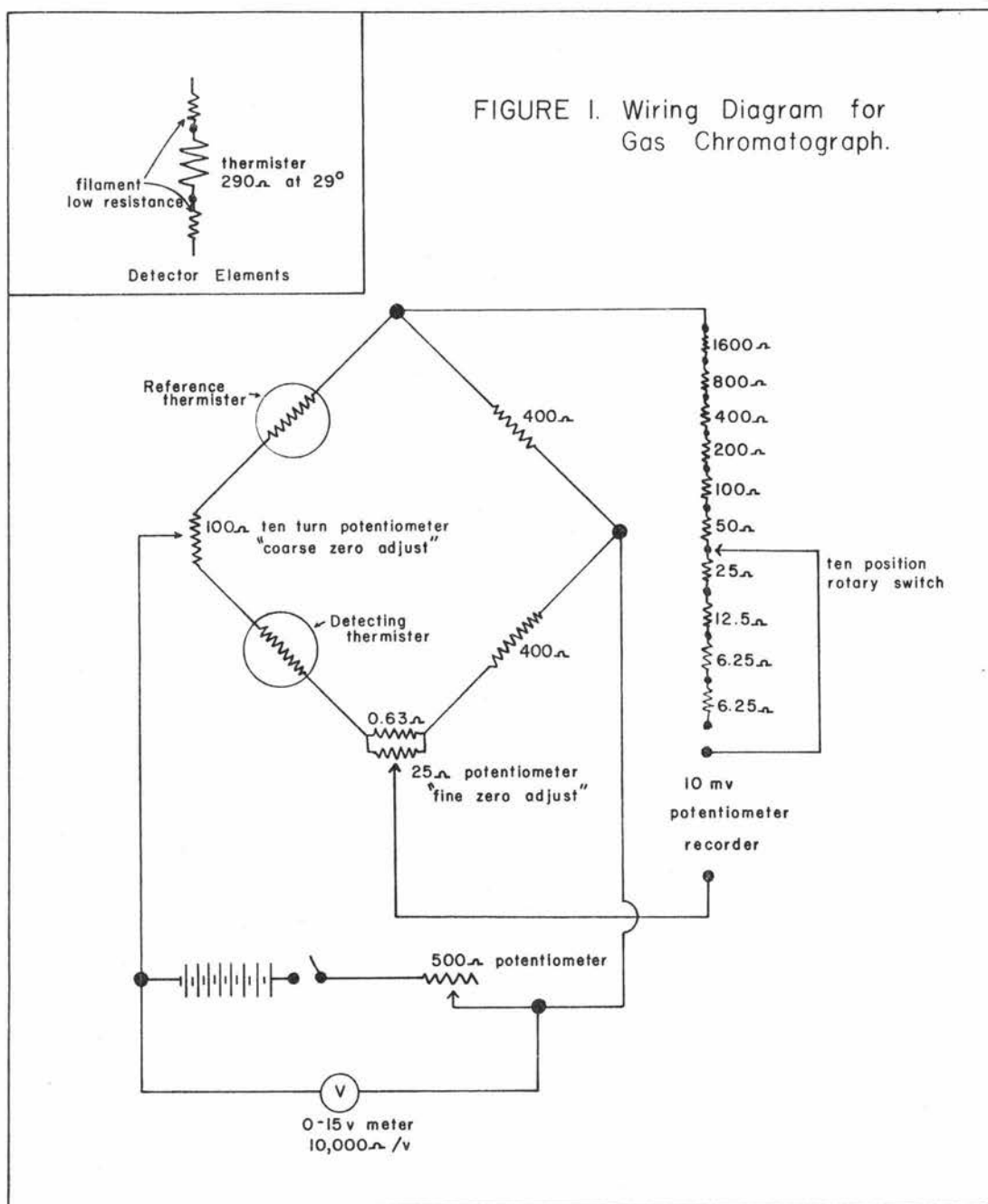
It is necessary in any investigation of an isotopic exchange reaction finally to separate the reactants reproducibly, as nearly quantitatively as possible, and without inducing exchange. In past work dealing with the $\text{SO}_2\text{-S}^{35}\text{OCl}_2$ exchange reaction (6, 12, 24) the reactants have been (incompletely) separated by taking a sample of the vapor over the liquid solution held at -20°C . Separation errors inherent in this procedure here led to rather large and inconsistent values for the apparent fraction of exchange at zero-time, i.e., exchange seeming to have occurred before the reaction has actually been initiated. The result has been scatter in the data -- in some cases enough to invalidate runs. Thus it was thought proper to investigate some other methods of separating the exchange reactants.

In view of the success of Burge (5, p. 11-16) in separating sulfur dioxide and thionyl chloride using a gas chromatograph, it seemed appropriate to attempt to develop a method utilizing this instrument for the separation of the exchange mixtures, and considerable effort was expended towards this end.

Although the method was eventually used only for analysis rather than practical reactant separation, it still appears to have potentialities for this purpose, and so it has seemed of interest to record details of this developmental effort. A gas chromatograph of conventional design was constructed. A commercial cell¹ with matched thermistor elements (290 ohm resistance at 29°C) was used as the detector. The thermistors of the cell were made two legs of a Wheatstone bridge (see Figure 1), the other two legs being 400 ohm resistors. The power supply (12 volts) was a pack of dry cells, the voltage supplied to the bridge was varied by a 500 ohm potentiometer and read by a voltmeter (15 volts full scale). The bridge imbalance was measured on a strip-chart, recording potentiometer² of 10 mv span fed through a voltage dividing circuit to increase the useful range

¹Available from Gow-Mac Instrument Co., Madison, New Jersey. Model 9680.

²Available from Varian Associates, Palo Alto, Calif. Model G-11 A.



of the instrument. Zero adjustment was by variable resistors at two "corners" of the bridge.

In this instrument, in practice, helium, the carrier gas, after passing through a rotameter, passes successively through the reference side of the detector cell, the vapor sampler, the column, the detector side of the cell and out through the sample collector. When only helium is flowing, the filaments in the detector and the reference side of the detecting cell are cooled to the same extent and the bridge is balanced. In the presence of a sample, which has a thermal conductivity less than that of helium, the detector filament becomes warmer than the reference filament and the bridge becomes unbalanced. (The amount of unbalance is a complex function of the change in resistivity of the thermistor with temperature change, the heat conductivity of the sample vapor and the amount of sample vapor.)

Figure 2a shows the vapor sampler employed. First, during a run, helium flows in and through the short "S"-shaped loop and on through the instrument. During this time the bridge can be balanced. Meanwhile, the sample loop, the longer loop, is filled (by expansion) with vapor from the vacuum system. With the bridge balanced and the sample in the long loop, both stopcocks are rotated 180° and the helium stream sweeps

FIGURE 2a. Vapor Sampler for Gas Chromatographic Analysis.

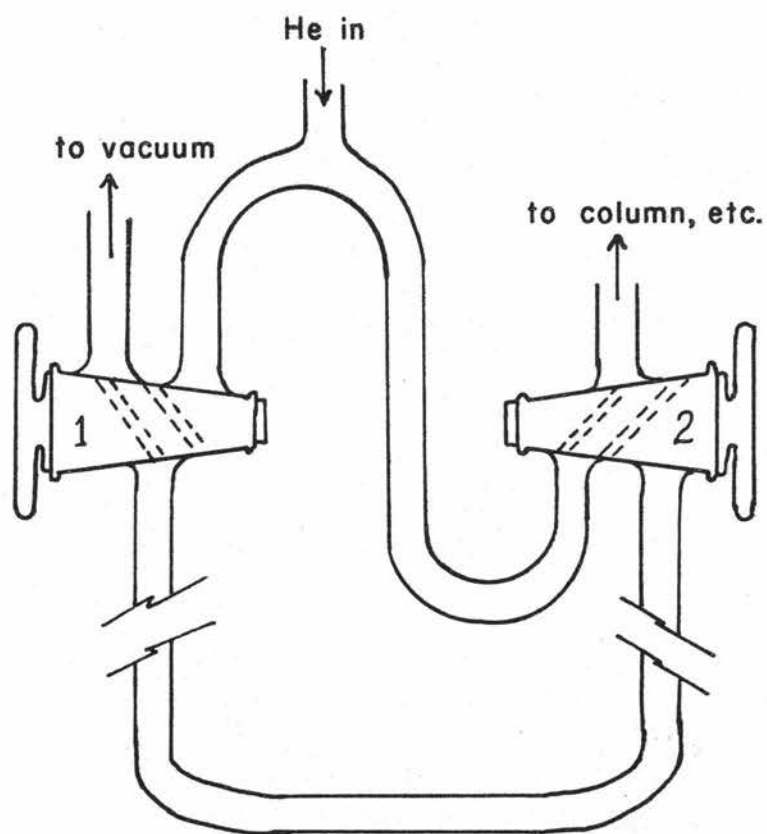
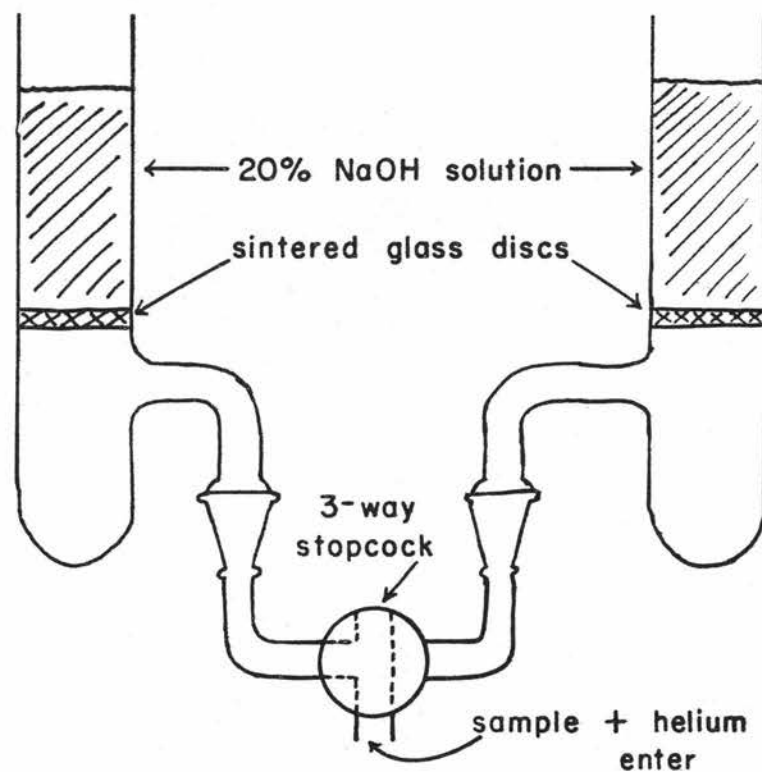


FIGURE 2b. Sample Collector for Gas Chromatographic Separation.



the sample into the column, through the detector and into the sample collection bubbler.

Columns were constructed of 8 mm o.d. glass tubing about one meter long, bent in the shape of a "U". A number of different packings were used and are listed in Table V. These packings were prepared in the following way: the liquid was dissolved in enough petroleum ether to make a thin slurry on addition of the solid support. The slurry was thoroughly mixed and then the petroleum ether was evaporated off. When the mixture appeared dry (and there remained no odor of petroleum ether) the packing was dried for at least 2 hours at 110°C. It was then packed into the column, the column attached to the instrument by means of ball and socket joints, and conditioned by passing several samples of thionyl chloride through it.

The sample collector is shown in Figure 2b. The effluent from the detector passes through a three-way stopcock, up through a fritted glass disc which supports several milliliters of 20% NaOH solution (which contains a few drops of octanol to reduce foaming). After the first portion of the sample has been collected in the sodium hydroxide solution, rotation of the stopcock 180° sends the gas stream through the other bubbler for collection of the second portion of sample.

TABLE V

Column Packings Used in Gas Chromatography Experiments

Solid Support		Liquid Phase		Retention Time $\text{SOCl}_2^{\text{a)}$		Comments
					Retention Time SO_2	
Celite 545 ^{b)} 40-100 mesh	10 g	Silicone oil ^{c)}	4 g		9	"Ideal" chromatograms about 10 minute separation of components ^{d)}
	10 g		5 g		11	"Tailing" of both peaks, about 6 minute separation of components
	50 g	Dibutyl phthalate	20 g			Extreme tailing, peaks overlap
	50 g		10 g		6	Tailing bad on SOCl_2 peak, about 6 minute separation
	10 g	Squalane	4 g			Only one peak
	10 g		3 g			Peaks not well resolved

(Continued on next page)

TABLE V - (Cont'd.)

Solid Support		Liquid Phase	Retention Time SOCl_2 ^{a)}		Comments
				Retention Time SO_2	
Chromosorb ^{e)} 30-60 mesh	10 g	Silicone oil ^{c)} 2 g		4	"Ideal" chromatograms, peaks well resolved 4 minutes apart
	10 g	Dibutyl phthalate 2 g		3	Some "tailing", peaks not well resolved
	10 g	Squalane 2 g			Peaks overlap
Silica gel	10 g	Silicone oil ^{c)} 2 g			No effluent

- a) The retention time of the sample is here taken as the time from when the sample is introduced into the instrument by rotation of the two stopcocks until the peak maximum appears on the chromatogram. These ratios of retention time are all for flow rates of $45 \text{ cm}^3/\text{min}$ and column held at room temperature.
- b) Celite 545 is the trade name for a diatomaceous filter aid and is supplied by Johns-Manville Co., San Francisco, Calif.
- c) Dow-Corning 200 Fluid is the designation of this silicone-type material of 50 centistokes viscosity at 20°C . It is available from the Dow-Corning Co., Midland, Michigan.
- d) Component separation is the time from when the chromatogram returns to the baseline after one component passes until the appearance of the second component.

(Continued on next page)

TABLE V - (Cont'd.)

- e) Trade name for a crushed, acid-washed fire brick. It is sold by Wilkins Instrument and Research, Inc., Walnut Creek, Calif.

The instrument was always operated at a filament voltage of 8.4 volts. Optimum flow rate seemed to be approximately $45 \text{ cm}^3/\text{min}$. At lower flow rates there was significant "tailing" in most columns and the helium pressure necessary for flow rates much greater than this caused leaks in the ball and socket joints. The detector and vapor sampler were open to the laboratory temperature fluctuations, while the column was placed in a constant temperature oven. In no case was there observed any advantage to heating the column, and, in general, it was maintained at room temperature along with the detector and sampler.

In Table V are given a list of the column packings used and some comment on the chromatograms obtained in using columns packed with these mixtures. Of the mixtures tried, the two best were clearly the silicone oil on Celite or fire brick. (The former column was used in all cases for analysis of thionyl chloride for volatile impurities.) Both columns were tested for their ability to separate labeled sulfur dioxide from thionyl chloride. Using the Celite column and a 1:1 molar mixture of thionyl chloride and labeled sulfur dioxide (in which, of course, no true exchange had occurred), three successive samples taken from the mixture showed an apparent fraction exchange, F , of less than 0.05. Here,

$$F = A/A_{\infty} \quad (13)$$

where F is the apparent fraction exchange, A is the observed specific activity of the effluent thionyl chloride, A_{∞} is the "complete exchange" specific activity of either the thionyl chloride or the sulfur dioxide calculated for complete randomization of the S^{35} on the basis of the actually observed specific activities and amounts of the effluent sulfur dioxide and thionyl chloride. With further successive samples from the same "no exchange" mixture, apparent F values increased to 0.05, 0.23, 0.41 and 0.57. Using the fire brick-silicone column, some improvement was noted, F increasing only from 0.001 to 0.20 in eight successive samples.

This unsatisfactory increase in apparent F values with succeeding samples is presumably due to the partial irreversible adsorption of the sample on the support material, the adsorbed material being then eluted by subsequent samples. With the large variety of support materials now available, it should be possible with sufficient effort to find one capable of separating mixtures of labeled sulfur dioxide and thionyl chloride more satisfactorily than the column packings so far tried. However, a problem other than the increase in apparent fraction exchange exists in that it was impossible, even

with the best column found, to separate more than approximately 0.05 mmole of the major component in a mixture without "overloading" the column. Thus, only about 10-15 mg of barium sulfate from the major component was available for assay, and this is not really sufficient for the preparation of good counting samples. This difficulty could be overcome by using larger diameter (and longer) columns or with the aid of other counting techniques, such as liquid scintillation counting. As a practical matter, however, at this stage of the experiments with the gas chromatographic technique, concurrent experiments in vacuum fractionation, mentioned earlier, had shown that this alternative technique could be used to separate the exchange solution components quite effectively and so the gas chromatograph was utilized thereafter only to analyze volatile mixtures.

Since the reproducible separation of reactants is such an important part of the investigation of exchange reactions, a detailed description of the procedure used in this particular study is in order. This procedure and the apparatus used in it evolved somewhat during the course of the study, but in no essential details did it differ from what follows. The apparatus is shown in Figure 3 and consists of three "U" traps in series; C,

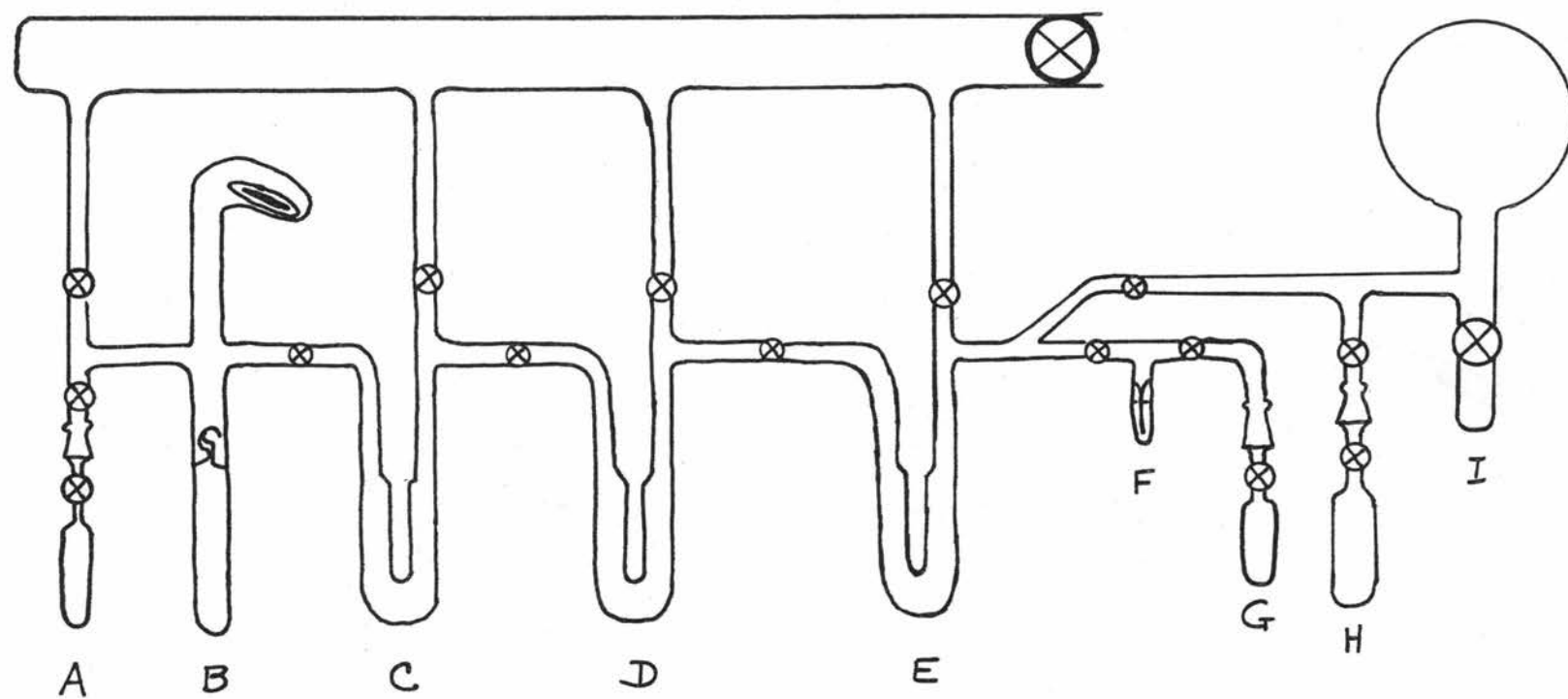


FIGURE 3. Separation System.

D, E, followed by the sample-taking sections for sulfur dioxide and thionyl chloride in parallel. The sulfur dioxide sampler consists of a bulb of 650 milliliter capacity connected through a large stopcock to a cold finger, I, below it and the sample collection tube, H, attached to the line by means of a standard taper joint. The thionyl chloride sampling section was made up of a capillary finger doser, F (calibrated to contain 0.3 mmoles of thionyl chloride), and the sample collection tube, G.

The separation procedure was slightly different depending on which of the three run procedures was used (see above), the sealed ampoule, the stopcock-ampoule containing excess thionyl chloride or the stopcock-ampoule with excess sulfur dioxide. The method where the solution was in a sealed ampoule is as follows: the sealed ampoule was provided with a break-tip. It was taken from the bath, frozen, sealed to the line (B in the diagram) and the system evacuated to 10^{-5} mm of Hg. When a good vacuum was attained, the separation system was isolated from the vacuum manifold and the ampoule opened. With trap C cooled with Dry Ice-acetone and trap D with liquid nitrogen, the sample was allowed to thaw slowly. When the sample had all evaporated, trap C was isolated from D, trap E was cooled with

Dry Ice-acetone and cold finger I with liquid nitrogen and the material in trap D (mostly sulfur dioxide) was allowed to warm slowly. At this point the procedure varied. If sulfur dioxide had been the major solution component, only about one-tenth the material in trap D was transferred to the cold finger; if sulfur dioxide had been the minor component, all of the material in trap D that would pass through trap E was transferred. In either case, the material remaining in traps D and E were condensed into cold finger A, the sulfur dioxide sampling section was isolated from the remainder of the system and I warmed to -80°C . After 10 minutes equilibration, the stopcock above I was closed, the material that had evaporated from I condensed into sample collection tube H which was then set aside for assay.

In the meantime, traps D and E were pumped out and flamed to remove any adsorbed sulfur dioxide. Most of the material in trap C was transferred to cold finger A, leaving behind perhaps 0.5-1 mmole of thionyl chloride. Trap D was then cooled with Dry Ice-acetone and the material in C allowed to warm slowly. The vapors passing through D were collected in A. This step was repeated with traps D and E and cold finger A. The material finally collected in trap E was transferred to the capillary doser, F. Any material in F above the

calibration mark was distilled back to A, and finally, the remaining thionyl chloride was distilled into sample tube G for analysis.

In the two procedures where stopcock-closed reaction ampoules were used, they were "A" in the drawing. Only the solution component in excess was taken as a sample and all material not separated for analysis was returned to the reaction ampoule.

This procedure served to separate the most volatile material from the least. In some cases it was necessary to change the procedure slightly. The exchange solutions contained, at the start at least, not only sulfur dioxide and thionyl chloride, but also triethylamine, acetone or mixtures of triethylamine and antimony pentachloride. In most instances, the catalysts did not interfere with the separation procedure since rather non-volatile products are formed during the course of the reaction. Where large amounts of catalyst were present, at least in the instances of triethylamine and acetone, enough of these substances evaporated in the first step of the separation so that not all the material that condensed into trap C could be transferred out, since there was formed a non-volatile reaction product between the catalyst and thionyl chloride. Thus, not the least volatile fraction but rather a middle cut of the least

volatile fraction was collected as the " SOCl_2 fraction."

Exchange ampoules involving acetone were found to yield materials other than sulfur dioxide (see below) which contained S^{35} and were collected in the " SO_2 fraction." Attempts to free the sulfur dioxide of these contaminants on a routine basis were unfortunately uniformly unsuccessful.

D. Non-equilibrium Conditions in Exchange Solutions

The rate equations most commonly used for interpreting isotopic exchange reaction results are based on the assumption that the solution involved is at chemical equilibrium in a single phase (35, p. 6-11). Rate equations have also been developed, however, for certain special instances of non-equilibrium behavior in homogeneous exchange solutions, for instance, where one of the exchanging species is being converted to the other while simultaneously undergoing exchange (20).

Either acetone or triethylamine dissolved in thionyl chloride or thionyl chloride-sulfur dioxide mixtures forms initially a colorless solution, which, in time, becomes colored. Hence, these evidently represent unstable systems. Spandau and Brunneck (33) observed that, upon addition of thionyl chloride to acetone, gases

were evolved with the formation of a colored solution. This, they believed, was due to the acid-catalyzed (SOCl_2 being the acid) aldol condensation of acetone to form mesityl oxide or phorone, the water, arising from the condensation reaction, then hydrolyzing the thionyl chloride to form sulfur dioxide and hydrogen chloride.

The results of the first exchange experiments in this research utilizing acetone tended to confirm this view. The separated sulfur dioxide fraction contained a very volatile material -- presumed to be hydrogen chloride. The apparent fraction exchange based on the change of specific activity in the sulfur dioxide fraction, F_{SO_2} , was greater than F_{SOCl_2} , the apparent fraction exchange based on the change of specific activity in the thionyl chloride fraction. This result is just as one would expect for such an exchange reaction where thionyl chloride is being converted to sulfur dioxide, and from a series of measurements of F_{SO_2} and F_{SOCl_2} one could, by the method of Luehr et al. (20), calculate both the rate of the exchange and of the condensation reaction, if this latter reaction were indeed taking place. Such calculations, however, actually yielded inconsistent and unreasonable values for the apparent rate of the condensation, suggesting a greater complexity in this system than that visualized by Spandau and Brunneck. So long

as any decomposition occurring in a system of the present sort involves nothing beyond the conversion of one exchange reactant into the other, and so long as the calculated exchange rate is based on the decomposing reactant, i.e., thionyl chloride, the calculated rate obtained will be the same as would be obtained in an equilibrium system. Unfortunately, however, while the second condition applies in the present calculations, it appears from the indicated results that the first one may not. Nevertheless, in all cases but one (Experiment 18, with acetone), good straight line McKay plots were obtained, and this fact would appear to provide adequate support for the validity of the exchange rate thus obtained. (See Calculations.)

When these exchange solutions are evaporated in order to separate the sulfur dioxide from the thionyl chloride, there is left in the reaction ampoule a non-volatile residue, yellow to orange in color, which rapidly darkens after isolation to form a black oily liquid, and over a period of several months sets to a black, asphalt-like, essentially solid material. This was first presumed to be phorone and/or mesityl oxide, which, with adsorbed thionyl chloride as catalyst, reacted further after the removal of the solvent. It was found, however, that the residue contained both sulfur

and chlorine and that the sulfur was generally of specific activity between that of the thionyl chloride initially and the thionyl chloride at the time the reaction was quenched. The analysis of a typical run is given in Table VI. (Several other run analyses are given in Appendix A.) The essential points, based on all such analyses, are these: (1) the amount of residue generally increases with time; (2) the fraction of the residue that is sulfur is approximately constant and corresponds approximately to a ratio of two acetones to one thionyl chloride unit in the residue; (3) the percent of chlorine tends to vary, generally between one and two chlorines per sulfur, perhaps reflecting the loss of some chlorine through a condensation reaction as hydrogen chloride; (4) the specific activity of the residue decreases with time more slowly than the specific activity of the thionyl chloride. From this last point it might be inferred that the residue is not exchanging sulfur with either sulfur dioxide or thionyl chloride, but rather is being continuously formed from thionyl chloride of decreasing specific activity.

Four solutions of acetone and thionyl chloride, some in the presence of, others without sulfur dioxide, were allowed to react under varying conditions, the volatile material evaporated and the molecular weights of the residues, oils which ranged in color from orange to

TABLE VI

Analysis of a Typical Residue from an Acetone-Catalyzed Run
Run 18Conditions: 0°C; 18.0 mmoles SO_2 ; 4.00 mmoles S^*OCl_2 ; 4.05 mmoles Me_2CO

Sample	Wt. Res.	Wt. % S	Wt. % Cl	$\frac{\text{moles Cl}}{\text{moles S}}$	$A^{\circ}_{\text{SOCl}_2}$ ^{a)}	A_{SOCl_2} ^{b)}	A_{res} ^{c)}	Time
	(mg)				(cpm/mg)	(cpm/mg)	(cpm/mg)	(hr)
5	146	20	19	0.87	594	582	543	5.00
1	125	19	d)		603	544	541	9.60
2	d)			1.9	603	358	520	15.0
3	208	19	34	1.6	600	373	570	20.0
4	263	17	29	1.6	600	162	530	24.4
6	d)			1.6	594	112	502	35.5

a) Initial specific activity of SOCl_2 .b) Specific activity of SOCl_2 at time noted.

c) Specific activity of residue at time noted.

d) Part of sample lost.

black, were estimated by cryoscopy in benzene. In Table VII are shown the results of these experiments. Unlike samples 1 and 3, only part of samples 2 and 4 were soluble in benzene, presumably the lower molecular weight fraction, so that these particular data are only lower limit estimates of the residue molecular weights. To compare these results with the sulfur analyses of the residues, if one assumes there is one sulfur per molecule of residue then the average of twenty-six sulfur determinations gives a molecular weight of 233 ± 80 . This figure would appear to correspond to one monomeric unit, formed initially and roughly corresponding to the molecular weights of samples 1 and 3 in Table VII. The molecular weights shown by samples 2 and 4 appear to bespeak a continuing polymerization of this initial product.

The infrared spectra of all four of the residues listed in Table VII were quite alike. All showed strong absorption in the carbonyl region (1730 cm^{-1})³ and the sulfone region ($-\text{SO}_2-$) (1350 cm^{-1} and 1160 cm^{-1}). Weaker bands were observed at $730\text{--}735 \text{ cm}^{-1}$ (C-Cl ?), at 1410 cm^{-1} ($-\text{SO}_2\text{Cl ?}$), and at 2840 cm^{-1} (C-H ?). With the exception of the band at $730\text{--}735$, the relative

³A carbonyl band at 1730 cm^{-1} precludes the possibility that acetone has undergone an aldol condensation since this reaction would give rise to an α - β unsaturated ketone, the carbonyl of which would absorb in another region (3, p. 132).

TABLE VII

Molecular Weight of Residues from Thionyl Chloride-Acetone

Sample	SOCl ₂	Me ₂ CO	Reaction Time	Temp.	Color	Mol. Wt.
	(mole-fraction)	(mole-fraction)	(hr)	(°C)		
1	0.50	0.50	10	0	brown-black	296
2	0.50	0.50	8 +0.03	0 35	black	340 ^{a)}
3 ^{b)}	0.15	0.15	20	0	orange-yellow	240
4 ^{c)}	0.50	0.007	1000 +44000	0 18-34	faint yellow black	500 ^{d)}

- a) Approximately 10% of sample not soluble in benzene.
 b) Solvent SO₂. At end of reaction period, the SO₂ was evaporated at -80°C and benzene added at that temperature.
 c) Reaction run 1000 hours at 0°C in SO₂; the solvent was then evaporated, the reaction ampoule sealed and the reaction continued for 185 days.
 d) Approximately 50% of sample not soluble in benzene.

absorptions of the various bands were about constant, regardless of reaction conditions.⁴

Identification of the residue as a sulfone (sulfur VI), with no evidence for any sulfur in any reduced state, led to a more complete examination of the volatile products of the thionyl chloride-acetone reaction. Several equimolar mixtures of thionyl chloride and acetone, after having been allowed to react for several hours at room temperature, were vacuum fractionated into four fractions: the first, the oily residue, described above, which is quite non-volatile (vapor pressure at room temperature < 0.005 mm); the second collected in a "U" trap at -80°C (Dry Ice-acetone); the third, collected in a "U" trap at -95°C (toluene slush); and the fourth, which passed through all the traps and was collected in a cold finger at -196°C (liquid nitrogen).

The second fraction was evidently a mixture of unreacted thionyl chloride and acetone. If a large excess of either one were used in the reaction, only that

⁴The author wishes to thank Charles Rowell for obtaining the infrared spectra and for his help in identifying or tentatively identifying the bands. Thanks are also due Drs. E. N. Marvell and J. L. Kice for their helpful discussions concerning this problem. All analyses were carried out on a Perkin-Elmer, Model 21, double-beam infrared spectrophotometer using sodium chloride optics. All samples were transferred directly from the freshly opened reaction ampoule to a sodium chloride-window "cap" cell. The bands were tentatively identified with the aid of reference 3.

component was found in the first trap. The third fraction was an evil-smelling, colorless liquid which melted below -95°C . The vapor pressure was ~ 1 mm at -95°C , ~ 3 mm at -80°C , ~ 11 mm at -64°C (chloroform slush), and 100 mm (± 2 mm) at -30°C (bromobenzene slush), leading to an extrapolated boiling point of -3°C . Freshly prepared aqueous "solutions" of this material gave no standard qualitative test for sulfide, chloride, sulfite or sulfate. Though hard to tell with the very small amount of material involved, typically perhaps about two drops, the material appeared to be incompletely soluble in water. The "solution" had the same unpleasant, perhaps mercaptan-like odor as did the original material. Hydrolysis of the material in 10N KOH solution overnight, followed by acidification gave rise to hydrogen sulfide gas, identified by its odor and its characteristic reaction with moist lead acetate paper. The evidence appears to suggest as a reasonable possibility, that this fraction was mostly methyl mercaptan, m.p. -123° , b.p. 6° (31, p. 880); vapor pressure expected -- 1 mm at -95°C , 2.5 mm at -80°C , 13 mm at -64°C , and 80 mm at -30°C (extrapolated from data of reference 36, p. 216). This fraction may contain other compounds, but from the qualitative analyses and the vapor pressure data it would appear that there is no great amount of any

other compound in this fraction.

The fourth fraction was also a colorless liquid at -95°C . Vapor pressure measurements were attempted at -95°C and -80°C several times, but the results were inconsistent, a fact due, probably, to there being more than one compound present. Absorption of the material in 10N KOH (it dissolved completely) gave rise to a solution containing carbonate, sulfide and chloride. Another portion of the fourth fraction was vaporized and bubbled through water and then through 1N KOH. After acidification with nitric acid and boiling, the solution in the first (aqueous) bubbler was found to contain only chloride (and no carbonate or sulfide, of course). The contents of the second bubbler, when fresh, appeared to contain only carbonate and a trace of chloride; however, after the solution had remained at room temperature for an hour, the presence of sulfide and carbonate was obvious (lead acetate paper test and acid soluble barium salt test, respectively). It is believed that the material retained in the first bubbler was hydrogen chloride, that in the second bubbler was carbonyl sulfide, COS. Carbonyl sulfide would simulate carbon dioxide in a qualitative test with the fresh solution, precipitating in the presence of barium ion as barium thiocarbonate, BaCSO_2 , which upon acidification would

evolve carbonyl sulfide, a colorless, odorless gas. In time, however, the carbonyl sulfide would undergo hydrolysis to form carbonate and sulfide. Thus, it seems reasonable to believe that the fourth fraction was probably a mixture of hydrogen chloride and carbonyl sulfide.

In contrast to the foregoing observations, no evidence has been seen for any obvious progressing reaction between acetone and sulfur dioxide. It seems clear that instability in these systems is related primarily, if not entirely, to reaction between acetone and thionyl chloride. It further may be seen that the reaction between thionyl chloride and acetone is complex -- more so than was visualized by Spandau and Brunneck. There is formed an oily residue, apparently from its progressive variation of viscosity, color and molecular weight, a polymer which retains the carbonyl functions but also has a sulfone function. In addition, there are formed hydrogen chloride, carbonyl sulfide and methyl mercaptan. Thionyl chloride is then not only losing sulfur-35 by exchange with sulfur dioxide but also by a side reaction with the catalyst.

Experiment IX, using amounts of reactants similar to Experiment VIII, was designed to test the affect on the rate of the exchange of allowing the thionyl chloride-acetone mixture to approach equilibrium prior to the

exchange. The thionyl chloride and acetone were dosed into a stopcock ampoule which was then closed, removed from the vacuum line, and the contents allowed to react for approximately 60 hours at room temperature. The color of the solution did not change perceptibly for the last 40 hours of this period; the solution was black and almost opaque. The ampoule was returned to the vacuum line, dosed with labeled sulfur dioxide and the exchange carried out as usual. To test the affect of light on the exchange reaction, Experiment XX, dosed essentially like XIX, was run in the dark. The reaction ampoules were dosed as usual and kept frozen until the reaction was initiated by thawing the ampoules and plunging them into the ice bath. The ice bath, kept in a photographic darkroom, was covered tightly with several layers of aluminum foil. Samples were removed from the bath and frozen and the ice in the bath was replenished in darkness. The results of these experiments will be discussed in section V.

The reaction of sulfur dioxide with triethylamine has been extensively studied (2; 15, p. 224-227, 283-293; 12, p. 7-31). Bateman, Hughes and Ingold, in agreement with earlier workers (Ulich, Cruse, Bright and Jasper, see 15, p. 284-285), believe that there is formed, between these compounds, a molecular addition

compound, $\text{Et}_3\text{N}\cdot\text{SO}_2$, a yellow oil. (This oil has been reported to darken with time to an orange-red (28), but this phenomenon was not observed during this study.) The vapor pressure of $\text{Et}_3\text{N}\cdot\text{SO}_2$ at room temperature is approximately 10 mm (12, p. 14-16). It has been shown to undergo rapid sulfur exchange with sulfur dioxide ((1-F) = 0 in the time to separate the reactants at Dry Ice-acetone temperatures (12, p. 17-21)). It has been observed in the present work that this material when fractionated at room temperature or at 0°C , dissociates completely into the starting materials.

While no suggestion of such an interaction is to be found in the reports of Spandau and Brunneck, it was observed in the present research that when thionyl chloride and triethylamine react at -80°C , a yellow oil is formed, very similar in appearance to the addition compound involving sulfur dioxide, $\text{Et}_3\text{N}\cdot\text{SO}_2$. The oil will react further, however, under a variety of conditions to form a white crystalline material and a brown to black tarry solid. For instance, in non-ionizing solvents such as hexane or toluene, thionyl chloride and triethylamine react at -80°C to form a yellow solution. On warming to room temperature, white crystals precipitate. Evaporation of the solvent at room temperature leaves behind a white non-volatile material (vapor pressure ~ 0.005 mm

at room temperature), while unreacted thionyl chloride and triethylamine are volatilized with the solvent. If the reaction is carried out in the presence of an ionizing solvent such as ether or sulfur dioxide, or in the absence of solvent, the solution, on warming, rapidly darkens and evaporation of the unreacted thionyl chloride and triethylamine (and solvent, when present) leaves as a non-volatile residue a brown, tarry mass (vapor pressure approximately 0.005 mm at room temperature). This non-volatile material may be resolved either by fractional crystallization from a chloroform-carbon tetrachloride mixture, or by careful sublimation in vacuo with the aid of a small flame, into a black-tarry material and a white crystalline material (the precipitate and sublimate, respectively), apparently the same as that mentioned above. (The dark material melts somewhat above 100° but remains non-volatile.)

The white material is soluble at room temperature in water with fuming or in base, e.g. 1N NaOH, with the release of triethylamine and in acid with the apparent formation of thionyl chloride (sulfur dioxide and hydrogen chloride appear to be evolved, as evidenced by odor). Analysis: S, 14.6%; Cl, 31.4%; expected for $\text{Et}_3\text{N} \cdot \text{SOCl}_2$, S, 14.53%; Cl, 31.75%. The black tarry fraction was soluble in carbon tetrachloride or chloroform

but insoluble in water. It was relatively insoluble in basic solution (20% sodium hydroxide solution) and soluble only with difficulty (slowly, though eventually completely) in boiling acid (approximately 1N HNO_3 , giving off sulfur dioxide fumes). In the presence of the strong oxidizing agent sodium hypobromite (approximately 0.1M NaOBr in 10% sodium hydroxide solution), this material dissolved incompletely to yield solutions containing sulfate. In boiling 1N nitric acid solution, this material dissolved in the presence of approximately 1% hydrogen peroxide completely, but slowly, to form solutions containing chloride, but only small amounts of sulfur (as sulfate). Thus these observations suggest that thionyl chloride and triethylamine form a 1:1 complex and, in ionizing media, a second material of less certain composition. It is possible, though not certain, that this latter material is polymeric in character, conceivably (though again not surely) formed by further reaction of the 1:1 complex in appropriate media.

The exchange solutions involving triethylamine, like those with acetone, when first thawed and mixed, were colorless. Upon reacting, however, they rapidly turned yellow to black, depending on the concentration of triethylamine -- the more catalyst, the more deeply colored were the solutions. The change in color, in

most instances, appeared essentially complete before the final two samples were removed for radio-assay. The final color of such solutions is quite stable, being apparently constant for over three years when the solution is in a sealed evacuated tube. When such a colored exchange solution is evaporated, there remains in the reaction tube a dark, non-volatile residue typical of those mentioned above, obtained from thionyl chloride and triethylamine alone. In most of the runs, too little residue was present to estimate the amounts of either the sulfur or the chlorine present. In runs at high concentration of base, typically there was present about six percent sulfur and about ten percent chlorine.⁵ For instance, there is given in Table VIII the sulfur analysis of Experiment 44. The essential points to be deduced from this table are that the percent sulfur is about constant, while the residue tends to increase in weight with time. In Table IX the specific activities of the residues (A_{res}) are compared with the specific activities of thionyl chloride (A^0) and at the time of quenching the sample (A_{SOCl_2}). The specific activity of the residue is seen to lie below A_{SOCl_2} in all cases.

⁵Sulfur analyses were carried out on all residues from Experiments 43 and 45. Chlorine analysis was carried out on only one residue each from Experiments 45 and 46.

TABLE VIII

Analysis of Residues
Experiment 44

Conditions: 0°C, 18.0 mmoles SO_2 , 0.711 mmoles S^*OCl_2 ,
1.53 mmoles Et_3N .

Sample	Wt. Residue	Sulfur	Time
	(mg)	(wt. %)	(hr)
1	74	5.5	0.300
2	69	5.5	0.496
3	164	6.2	1.00
4	244	5.5	2.00
5	255	4.2	3.50

TABLE IX

Specific Activity of Residues
in a Typical Experiment with Triethylamine
Experiment 24

Conditions: 0°C , 28.3 mmoles SO_2 , 0.522 mmoles S^*OCl_2 ,
0.0782 mmoles Et_3N .

Sample	A_{res}	A_{SOCl_2}	A°	Time
	(cpm/mg)	(cpm/mg)	(cpm/mg)	(hours)
1	1582	2166	2533	5.00
2	1182	2101	2533	10.0
3	982	1656	2533	18.2
4	1095	1237	2526	24.0
5	837	957	2483	30.0

Presumably, then, the residue is formed, in part, from sulfur dioxide and triethylamine as well as from thionyl chloride and triethylamine, although in appearance it was indistinguishable from the reaction product of thionyl chloride and triethylamine. Fractionation of the volatile materials in such solutions yielded only starting materials and the non-volatile residue, i.e., in contrast to the acetone experiments, there were no volatile products of a side reaction. There was no evidence that the sulfur had been oxidized. On the contrary, the implication is that the sulfur remains in the +4 state since the residue, when dissolved in acid solution (either dilute nitric or hydrochloric acid), evolved sulfur dioxide and thereafter contained little or no additional sulfur.

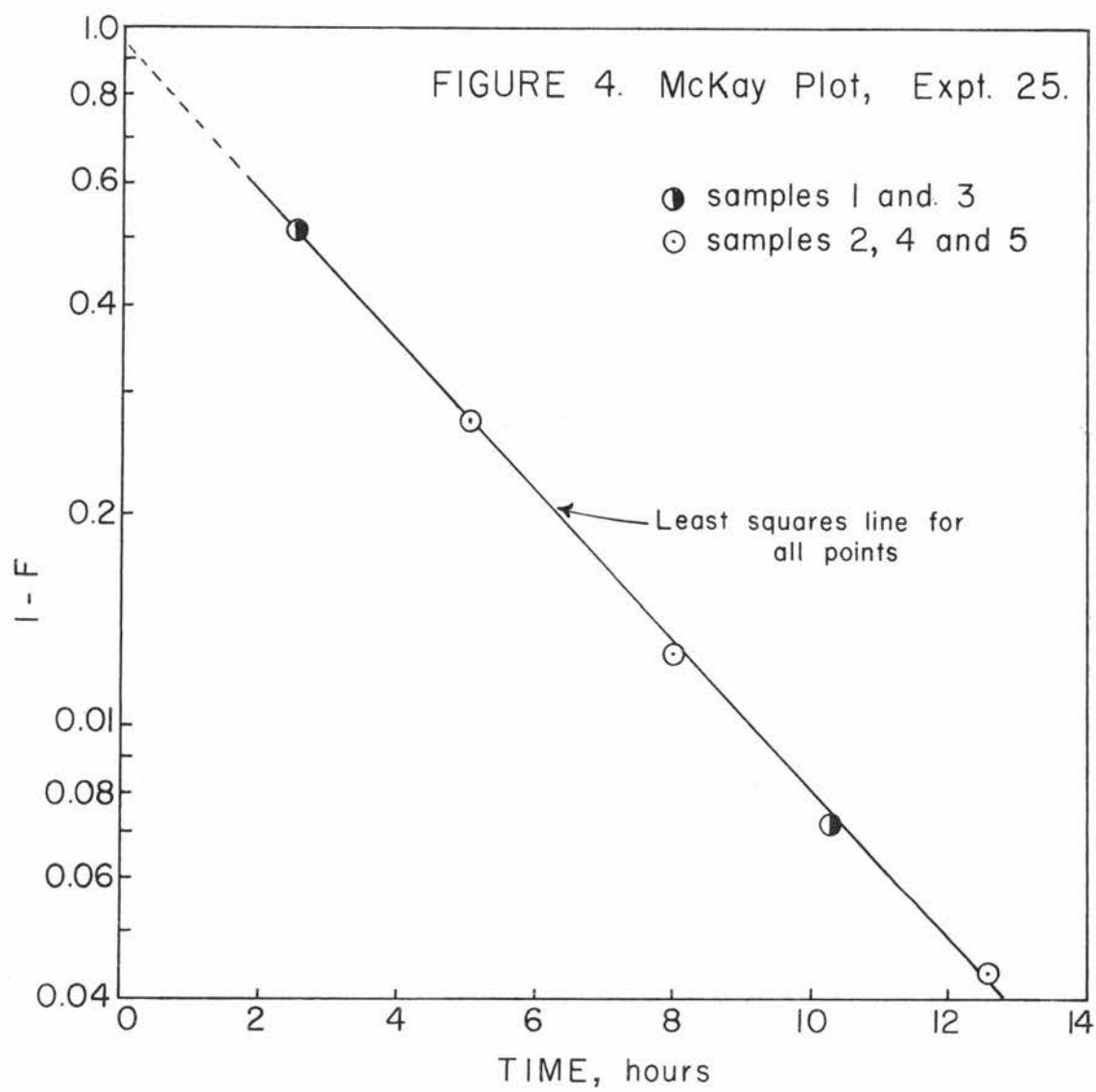
These exploratory experiments with the residues obtained in systems involving acetone or triethylamine lack elegance. The results of the chemical analyses varied considerably from one residue to the next and the specific activities in many cases were determined using samples of less than five milligrams of barium sulfate. It was felt that an attempt at more precise measurements was not justified, however, since the residue isolated bears only a loose relationship to what is in solution at a given time. This is so simply because, during the

isolation step, the sulfur dioxide evaporates more rapidly than the other components, the concentration of reactants primarily involved in residue formation increasing drastically in the process, to an extent which unquestionably radically affects the amount and nature of the residue ultimately left behind. Certainly, the results of the experiments confirm definitely that these are non-stable exchange systems, but no definite conclusions are to be drawn about the extent of the formation of the compounds -- the ketone-sulfone in the acetone experiments and the residue in the triethylamine experiments -- in the exchange solutions themselves prior to the evaporation of the reactants.

The possible effect on the exchange results of the non-equilibrium behavior here described in the exchange solutions containing triethylamine was tested in several experiments. For instance, in Experiment 25, in ampoules 1 and 3 the triethylamine and thionyl chloride were allowed to react briefly at -10° before the sulfur dioxide was dosed in, the ampoules sealed, and the exchange reaction started. In the remaining three ampoules, the exchange was run as usual. The triethylamine and thionyl chloride reacted to give a strongly-colored solution. On being dissolved in sulfur dioxide,

the solutions were wine-red and did not change color perceptibly over the course of the reaction. The three conventional ampoules were, of course, initially much less colored. Sample 5 of this run attained the color of sample 1 in about eight hours (the rest of the samples had been removed for assay by this time). Despite the obvious differences between the two sets, there was no perceptible difference in apparent rate of exchange between samples 1 and 3 on the one hand and the remaining samples on the other. Thus, Figure 4 shows the $\log (1-F)$ versus time plot for this experiment; it may be seen that a good straight line fits all five points about equally well.

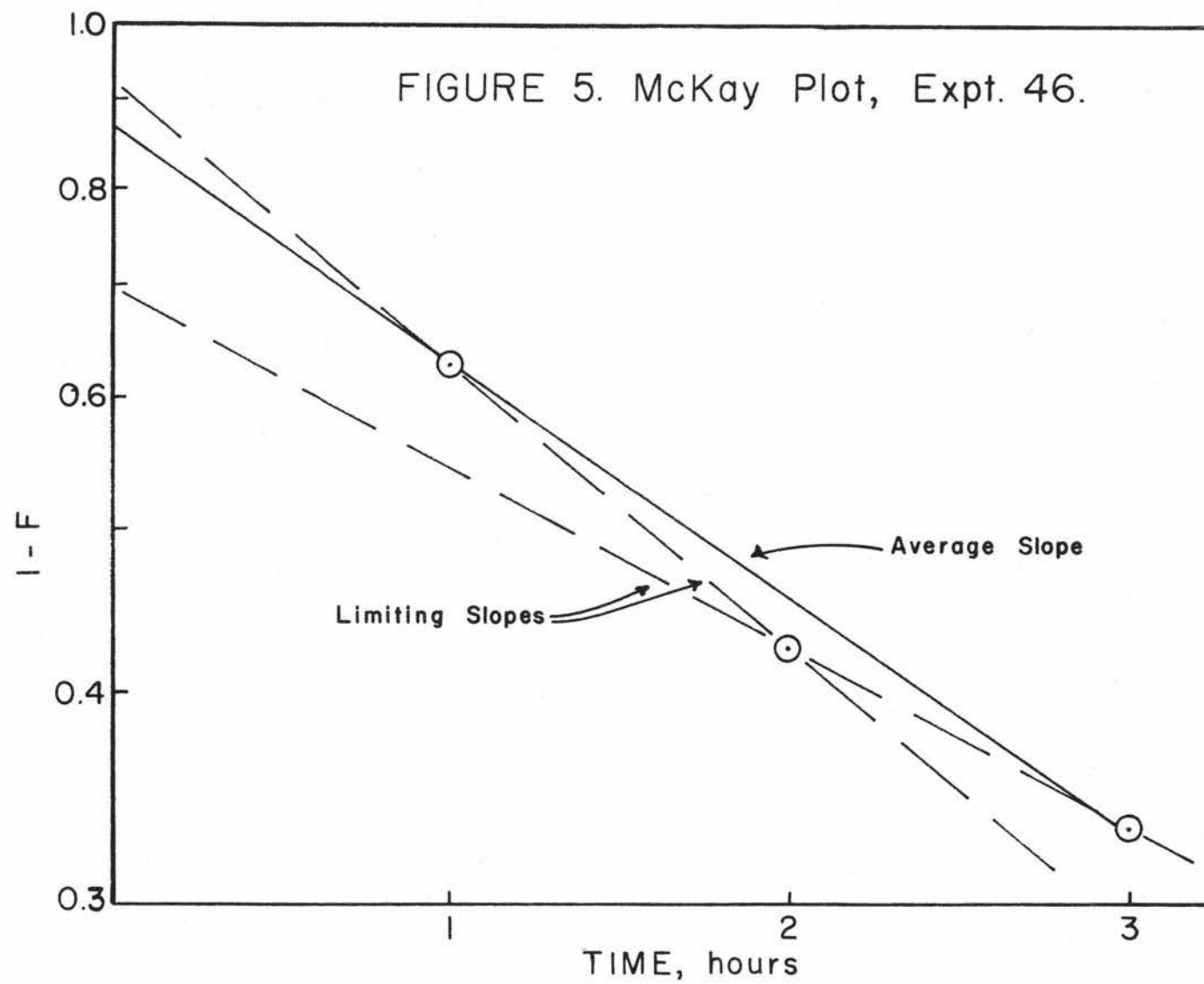
In Experiment 46, the effect on the rate of pre-reacting thionyl chloride-triethylamine mixtures was further investigated. Here, each ampoule was dosed with 0.765 mmoles of triethylamine and 0.710 mmoles of labeled thionyl chloride. This mixture was thawed and allowed to react at 0° for one-half hour, after which all volatile materials were distilled away. To the non-volatile residue was added another 0.710 mmoles of labeled thionyl chloride plus 18.0 mmoles sulfur dioxide. The exchange reaction was then carried out as usual. The volatile material from the first step proved to be thionyl chloride uncontaminated with triethylamine. The amount of

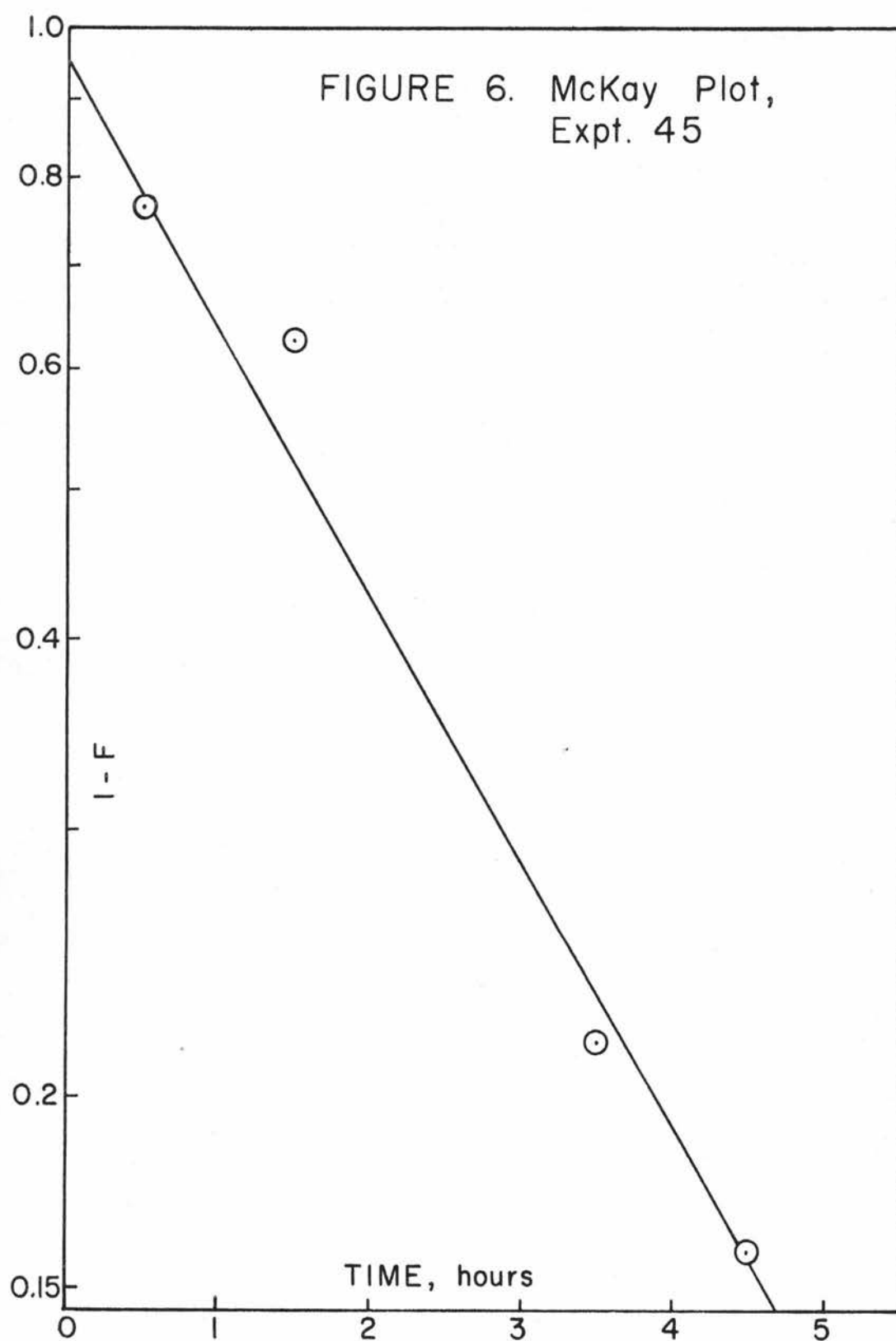


reactants in the solution were taken to be the amounts dosed in less the amount of labeled thionyl chloride removed (determined by chloride analysis of the volatile material).

Experiment 45 was designed to test the effect of allowing the sulfur dioxide and triethylamine to react before adding labeled thionyl chloride and initiating the exchange reaction. In this experiment, 0.765 mmoles triethylamine and about 1.5 mmoles sulfur dioxide were allowed to interact at 0° for one-half hour. Excess sulfur dioxide was then distilled off of the solution at 0° for 3.0 minutes. (Some triethylamine evaporated along with the sulfur dioxide.) One ampoule was removed for analysis, the remaining were dosed with 0.711 mmoles labeled thionyl chloride and 17.1 mmoles of sulfur dioxide and the exchange carried out as usual. From the total weight of material and the amount of sulfur dioxide in the analysis ampoule (0.66 mmoles), it was deduced that about 0.1 mmoles of triethylamine were volatilized along with the sulfur dioxide (in that sample, at least). It was assumed that this was true in all of the ampoules and 0.66 mmoles triethylamine was taken as the amount of triethylamine in each.

Figures 5 and 6 show the McKay plots for Experiments 45 and 46. These figures show a significant





scatter in the data for these runs, which is not unexpected considering the dosing procedure. In Experiment 45 the points on the McKay plot were fitted to a straight line by a least squares treatment. In Experiment 46 the limiting slopes, as shown, were used to determine the approximate value of the rate. The conclusions to be drawn from these experiments are discussed under Results and Discussion.

IV. METHODS OF CALCULATION

A. The Concentration

In all cases, the molar concentrations were calculated from the known amounts of reactants and their known densities, assuming additivity of volumes. The densities used were as follows (units, g/ml):

Temp.	SO ₂ ^{a)}	SOCl ₂ ^{b)}	Me ₂ CO ^{c)}	Et ₃ N ^{d)}	SbCl ₅ ^{e)}
0°C	1.435	1.677	0.8125	0.74551	2.336
15°	1.397	1.648	0.7874	0.73199	
25°	1.368	1.628		0.72224	
35°	1.341	1.608		0.71346	

a) Given as specific volume (37, p. 236).

b) Given as $d_4^t = 1.6767 - 1.951 \times 10^{-3}t + 6.65 \times 10^{-7}t^2 - 1.17 \times 10^{-8}t^3$ (37, p. 22).

c) Given as $d_s = 0.81248 - 0.991(t-t_s) \times 10^{-3} - 0.553(t-t_s)^2 \times 10^{-6}$; $t_s = 0^\circ\text{C}$ (37, p. 28).

d) (34).

e) Density as 20°C (37, p. 111).

The only density found for antimony pentachloride was for 20°C and this value was used for the runs at 0°C since in all cases antimony pentachloride was a minor contributor to the volume, thus the error involved is small -- probably smaller than the assumption of additivity of volume.

B. Break-tip Ampoule Experiments (Procedure I)

In these experiments, the samples were fractionated to obtain, where possible, two volatile fractions, thionyl chloride and sulfur dioxide. Thus it was possible to calculate the fraction exchange, F , on the basis of either one or both of these fractions. Where triethylamine was present in the exchange solution in amounts comparable to the amount of thionyl chloride, it was usually not possible to obtain a thionyl chloride fraction large enough for assay due to the formation of the non-volatile residue; in these cases, the fraction exchange, F , could only be calculated from the sulfur dioxide fraction.

The fraction exchange, F_i , was calculated from either fraction using the expression for a simple exchange system,¹ i.e.,

$$1-F_i = \frac{A_i - A^\infty}{A^\circ_i - A^\infty} \quad (14)$$

¹This expression applies to a simple, i.e., only one exchanging atom, and stable system. The justification for using it in the present, admittedly non-equilibrium systems (where it might or might not apply) rests on at least four arguments. (1) In all cases but one (Experiment XVIII) with acetone, good straight line $\log(1-F_i)$ versus time plots (McKay plots) were obtained so long as F_i referred to F_{SOCl_2} in the acetone experiments or to the minor (and initially active) component

where i refers to the i^{th} component, either thionyl chloride or sulfur dioxide,

A_i is the specific activity of that component at the time, t ,

A^∞ is the specific activity both components would have if the activity were completely randomized, and

A_i° is the initial specific activity of the i^{th} component and was zero for the major solution species (i.e., the "solvent") in all cases in this research.

The experimental quantities were A_i° and A_i . The value of A^∞ was deduced from the initial specific activities of the two exchanging species and the known quantities

in the triethylamine and mixed catalyst experiments.

(2) In the latter two systems, the use of either F_{SO_2} or F_{SOCl_2} , wherever a comparison was made, gave essentially the same good straight line McKay plots and hence the same rates. (3) The kinetic data obtained showed an overall self-consistency which would not have been expected unless equation (14) were valid. (4) Special experiments (IX with acetone and 25, 45 and 46 with triethylamine) designed to show up any kinetic effect on the exchange results due specifically to the non-equilibrium character of the systems, failed to indicate any such effect. These comments regarding the validity of equation (14) apply with equal force to all three procedures, I, II and III, used in this research.

of the exchanging species in solution, i.e.,

$$A^{\infty} = \frac{A^{\circ}_{\text{SO}_2} n_{\text{SO}_2} + A^{\circ}_{\text{SOCl}_2} n_{\text{SOCl}_2}}{n_{\text{SO}_2} + n_{\text{SOCl}_2}} \quad (15)$$

where n_{SO_2} and n_{SOCl_2} refer, respectively, to the number of millimoles of sulfur dioxide and thionyl chloride put into solution. A^{∞} was also determined experimentally in a few cases to check the radioactivity balance, good agreement (within $\pm 5\%$) being found in all cases. Values of $1-F_{\text{SO}_2}$ and/or $1-F_{\text{SOCl}_2}$ were calculated for all available (both sulfur dioxide and thionyl chloride fractions were not collected in all cases) samples of a given run as shown in Tables IIa, IIIa and IV and then $\log(1-F)$ was plotted as a function of time. In most cases, good straight lines were obtained. The one exception is considered later. The exchange rate was found from the slope of the resulting straight line by the relation

$$\text{Rate} = -2.3 \frac{(\text{SO}_2)(\text{SOCl}_2)}{(\text{SO}_2) + (\text{SOCl}_2)} \frac{d}{dt} \log(1-F) \quad (16)$$

Here (SO_2) and (SOCl_2) represent molar concentrations of the reactants as dosed. Of course, it was not possible to calculate meaningful rates from the $1-F_{\text{SO}_2}$ versus time values for the runs involving acetone, since the

sulfur dioxide fractions in these instances were contaminated with a S^{35} -tagged decomposition species, as mentioned earlier. In the case of the triethylamine experiments the rate used in further calculations was calculated, where possible, from the change in specific activity of the species initially active (the minor solution component) since the change here is larger than the change in specific activity of the species not originally tagged. In general, the difference between the rates calculated by the two methods, $\text{Rate}_{(SO_2)}$ and $\text{Rate}_{(SOCl_2)}$, was small and can be attributed to experimental error in dosing and/or to the large error in counting samples of low activity (about 3%).

C. Stopcock Ampoule Experiments (Procedure II)

In all runs using procedure II, acetone was the catalyst, sulfur dioxide was initially active and thionyl chloride was the major species present. The concentrations were calculated as above. Several small samples of thionyl chloride were taken at periodic intervals throughout the course of the experiment and the specific activities determined. The known quantities were then $A^\circ_{SO_2}$, $A^\circ_{SOCl_2}$ and the amounts and concentrations of the reactants. The value of A^∞ was calculated using

equation (15), $1-F_{\text{SOCl}_2}$ was calculated using equation (14) ($A^\circ_{\text{SOCl}_2} = 0$) and the rate calculated from the slope of the plot of $\log (1-F)_{\text{SOCl}_2}$ versus time, which in all cases was a good straight line. The validity of this treatment has already been discussed as a footnote under Procedure I above. There is introduced here a small error, since in withdrawing small samples of thionyl chloride from the solution, the concentration is changed. In these experiments a total of only about one mmole (at most) of thionyl chloride was used for radio-assay out of at least 50 mmoles of thionyl chloride in the solution. The error introduced is certainly less than the uncertainty in A_{SOCl_2} , or for that matter, it is not large compared to the uncertainty in the initial dosing.

D. Stopcock Ampoule Experiments (Procedure III)

In these two runs (II and VI), sulfur dioxide was in excess (18.0 mmoles) and thionyl chloride (4.00 mmoles) was initially active. Small samples of sulfur dioxide were periodically removed from the solution through the stopcock (about 0.25 mmoles), the amount of sulfur dioxide determined by weighing the barium sulfate produced for radio-assay and the specific activity determined.

In this case it was necessary to correct for the change in concentration resulting from the withdrawal of sulfur dioxide. This was done by determining the rate of exchange between successive samples, correcting back to the original concentration and graphically averaging the rates found during all the reaction periods. A detailed account of the method is given by Masters (22, p. 83-89) and Burge (15, p. 65-73).

E. Least Squares Calculations

The problem arises, as will be discussed under Results and Discussion, of finding the best values of two constants, k' and K' , so as to fit the data from a series of experiments to the equations

$$\text{Rate} = k_1(b-x_2)(x_1) + k_2(a-x_1)(x_2) \quad (18)$$

$$K_1 = \frac{x_1}{(a-x_1)(c-x_1-x_2)} \quad (19)$$

$$K_2 = \frac{x_2}{(b-x_2)(c-x_1-x_2)} \quad (20)$$

In these equations

Rate = the rate of sulfur exchange

x_1 = concentration of $\text{Et}_3\text{N} \cdot \text{SO}_2$ at equilibrium

x_2 = concentration of $\text{Et}_3\text{N} \cdot \text{SOCl}_2$ at equilibrium

a = concentration of SO_2 put into solution and
 $a-x_1$ is the equilibrium concentration

b = concentration of SOCl_2 put into solution
 and $b-x_2$ is the equilibrium concentration

c = concentration of Et_3N put into solution
 and $c-x_1-x_2$ is the equilibrium concentration

K_1 = the equilibrium constant for the association
 of SO_2 and Et_3N

K_2 = the equilibrium constant for the association
 of SOCl_2 and Et_3N

k_1 = the bimolecular rate constant for exchange
 of SOCl_2 with $\text{SO}_2 \cdot \text{Et}_3\text{N}$

k_2 = the bimolecular rate constant for exchange
 of SO_2 with $\text{SOCl}_2 \cdot \text{Et}_3\text{N}$.

Now, in all the experiments under consideration, those involving catalyst triethylamine at 25° , $c \ll a$ and $c \ll b$, so that $x_1 \ll a$ and $x_2 \ll b$, consequently a is, to a good approximation, equal to the equilibrium concentration of sulfur dioxide and b is about equal to the equilibrium thionyl chloride concentration. Substituting in (18), (19) and (20) a for $(a-x_1)$ and b for $(b-x_2)$, dividing (19) by (20) and rearranging yields

$$x_2 = \frac{K_2}{K_1} \frac{b}{a} x_1 = K' \frac{b}{a} x_1 \quad (21)$$

Substituting (21) into (18) yields

$$\text{Rate} = k_1 + k_2 \frac{K_2}{K_1} x_1 = k' b x_1 \quad (22)$$

where now

$$K' = \frac{K_2}{K_1} \quad (23)$$

$$k' = k_1 + k_2 K' \quad (24)$$

Consider each experiment as yielding an equation

$$\text{Rate} = k' b x_{1i} + E_i \quad (25)$$

analogous to (22) but containing an error term E_i . This equation contains values of K' , x_2 and a , implicitly and the error term represents the deviation of the observed rate from a value predicted by a choice of k' and K' , the choice being directed toward a minimum error in calculated rate, i.e., "best fit" values for k' and K' . The least squares method is actually utilized to find the values of k' and K' which minimize the summation of the $(E_i)^2$ terms. In the present case, the percentage error in R_i was assumed constant and a weight factor $(1/R_i)^2$ was introduced to make all the terms of the summation of the same order of magnitude (38, p. 217-219). Then we have

$$\sum_i (E_i/R_i)^2 = \sum_i (1/R_i)^2 (R_i - k' b x_{1i})^2 \quad (26)$$

and the summation is to be minimized by proper choice of K' and k' . If one assumes that K_1 and K_2 are at least moderately large, say at least about 1, then

$$c - x_1 - x_2 \simeq 0 \quad (27)$$

Substituting this into (21) leads to

$$x_1 = \frac{ac}{a + bK'} \quad (28)$$

The justification for assuming K_1 and K_2 are large will be given in the Results and Discussion section. From (28), then, one may, with a choice of K' , calculate, for each experiment, values for x_1 , the x_{1i} 's of equation (26). With these, the values of the summation may be computed for a series of choices of k' and the minimum established graphically for this particular K' . Repeating this procedure for a series of values of K' , there arises a series of minima in the summation as a function of k' , at various values of K' . These minima of the summation are then plotted as a function of K' , thus establishing the minimum of the summation as a function of both k' and K' .

As a specific example, consider the evaluation of

the constants for all of the experiments using triethylamine at 25°C. (Here, the conditions are met that $a \ll x_1$, $b \ll x_2$, since $c \ll a$ and $c \ll b$.) The values of $\sum_i (E_i/R_i)^2$ for various values of k' and K' are given in Table X.

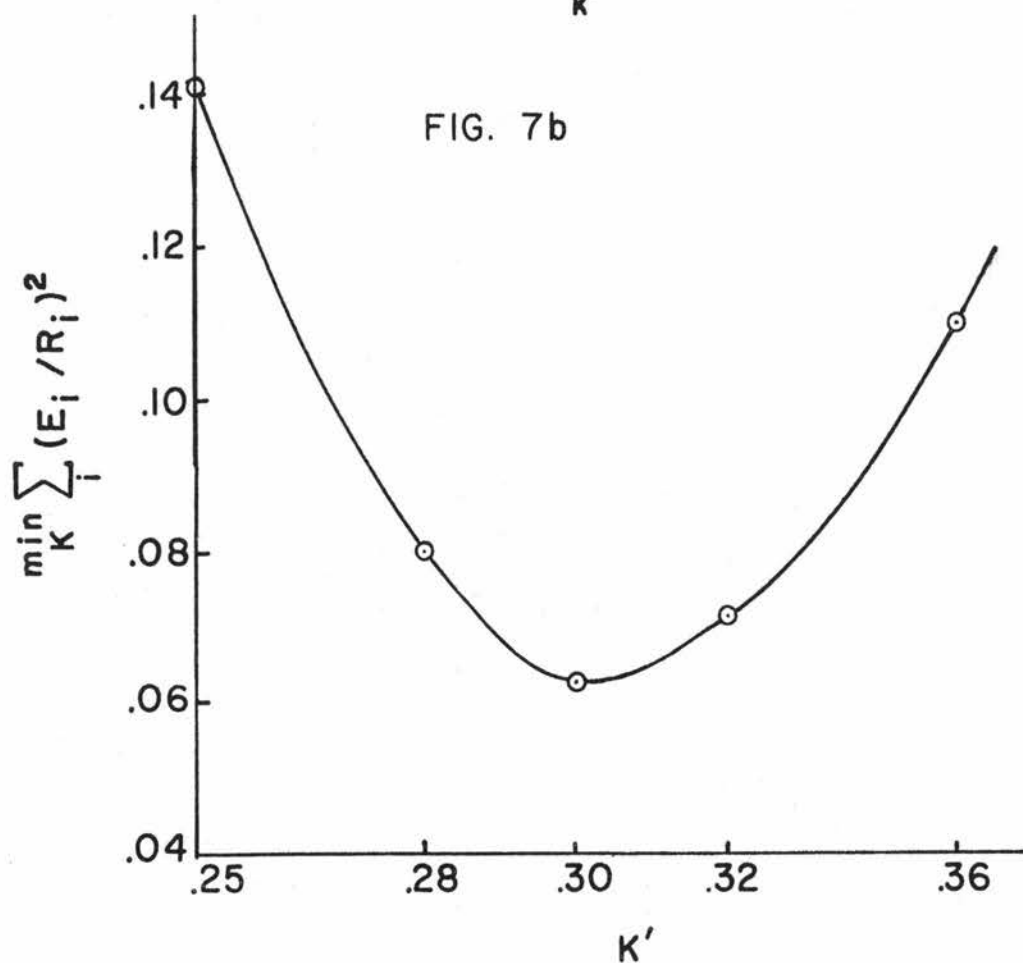
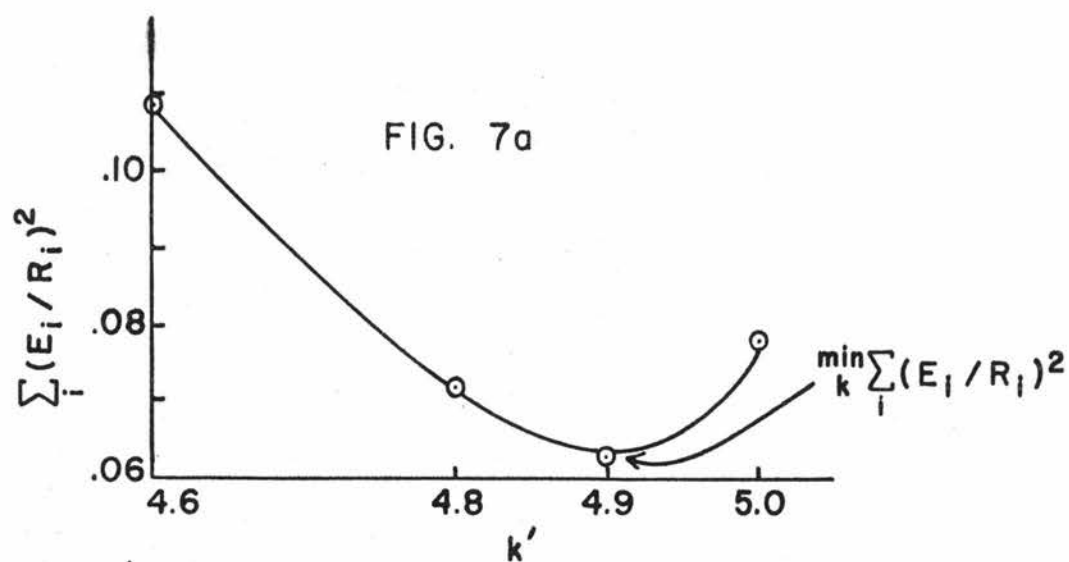
By plotting $\sum_i (E_i/R_i)^2$ versus k' , a value of $\min_{k'} \sum_i (E_i/R_i)^2$ was found for each K' . As an example see Figure 7a. These minimum values were plotted as a function of K' to establish an overall minimum for

$\sum_i (E_i/R_i)^2$, as shown in Figure 7b. From this graph we see that the best value for K' is 0.3 and looking back to Figure 7a we see that the minimum occurs at $k' = 4.9$.

TABLE X

$(E_1/R_1)^2$ as Function of k' and K'
for Triethylamine Experiments at 25°C.

$K' \backslash k'$	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.5
0.28	0.09180	0.08177	0.08202	0.09414				
0.30	0.1089		0.07199	0.0631	0.0779			
0.32			0.0997		0.07138	0.07620	0.0920	
0.36	0.3580				0.1367		0.115	0.1510



FIGURES 7a and 7b. Plots for Least Squares Analysis.

V. RESULTS AND DISCUSSION

A. Triethylamine Experiments

The results of the experiments with triethylamine as catalyst are presented in Table XI. All quantities of reactants have been converted to molar concentration units assuming additive volumes of reactants as explained in Section IV. The observed rates are expressed in mole liter⁻¹ hour⁻¹ and the termolecular rate constants in liter² mole⁻² hour⁻¹. These latter will be discussed later. While in general the experiments involve sulfur dioxide as the solvent, it will be noted that Experiments 34 through 42 form a group in which thionyl chloride is the major solution component and thus should be considered the solvent. This group of experiments are henceforth referred to as "excess thionyl chloride experiments (or runs)".

1. Dependence of the Rate on Et₃N Concentration

It will be assumed, at first, that the rate law for the exchange is of the form

$$\text{Rate} = k(\text{SO}_2)^a(\text{SOCl}_2)^b(\text{Et}_3\text{N})^c \quad (29)$$

where $(\text{SO}_2)^a$ is the stoichiometric concentration in

TABLE XI
Rate and Rate Constants
For Triethylamine Experiments

Exp.	Temp.	(SO ₂)	(SOCl ₂)	(Et ₃ N)	Rate ^{a)}	k ₃
	(°C)	(M/l)	(M/l)	(M/l)	(M/l-hr)	(l ² /M ² -hr)
13	0	16.42	3.65	0.0540	0.0805	0.0249
14	0	14.69	3.27	0.824	1.089	0.0275
15	0	11.03	2.45	2.45	1.945	0.0294
21	0	20.83	0.859	0.0584	0.0249	0.0238
22	0	20.52	0.847	0.167	0.0785	0.0270
23	0	19.06	0.768	0.679	0.168 ^{b)}	0.0169
24	0	21.56	0.398	0.0596	0.0134	0.0262
25 ^{c)}	25	20.61	0.378	0.0566	0.0917	0.208
26	25	20.98	0.210	0.0206	0.0230	0.253
27	25	19.52	1.078	0.0546	0.294	0.256
28	25	15.75	3.487	0.0556	0.888	0.291
29	25	8.34	8.27	0.0416	1.147	0.400
30	25	15.87	3.511	0.00480	0.0834	0.312
31	25	15.85	3.506	0.0239	0.414	0.312
32	35	19.83	0.576	0.0548	0.334	0.533
33	15	20.78	0.603	0.0218	0.0338 ^{d)}	0.130 ^{d)}
34	25	0.214	13.52	0.0137		^{e)}
35	25	1.346	12.81	0.0136	0.221	0.942
36	25	1.347	12.82	0.00850	0.140	0.952
37	25	1.339	12.74	0.0709	1.14	0.963
38	25	3.23	11.61	0.00854	0.258	0.806
39	25	0.446	13.38	0.00972	0.0629	1.038

(Continued on next page)

TABLE XI - (Cont'd.)

Exp.	Temp.	(SO ₂)	(SOCl ₂)	(Et ₃ N)	Rate ^{a)}	k ₃
	(°C)	(M/l)	(M/l)	(M/l)	(M/l-hr)	(l ² /M ² -hr)
40	25	0.213	13.55	0.00880	0.0273	1.075
41	0	1.378	13.22	0.00961	0.0214	0.122
42	35	1.325	12.66	0.00916	0.307	2.01
43	0	18.81	0.743	0.800	0.190 ^{b)}	0.0170
44	0	16.97	0.669	1.44	0.330 ^{b)}	0.0226
45 ^{c)}	0	19.2	0.78	0.66	0.24 ^{b)}	0.024 ^{f)}
46 ^{c)}	0	18.2	1.27	0.773	0.36 ± .04 ^{b)}	0.022 ± .002 ^{g)}

- a) Unless otherwise noted, the rate is calculated on the basis of the change in specific activity of the sulfur species of lower concentration, i.e., that initially active.
- b) Calculated from change in specific activity of sulfur dioxide.
- c) Runs designed to test for effect of non-equilibrium conditions. See Run Procedures.
- d) Bad run; bath relay stuck. Estimated error + 30% (see Table IV).
- e) Exchange complete by the time the first sample was assayed, 5 hours.
- f) Uncertainties in amount of triethylamine (perhaps 20% high) make the k₃ value uncertain.
- g) Only three samples available, with considerable scatter. Error estimated from maximum range in the slopes which might be drawn (Figure 6) is ± 10%.

moles/liter of sulfur dioxide put into solution, raised to the a^{th} power. $(\text{SOCl}_2)^b$ and $(\text{Et}_3\text{N})^c$ are defined similarly.

Experiments 13, 14 and 15; 21, 22 and 23; 28, 30 and 31; and 35, 36 and 37 form four sets of runs in which the concentrations of sulfur dioxide and thionyl chloride are varied only moderately within a set, while the concentration of triethylamine is varied extensively. The logarithm of the rate has been plotted as a function of $\log (\text{Et}_3\text{N})$ in Figure 8. Lines of unit slope have been drawn through the four sets of data, illustrating that the order with respect to triethylamine concentration ("c" of equation 29) is one both in excess thionyl chloride and excess sulfur dioxide at 25° (runs 35, 36, 37 and 28, 30, 31, respectively) (the occurrence of a common line for these two sets is coincidental only) and at 0° in excess sulfur dioxide (runs 13, 14, 15 and 21, 22, 23). The apparent decrease in slope with increasing concentration of triethylamine in the last two sets, those in excess sulfur dioxide at 0° , is due to the fact that the concentration of triethylamine cannot be varied independently of the concentrations of sulfur dioxide and thionyl chloride and still obtain conveniently measurable rates. Since the order of the reaction is positive with respect to both sulfur dioxide and thionyl chloride, the

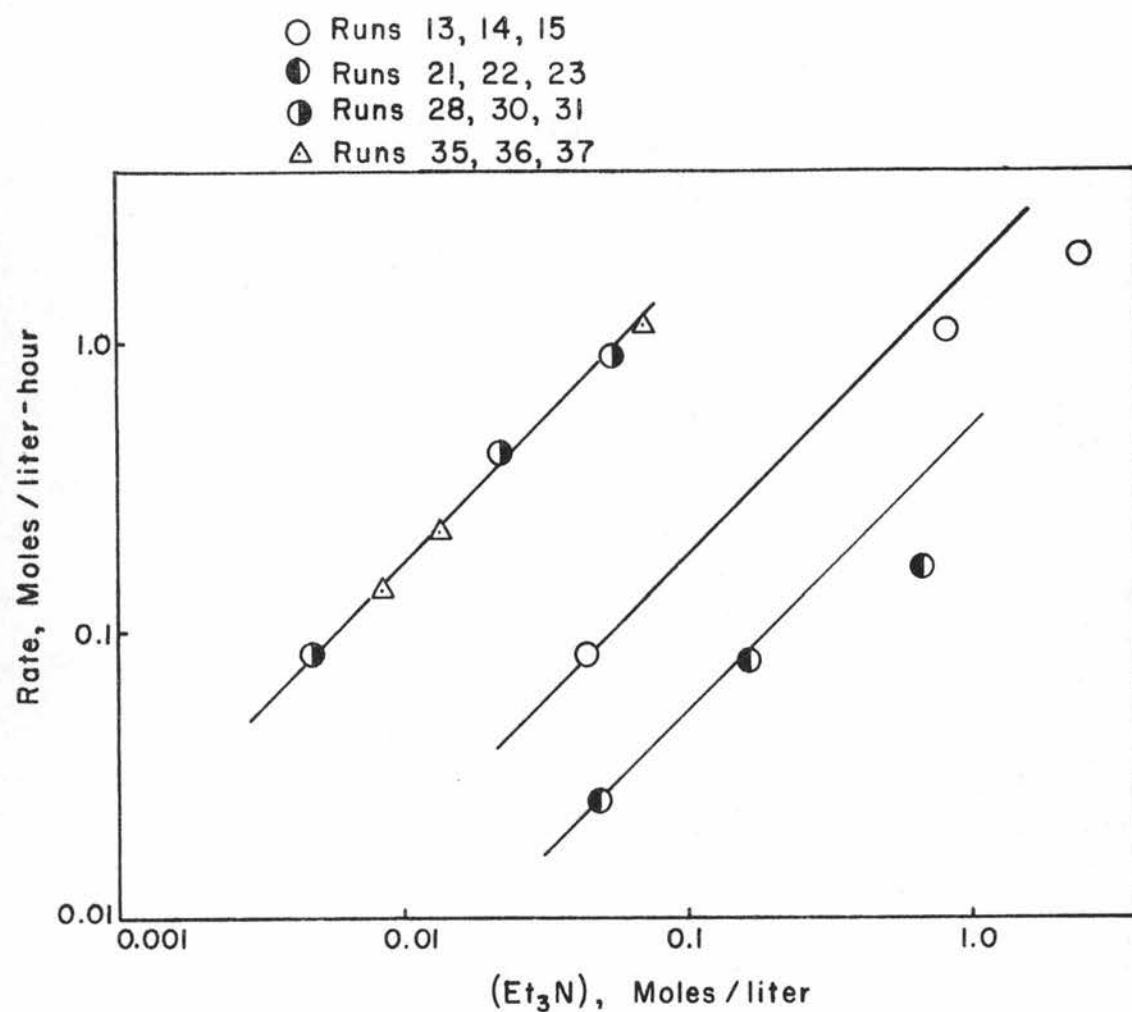


FIGURE 8. The Rate Dependence on Et_3N Concentration.

plot of rate versus triethylamine concentration falls off at higher concentrations of triethylamine. It appears, however, that over approximately a 50-fold range of triethylamine concentration in excess sulfur dioxide and an 8-fold range of triethylamine concentration in excess thionyl chloride, the reaction is first order with respect to triethylamine concentration.

2. Dependence of the Rate on SOCl_2 and SO_2 Concentrations

In the systems here being studied, it is impossible to vary the concentration of sulfur dioxide or thionyl chloride independently of one another. In Experiments 36, 38, 39 and 40, sulfur dioxide concentration is varied over a 15-fold range while thionyl chloride concentration varies only approximately 15%. (In these experiments, triethylamine concentration also varies approximately 13%.) The rates of these experiments are plotted as a function of sulfur dioxide concentration in Figure 9. It is seen that at lower concentrations of sulfur dioxide, where variation of this factor has less effect on the thionyl chloride concentration, the points approach unit slope. The order with respect to sulfur dioxide concentration, at least in excess thionyl chloride, is evidently one. Similarly, in Experiments 13, 21 and 24,

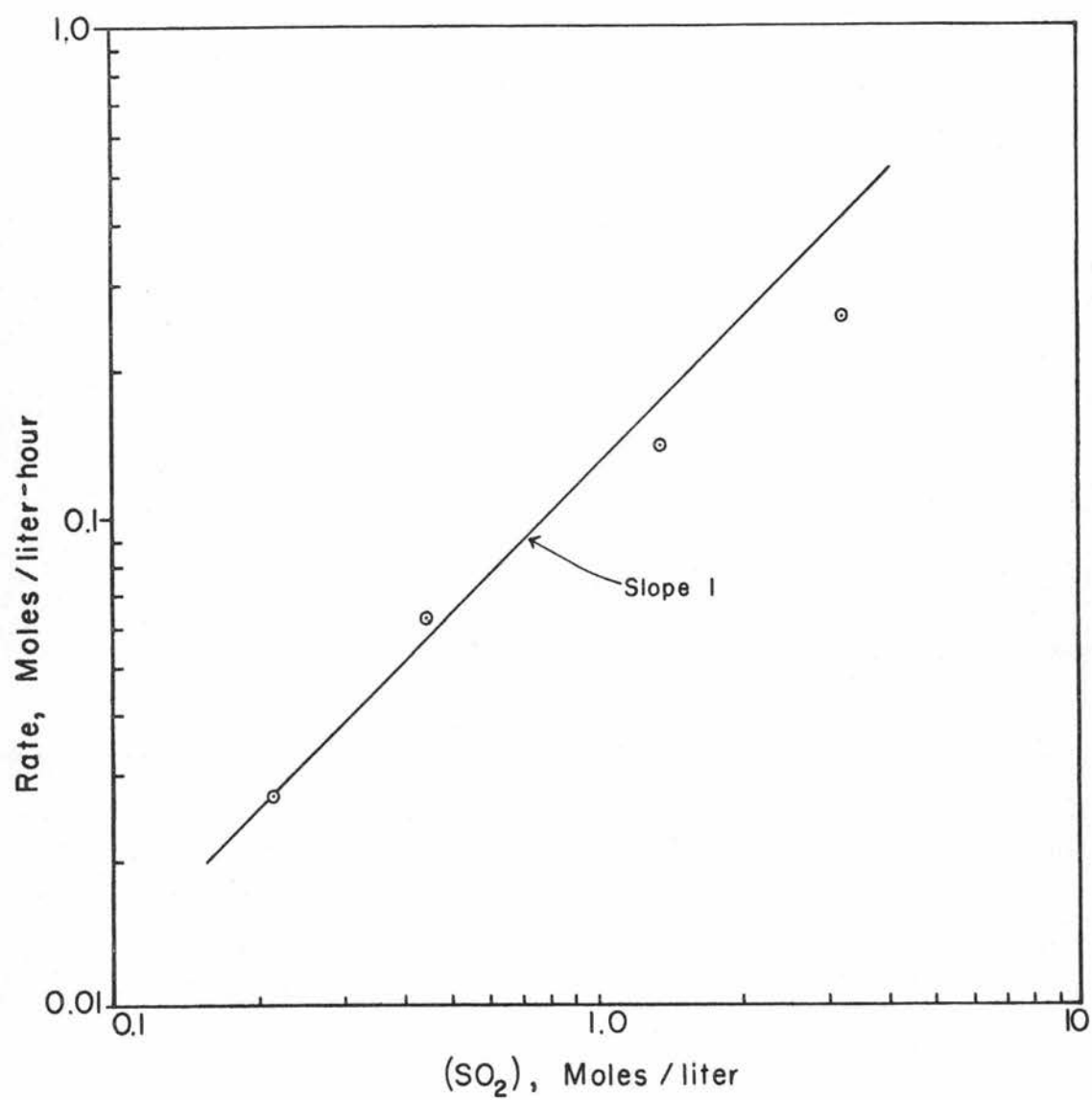


FIGURE 9. The Rate Dependence on SO_2 Concetration.

thionyl chloride concentration is varied, at 0°, over about a 9-fold range ((SO_2) variation approximately 30%, (Et_3N) variation approximately 10%) and in Experiments 25, 27 and 28 the concentration of thionyl chloride is varied, at 25°, over a 9-fold range ((SO_2) varying approximately 30%, (Et_3N) varying approximately 4%). The plot of $\log(\text{Rate})$ as a function of $\log(\text{SOCl}_2)$ for these two sets of data is shown in Figure 10. Lines of unit slope drawn through the points indicate that the order with respect to thionyl chloride concentration in excess sulfur dioxide is also one.

3. The Termolecular Rate Constant

The foregoing kinetic treatment indicates that, under the conditions investigated, a, b and c in equation (29) all have the value of one and that, provisionally, one may take the rate law to be

$$\text{Rate} = k_3(\text{SO}_2)(\text{SOCl}_2)(\text{Et}_3\text{N}) \quad (30)$$

The provisional aspect of this rate law is related to the fact, already indicated, that the kinetic dependence on sulfur dioxide and on thionyl chloride cannot be established under the same solution conditions. Thus, finding the order of the reaction to be one with respect to sulfur dioxide concentration in excess thionyl chloride is

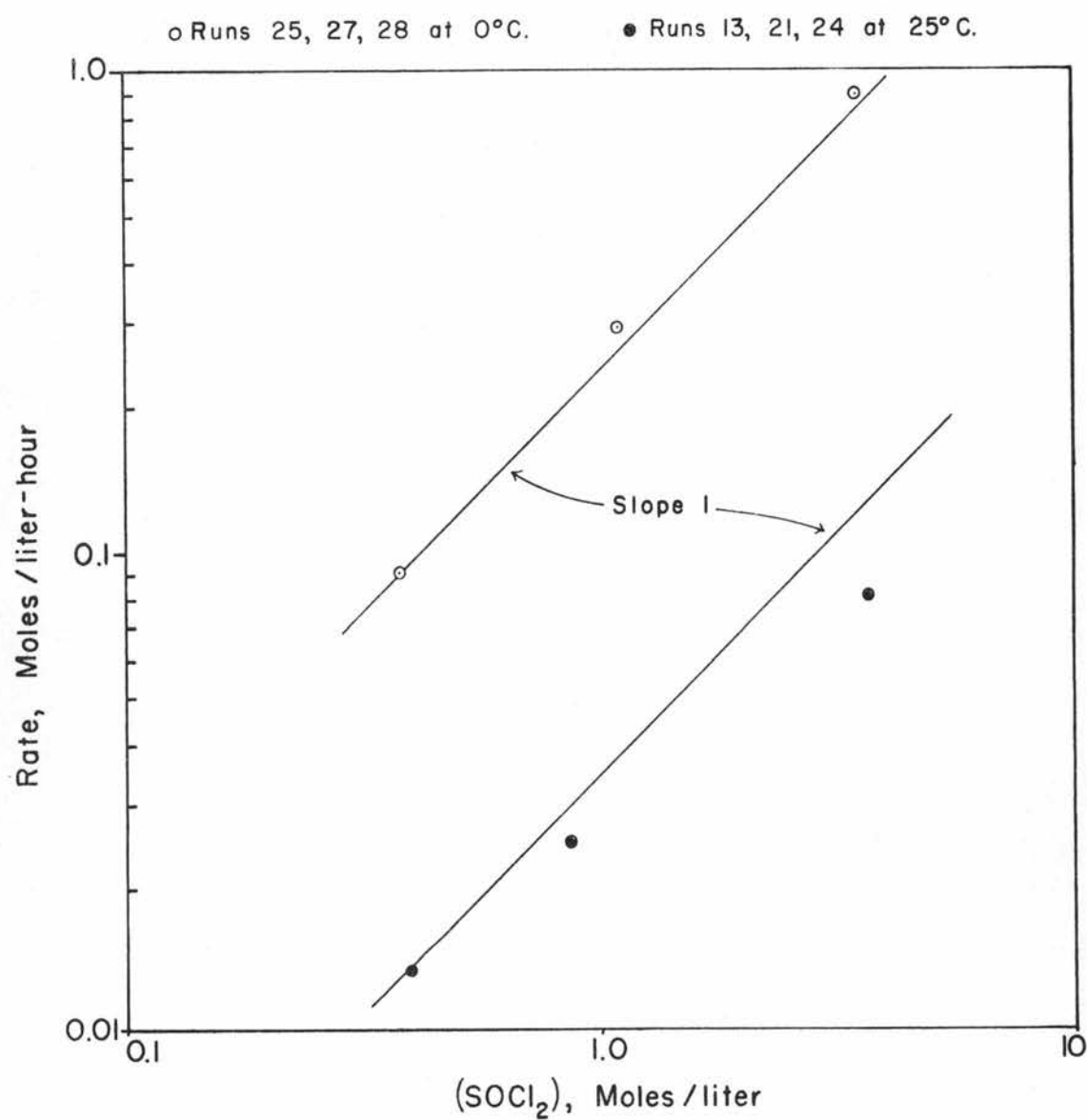
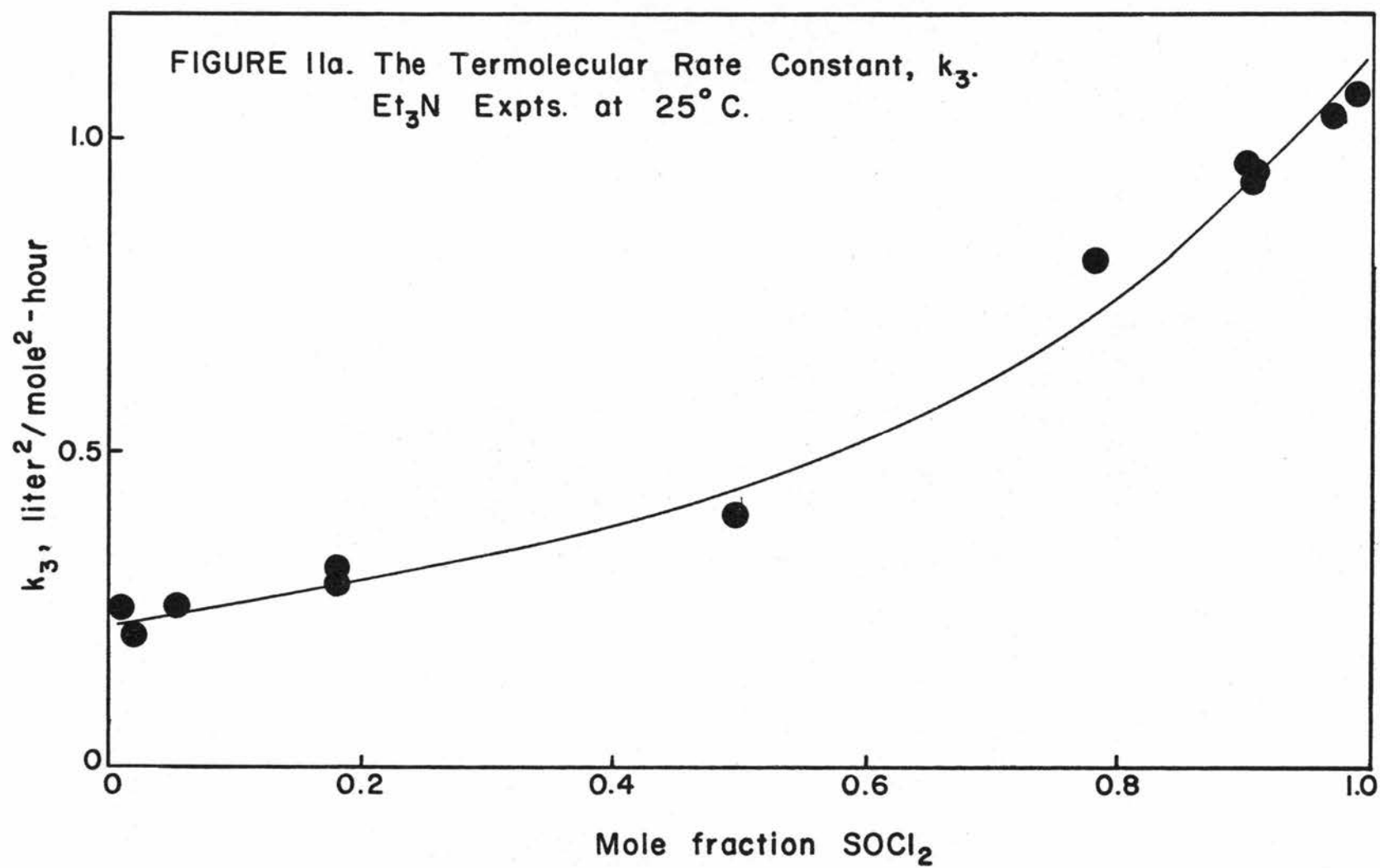
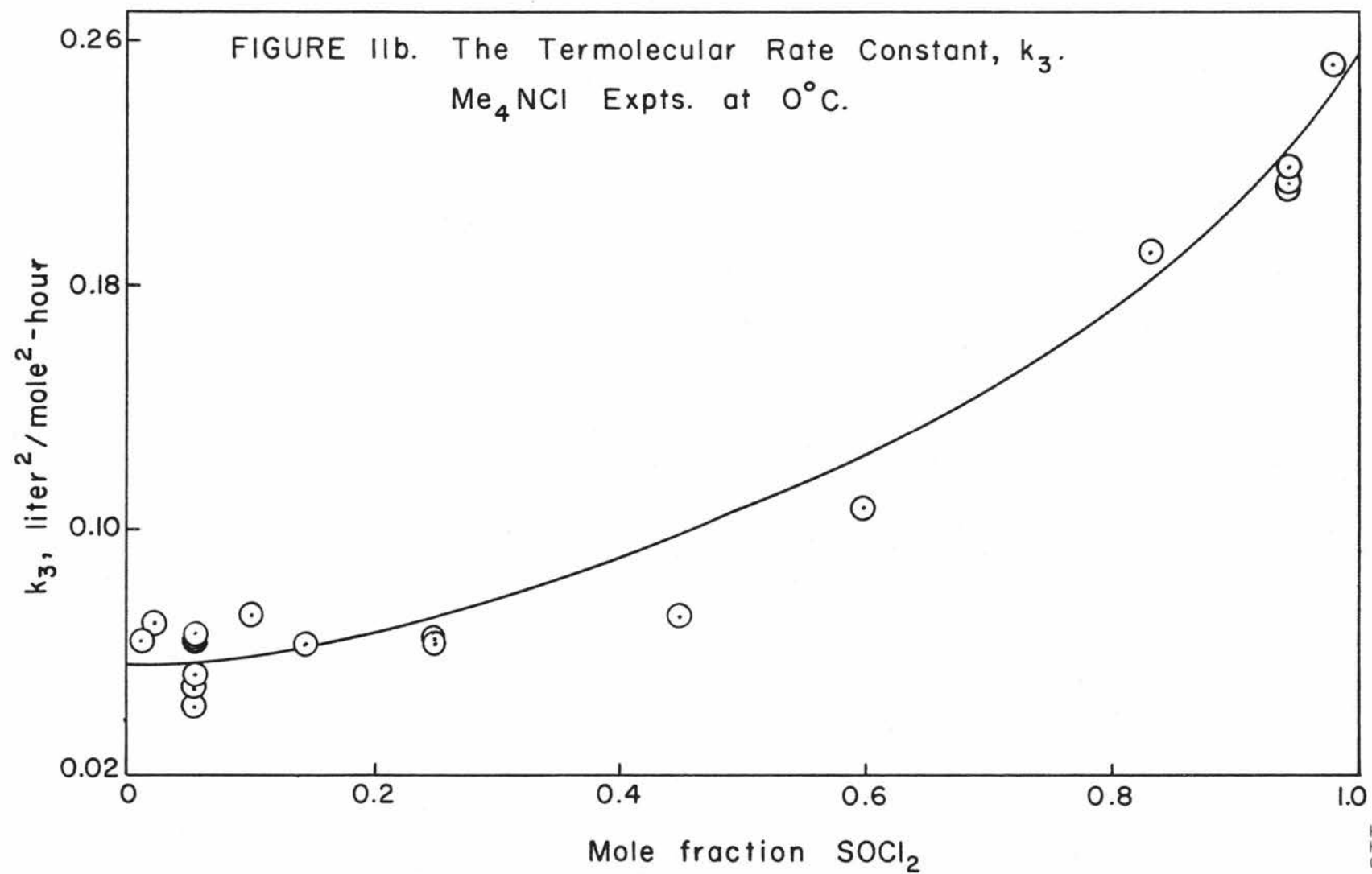


FIGURE 10. The Rate Dependence on SOCl₂ Concentration.

no necessary indication that the same order will be found in excess sulfur dioxide. Similarly, the order found in excess sulfur dioxide for thionyl chloride need not necessarily be the correct order of the reaction with respect to thionyl chloride in excess thionyl chloride. The drastic change in solvent, from almost pure sulfur dioxide to almost pure thionyl chloride, could quite possibly cause a change in mechanism for the reaction. The success of Burge and Norris (6) in accounting for the results of their study of the acid-catalyzed exchange over the entire solution range by one rate law, however, leads one to hope that the same can be done here. Therefore, always with the above reservation in mind, we will consider the termolecular rate constant that satisfies equation (30). The values calculated from the observed rates and the known concentrations are presented in Table XI in the right-hand column. Briefly, considering all of the reactions at 25°, the most complete set, we see that while the trend is a reasonably smooth one, k_3 is not in fact constant over the entire solvent range, varying by a factor of about five in going from solutions in excess sulfur dioxide to those in excess thionyl chloride. This is illustrated graphically in Figure 11a where there is plotted k_3 as a function of mole fraction thionyl chloride for the 25° experiments with





triethylamine (points). (The curve is a derived one and will be discussed below.) A similar trend is noted in the 0° runs, although the data are more scattered. There is again about a 5-fold increase in k_3 as the concentration of thionyl chloride increases. The reason for k_3 not being constant will be discussed further in part V,5, below.

4. The Temperature Dependence of the Rate

The temperature dependence of the rate of sulfur exchange has been studied in excess thionyl chloride and in excess sulfur dioxide. The results are summarized in Table XII. For the excess sulfur dioxide case, the values of k_3 for several experiments at about constant sulfur dioxide concentration were averaged together to get values of k_3 at 0° and at 25°. The k_3 's were treated similarly for the excess thionyl chloride case.

The experimental activation energies, E_{exp} , have been calculated from the slopes of plots (Figure 12) of $\log k_3$ versus the reciprocal of the absolute temperature by means of the Arrhenius equation

$$k = Ae^{-(E_{\text{exp}}/RT)} \quad (31)$$

where k is the observed rate constant, here k_3 , R is the gas constant (1.99 cal/degree-mole), A is the

TABLE XII
Variation of k_3 with Temperature

Exp.	Temperature (°C)	SO ₂ (M/l)	k ₃ (l ² /M ² -hr)
Excess SO ₂ Experiments			
21, 22, 24	0	20.97 (ave.)	0.0257 (ave.)
33	15	20.78	0.130 ^a)
25, 26, 27	25	20.37 (ave.)	0.239 (ave.)
32	35	19.83	0.533
Excess SOCl ₂ Experiments			
41	0	13.22	0.122
35, 36, 37	25	12.79 (ave.)	0.921 (ave.)
42	35	12.66	2.01

a) Bad runs due to stuck relay on thermostatted bath.
Excessive scatter on last three points. See
Table IV. Error estimated to be $\pm 30\%$.

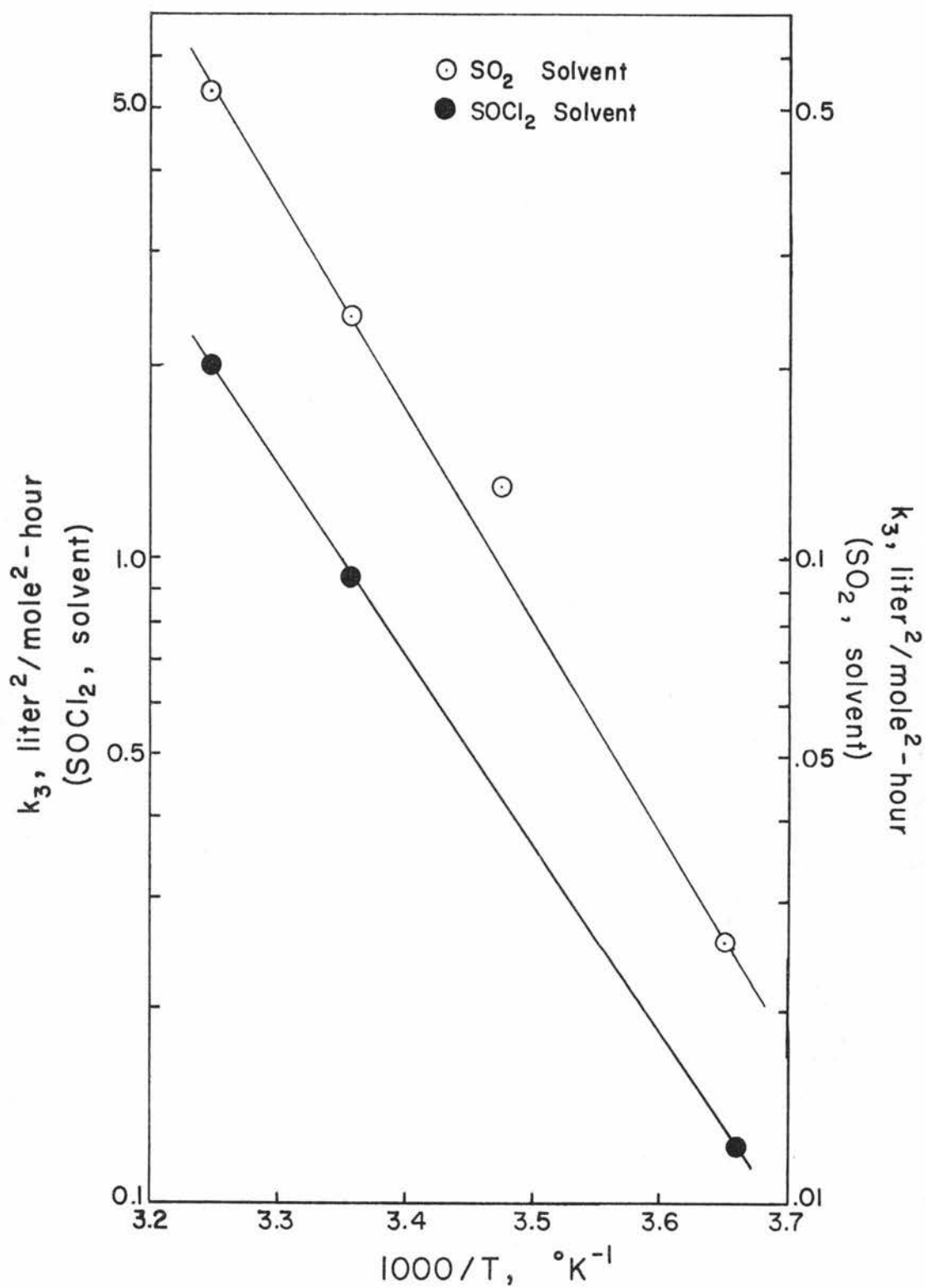


FIGURE 12. The Temperature Dependence of the Rate: Et_3N Experiments.

"frequency factor", and T is the absolute temperature.

The values of A and E_{exp} thus calculated are:

in excess SOCl_2 , $E_{\text{exp}} = 13.5 \text{ Kcal/mole}$

$$A = 2.08 \times 10^6 \text{ liter}^2/\text{mole}^2\text{-second}$$

in excess SO_2 , $E_{\text{exp}} = 14.6 \text{ Kcal/mole}$

$$A = 3.42 \times 10^6 \text{ liter}^2/\text{mole}^2\text{-second.}$$

The estimated accuracy of E_{exp} is approximately

$\pm 0.5 \text{ Kcal/mole}$. From the relation given by Glasstone,

Laidler and Eyring (10, p. 199)

$$k = e \frac{\bar{k}T}{h} e^{-(E_{\text{exp}}/RT)} e^{\Delta S^\ddagger/R} \quad (32)$$

the entropy of activation, ΔS^\ddagger , has been calculated.

Here \bar{k} is the Boltzman constant, h is Planck's constant

and k is the rate constant, in our case, k_3 . Substi-

tution into this equation leads to the value

$-31.0 \text{ cal/degree-mole}$ based on all experiments at all

temperatures. Considering excess sulfur dioxide experi-

ments separately from the excess thionyl chloride ex-

periments, in excess SO_2 $\Delta S^\ddagger = -30.6 \text{ cal/degree-mole}$

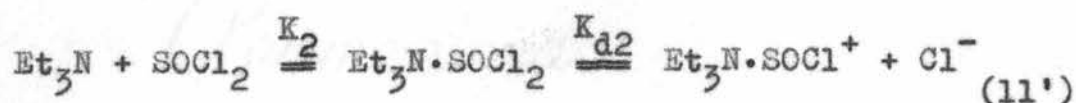
(from data on fifteen runs), in excess SOCl_2 $\Delta S^\ddagger =$

$-31.7 \text{ cal/degree-mole}$ (from data on eight runs).

5. Discussion

First, we would like to consider the question:

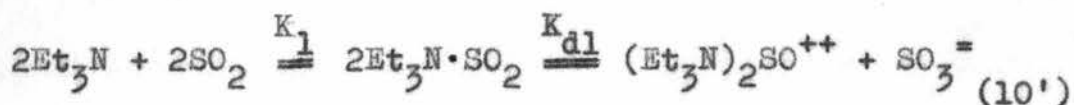
does triethylamine react with thionyl chloride to form chloride ion, which in turn is the catalyst for the exchange? Returning to equation (11) we have, according to Spandau and Brunneck (32)



The rate law for the exchange catalyzed by ionic chlorides, according to Masters and Norris (24), is

$$\text{Rate} = k(\text{catalyst})(\text{SOCl}_2)(\text{SO}_2) \quad (3')$$

where (catalyst) refers to the stoichiometric concentration of ionic chloride put into solution, e.g., rubidium chloride; in the present instance, this would be the triethylamine-thionyl chloride complex. The concentration of this complex ($\text{Et}_3\text{N} \cdot \text{SOCl}_2$) is dependent not only on the concentration of amine and thionyl chloride, but also on the concentration of sulfur dioxide since sulfur dioxide also reacts with triethylamine to form a 1:1 complex (see Run Procedures and also below), a reaction suggested by Jander (15, p. 289-291) to involve the equilibria shown in equation (10)



From the consideration of the equilibrium constants K_2 and K_1 , one finds that the concentration of the triethylamine-thionyl chloride complex is given by

$$[\text{Et}_3\text{N} \cdot \text{SOCl}_2] = \frac{K_2 (\text{Et}_3\text{N}) [\text{SOCl}_2]}{K_2 [\text{SOCl}_2] + K_1 [\text{SO}_2] + 1}$$

In this equation and the following, parentheses indicate the stoichiometric concentrations of reactants put into the solutions and square brackets refer to equilibrium concentrations.

In order for equation (3') to be valid in its given form, it seems best to restrict our discussion at first to experiments where triethylamine concentration is clearly less than that of either the sulfur dioxide or the thionyl chloride. Under these circumstances no significant amounts of either of these substances would then be lost to complex formation as shown in (11') and (10'). Doing so, then, one may substitute this last expression for the triethylamine-thionyl chloride complex "catalyst" concentration in equation (3'), thus obtaining the trial rate law

$$\text{Rate} = \frac{k K_2 (\text{Et}_3\text{N})(\text{SOCl}_2)(\text{SO}_2) [\text{SOCl}_2]}{K_2 [\text{SOCl}_2] + K_1 [\text{SO}_2] + 1}$$

Upon examining this equation, we see that, in excess

sulfur dioxide, and hence at low thionyl chloride concentration, so long as K_2 and K_1 are of the same order of magnitude, the rate law requires that the reaction be second order in thionyl chloride concentration. Such a reaction order, however, is at variance with the experimentally observed order of unity under these conditions. Only by assuming K_2 to be very much larger than K_1 is it possible to make the above equation match the experimentally observed rate law.

A lower limit for the possible value of K_2 may be estimated on the basis of the following points. With tetramethylammonium chloride as catalyst, Masters and Norris (24) found k in (3') to have a value in excess thionyl chloride solution ~ 3.5 times as great as in excess sulfur dioxide solution. On the other hand, in the present results with triethylamine as catalyst, the rate constant in excess thionyl chloride was ~ 4.25 times as great as in excess sulfur dioxide (this comparison being based actually on two particular experiments, viz. Runs 40 and 26, respectively). One may account for the difference between these two factors (4.25 versus 3.5) in terms of a particular value of K_2 , assuming $K_1 \geq 200$ (see below in this section). Making this calculation, one obtains $K_2 \geq 94,000$. The exact values here are not so important as the fact that K_2 is very large and much

greater than K_1 . It should also be noted that if the difference between the factors, 4.25 and 3.5, is not really significant, and therefore might be much less than it appears to be (or perhaps actually zero), the K_2 value becomes far larger still.

Thus if K_2 is in fact very large, it appears that, in fact, the complex $\text{Et}_3\text{N} \cdot \text{SOCl}_2$ might be functioning as the equivalent of an ionic chloride catalyst in the rate law, equation (3'). However, an insurmountable difficulty presents itself relative to this mechanism when we consider the experimental results at triethylamine concentrations comparable to or higher than thionyl chloride concentration. Thus, for example, in Run 44, where $(\text{Et}_3\text{N}) = 1.44$ and $(\text{SOCl}_2) = 0.669$ (and $(\text{SO}_2) = 16.97$), one may use the above estimated values of K_1 and K_2 to calculate equilibrium concentrations for the two complexes, viz. $(\text{Et}_3\text{N} \cdot \text{SOCl}_2) = 0.64$ molar and $(\text{Et}_3\text{N} \cdot \text{SO}_2) = 0.80$. This means that the residual thionyl chloride concentration in solution, left over from that used in forming the complex, amounts to only 0.03 molar in place of the dosed concentration of 0.67 molar. Now it has been observed experimentally in the present work that a third order rate law of exactly the form of (3') is followed quite closely, with (SO_2) , (SOCl_2) and (Et_3N) representing dosed concentrations. This applies even to the

higher triethylamine concentration runs, including Run 44. Yet if we are to interpret this observed rate law as relating to catalysis by the complex $\text{Et}_3\text{N} \cdot \text{SOCl}_2$ functioning essentially as an ionic chloride catalyst in (3'), we have two specific major difficulties.

In the first place, as we have just seen, the catalytic complex concentration would be only 0.64 in place of the dosed Et_3N concentration of 1.44 molar. This effect alone should lead to an observed rate only about one-half as high as would be expected on the basis of the dosed concentration, the observed value, as reflected in the calculated rate constant is 0.0226, a figure quite comparable to runs at lower triethylamine concentration (and comparable thionyl chloride concentration. Cf. Run 21, $k = 0.0238$).

In the second place, the equilibrium thionyl chloride concentration would be (for K_1 and K_2 as estimated) far less in Run 44 than that dosed (0.03 versus 0.67). Since presumably the equilibrium concentrations rather than that dosed would apply in equation (3'), we should, on the basis of this effect, find only about one-twentieth the rate in Run 44 as compared to that expected for the dosed thionyl chloride concentration. As already indicated, no significant decrease at all in this run was observed as compared to those at lower

triethylamine concentration.

On the basis of the foregoing points, it is clear that K_2 cannot be vastly larger than K_1 if the ionic chloride catalysis scheme is to apply to the present results. Yet it has already been shown that unless K_2 is much larger than K_1 , the expected rate law in excess sulfur dioxide would be second order in thionyl chloride, a conclusion at variance with what is actually observed. Hence we must conclude that the ionic chloride catalysis mechanism scheme cannot be made to fit the present results.

Finally, relative to the above discussion, it is of interest to calculate the thionyl chloride equilibrium concentration to be expected in Run 44 on the basis of the K_1 and K_2 values deduced for $\text{Et}_3\text{N}\cdot\text{SO}_2$ and $\text{Et}_3\text{N}\cdot\text{SOCl}_2$ complex formation in the kinetic treatment offered below, which appears to fit the present data satisfactorily. With $K_1 = 200$ and $K_2 = 67$, one obtains an equilibrium thionyl chloride concentration of 0.66, very little lower than the dosed concentration of 0.67 molar. Now, throughout the excess sulfur dioxide range, the rate law to be presented reduces essentially to (3'), and the assumption is made that complex formation is never great enough to decrease the thionyl chloride or sulfur dioxide concentrations substantially. Thus the above calculated

equilibrium thionyl chloride concentration is quite acceptable in terms of this rate law, as is the observed rate in Run 44, a situation in marked contrast to that presented by the hypothetical ionic chloride catalysis scheme.

To summarize, then, it would seem clear that, on the basis of the foregoing discussion, any chloride ion concentration which may possibly be produced in such an equilibrium as the second half of (11') must be in too low concentration to represent an effective catalytic entity, at least as a competitor relative to the alternative exchange mechanism presented below.

It is of interest now to make a further comparison of the present exchange results with those obtained in the experiments involving catalysis by ionic bases (24). Reference to Table XIII shows that the energy of activation of the exchange is almost the same for catalysis by ionic chlorides as by triethylamine. The entropy of activation for the latter catalyst is somewhat lower than, but comparable to that for tetramethylammonium chloride (2.5 cal/mole lower in excess sulfur dioxide and 2.1 cal/mole lower in excess thionyl chloride). In both instances, furthermore, the rate law is

$$\text{Rate} = k_3(\text{catalyst})(\text{SO}_2)(\text{SOCl}_2) \quad (33)$$

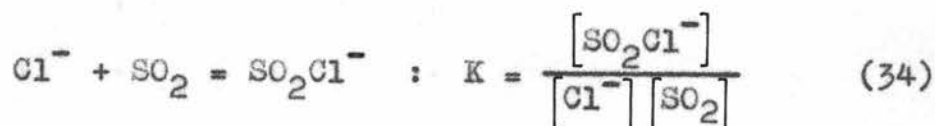
TABLE XIII
 A , E_{exp} and ΔS^\ddagger
 for Base Catalyzed Exchange

Catalyst	"Solvent"	A ($l^2/M^2\text{-sec}$)	E_{exp} (Kcal/ $^\circ\text{C-M}$)	ΔS^\ddagger (cal/Mole)
Et_3N	SO_2	3.42×10^6	14.6	-30.6
	SOCl_2	2.08×10^6	13.7	-31.7
RbCl	SO_2	5.31×10^6	14.7	-29.5
Me_4NCl	SO_2	1.08×10^7	14.7	-28.1
	SOCl_2	5.11×10^6	13.6	-29.6

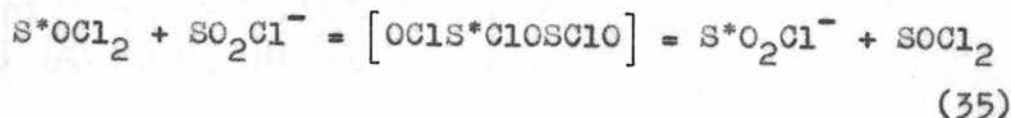
and in both instances k_3 increases on going from an excess sulfur dioxide to an excess thionyl chloride solution.

To illustrate this last point, the values of Masters and Norris (24) for k_3 for all experiments with tetramethylammonium chloride at 0° have been plotted as a function of mole-fraction of thionyl chloride, f_{SOCl_2} (Figure 11b).

This is to be compared with Figure 11a, which shows the results of all the triethylamine experiments at 25° plotted similarly. It is seen that the parallel is striking. Now, the interpretation by Masters and Norris of this reaction was, as mentioned in the Introduction, that there is a preliminary rapid solvation of the base, chloride ion, by the sulfur dioxide,



followed by the rate-determining step, the simultaneous exchange of a chlorine and an oxygen through a symmetrical binuclear bridge complex, thus,



The equilibrium constant, K , for (34) was presumed to be small.

The equilibrium constant for the solvation of

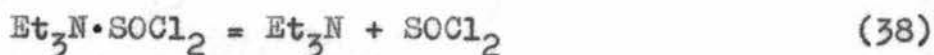
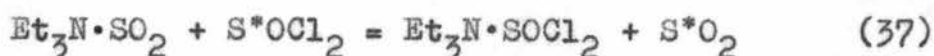
triethylamine by sulfur dioxide, on the other hand, cannot be small. Herber (12, p. 12-16) measured the vapor pressure of sulfur dioxide-triethylamine mixtures at 20-25° and found a minimum vapor pressure at an equimolar mixture of the two compounds. If the assumptions are made that sulfur dioxide is the major species in the vapor and that the solution at a 1:1 molar ratio is an ideal solution, we can estimate, from Herber's data, the equilibrium constant for the reaction



Doing so, we find a value of $200 \leq K_1 \leq 10,000$, depending on which of Herber's vapor pressures we take.¹ At present, the absolute value of K_1 is unimportant as long as it is large enough so that most of the amine can be considered solvated. We find that in Run 40, where we would expect the lowest amount of solvated amine ($(\text{SO}_2) = 0.213$ moles/liter and $(\text{Et}_3\text{N}) = 0.0088$ moles/liter), 94% of the triethylamine in the solution would be in the form of $\text{Et}_3\text{N} \cdot \text{SO}_2$, assuming $K_1 = 200$. This, of course, ignores the fact that thionyl chloride is present

¹In three experiments, the minimum vapor pressure for an equimolar mixture of SO_2 and Et_3N was 5 mm at 25°, 12 mm at 20° and 20 mm at 24°. Above, $K_1 = 200$ corresponds to the vapor pressure 20 mm, $K_1 = 10,000$ corresponds to the vapor pressure 5 mm.

in much greater amounts than sulfur dioxide and also forms a complex with triethylamine. The point is, the amine can be considered as essentially all solvated in all the present experiments. It would seem reasonable to suppose that the first step in the amine-catalyzed exchange is like that given in equation (34), the solvation by sulfur dioxide of the base -- in this instance, the amine. This would next be pictured as reacting to exchange a sulfur with $S^{35}OCl_2$, via a binuclear bridged activated complex similar to that postulated for chloride-catalyzed exchange.



The situation here appears less straightforward than in the case of chloride catalysis, however, for reaction (37) cannot be pictured as a simple step. The obvious route to exchange requires the formation of the binuclear complex and a bond flip-flop, as is assumed the case in the mechanism of the chloride-catalyzed exchange. In this case, there would be required, in addition, the formation of an ion pair (or free ions), chloride ion plus a complex cation, sometime in the transition state. After the bond flip-flop, the resulting $(Et_3N \cdot SOCl)^+$

would be pictured as reacting with the chloride ion to form $\text{Et}_3\text{N} \cdot \text{SOCl}_2$. Alternatively, the activated complex could be considered a trinuclear bridge, a six-center affair, but this seems beyond the bounds of credibility. The large, negative entropy of activation does suggest an involved structure, but a binuclear bridge, four-center complex appears quite sufficiently involved.

Looking more closely at the reaction steps (36) through (38), we see that an exchange path is provided by the reverse of the path therein outlined -- that is, by following steps (38) through (36) backward. Thus, if both the forward and reverse paths are to be considered, we must write the rate law as

$$\text{Rate} = k_1 [\text{SOCl}_2] [\text{SO}_2 \cdot \text{Et}_3\text{N}] + k_2 [\text{SO}_2] [\text{SOCl}_2 \cdot \text{Et}_3\text{N}] \quad (39)$$

$$[\text{SO}_2 \cdot \text{Et}_3\text{N}] = K_1 [\text{SO}_2] [\text{Et}_3\text{N}] \quad (40)$$

$$[\text{SOCl}_2 \cdot \text{Et}_3\text{N}] = K_2 [\text{SOCl}_2] [\text{Et}_3\text{N}] \quad (41)$$

Assuming that K_1 or K_2 (or both) are large, combination of (40) and (41) with (39) yields the new rate law

$$\text{Rate} = \frac{k' [\text{SO}_2] [\text{SOCl}_2] (\text{Et}_3\text{N})}{K' [\text{SO}_2] + [\text{SOCl}_2]} \quad (42')$$

As before, dosed concentrations are indicated by

parentheses, and equilibrium concentrations by square brackets. As noted in Section IV, $K' = K_2/K_1$ and $k' = (k_1 + \frac{K_2}{K_1} k_2)$. Now in the large majority of cases the total dosed concentration of triethylamine is much lower than either the sulfur dioxide or the thionyl chloride. Even where this is not so, the values of K_1 and K_2 which emerge from the treatment below are such that, in no experiment is sufficient complex formed to constitute a significant drain on the dosed concentrations of either of the two exchanging reactants. (This point has already been brought out in our discussion given above, of the equilibrium thionyl chloride concentration in Run 44.) Under these circumstances (42') can be written in the more useful form

$$\text{Rate} = \frac{k'(\text{SO}_2)(\text{SOCl}_2)(\text{Et}_3\text{N})}{K'(\text{SO}_2) + (\text{SOCl}_2)} \quad (42)$$

We see that, qualitatively, this rate law fits the data. At high concentrations of sulfur dioxide, $\text{Rate} \propto (\text{Et}_3\text{N})(\text{SOCl}_2)$, and where thionyl chloride concentration is large, $\text{Rate} \propto (\text{Et}_3\text{N})(\text{SO}_2)$.

The constants, k' and K' , have been evaluated by a least squares treatment and are found to be $K' = 0.3$, $k' = 4.9$. From the relation

$$k_3 = \frac{k'}{K'(SO_2) + (SOCl_2)} \quad (43)$$

where k_3 refers to $\frac{\text{Rate}}{(SOCl_2)(SO_2)(Et_3N)}$, values of k_3 have been calculated. The solid line in Figure 11a is the result of this calculation and it is seen that the agreement here is excellent.

If it is now assumed that a similar rate law is operative in all cases of the base-catalyzed exchange, i.e., that we may write

$$\text{Rate} = k_1[SOCl_2][\text{Base} \cdot SO_2] + k_2[SO_2][\text{Base} \cdot SOCl_2] \quad (44)$$

$$K_1 = \frac{[\text{Base} \cdot SO_2]}{[\text{Base}][SO_2]} \quad (45)$$

$$K_2 = \frac{[\text{Base} \cdot SOCl_2]}{[\text{Base}][SOCl_2]} \quad (46)$$

In the instance where

$$(\text{Base}) \ll (SO_2) \text{ or } (SOCl_2) \quad (47)$$

a general expression results (48).

$$k_3 = \frac{(k_1K_1 + k_2K_2)}{K_1(SO_2) + K_2(SOCl_2) + 1} \quad (48)$$

Where, in the case of triethylamine, K_1 and K_2 are large, this expression reduces to (43).

Let us consider, again, the exchange reaction catalyzed by tetramethylammonium chloride. Here, we can hardly expect that either K_1 and K_2 will be large.² On the other hand, if both K_1 and K_2 are very small, say less than 0.01, k_3 will be approximately constant, at the most varying approximately 22% (this is calculated for $K_2 = 0$, $K_1 = 0.01$; if K_2 is taken as greater than zero, there is less variation in the rate).

Here then, we apparently may have a means of accounting for the variation in k_3 observed by Masters and Norris on going from excess sulfur dioxide to excess thionyl chloride solutions. In principle, the values of K_1 , K_2 and $(k_1K_1 + k_2K_2)$ can be determined by taking any three values of k_3 at different concentrations of sulfur dioxide and thionyl chloride and solving three simultaneous equations. Masters and Norris' data have therefore been treated accordingly. Picking three points, one from the thionyl chloride rich, one from the sulfur dioxide rich, and one from approximately equimolar SO_2 - SOCl_2 mixtures, and solving for the three constants leads to quite small, negative values for K_2 -- a physically

²For instance, no reports have been made of the preparation of and isolation of ionic chlorosulfinates (species containing the ion SO_2Cl^-), though the analogous fluorosulfinates have been isolated and well characterized (11, p. 451-462).

nonsensical result. (These calculations were repeated for several sets of points.) If we take this as an indication that K_2 is zero, then the expression for k_3 reduces to

$$k_3 = \frac{k_1 K_1}{K_1(\text{SO}_2) + 1} \quad (49)$$

Now, this equation may be solved for K_1 and k_1 from the values of k_3 and (SO_2) at any two points. Doing so, we arrive at a value of $K_1 = 0.17$ liter/mole and $k_1 = 1.5$ liter/mole-hour. The value of k_3 calculated using these values is shown (solid line) in Figure 11b. The agreement of the derived curve with the experimental points, while giving a rough fit, is definitely poorer than one might have hoped for. This does not necessarily mean, however, that the mechanism is fundamentally different in the two exchange reactions. At the time that the tetramethylammonium chloride catalysis work was published, no adequate quantitative data were available concerning the degree of ion-pairing in the solutions. At the time, the best assumption appeared to be that ionic chlorides were effective catalysts for the exchange reaction whether in the form of ion-pairs or free ions.

We are now in a better position to calculate the

extent of ion-pairing in these solutions. The dissociation constant, K_d , for the tetramethylammonium chloride in liquid sulfur dioxide (9.4×10^{-4} at 0°) has been generously made available to us by Lichten.³ From the relation (50), the mass action law, α may be deduced assuming values of f_{\pm} are available.

$$K_d = \frac{\alpha^2 f_{\pm}^2 (\text{Me}_4\text{NCl})}{1 - \alpha} \quad (50)$$

where f_{\pm} is the mean molar ionic activity coefficient of tetramethylammonium chloride, the activity coefficient of the ion pair is assumed to be one, α is the degree of dissociation, and (Me_4NCl) is the stoichiometric molar concentration of tetramethylammonium chloride. The Debye-Hückel equation, equation (51), where a_{DH}° is the distance of closet approach parameter in Ångströms, D is the dielectric constant of the solvent and T is the absolute temperature, can be used for attaining values of f_{\pm} .

$$-\log f_{\pm} = \frac{1.814 \times 10^6 (DT)^{-3/2} [\alpha(\text{Me}_4\text{NCl})_s]^{1/2}}{1 + 50.30 a_{\text{DH}}^\circ (DT)^{-1/2} [\alpha(\text{Me}_4\text{NCl})_s]^{1/2}} \quad (51)$$

In the present instance, where we are looking for nothing more than an estimate of α , it will suffice to substitute

³Norman N. Lichten, private communication.

for $\overset{\circ}{a}_{DH}$, the quantity $\overset{\circ}{q}$, defined by

$$\overset{\circ}{q} = \frac{10^8 e^2}{2D\bar{k}T}$$

(where e is the electronic charge and \bar{k} is the Boltzman constant) which refers to the closest approach singly charged ions make without forming ion pairs.⁴

Substituting the expression for $\overset{\circ}{q}$ into (51) in place of $\overset{\circ}{a}_{DH}$ and solving the result simultaneously with (50)(graphically) leads to the values of f_{\pm} and α . Masters and Norris' values for six experiments at fixed sulfur dioxide and thionyl chloride concentrations are shown in Table XIV (first six entries). Although the data presented are not conclusive, it would seem that as α decreases there is a trend toward lower k_3 values. If this trend in k_3 is real, it would seem that free ions are rather more effective catalysts than ion pairs. Such an effect would be of considerable interest in presenting a distinct parallel to the recent observations of Lichtin and Rao (19) in their study of radiobromine exchange between p-nitrobenzyl bromide and ionic bromide in liquid sulfur dioxide solution. Although no precise quantitative conclusion with regard to Masters and Norris' tetramethylammonium chloride data is possible at this time,

⁴

This follows the Bjerrum treatment (27, p. 395-397).

TABLE XIV

Degree of Dissociation and Rate Constants
for Tetramethylammonium Chloride-Catalyzed Exchange at 0°

Exp ^{a)}	(Me ₄ NCl) x 10 ²	(SO ₂)	(SOCl ₂)	α	k ₃ (obs) x 10 ³	k ₃ (calc) x 10 ³
	(M/l)	(M/l)	(M/l)		(l ² /M ² -hr)	(l ² /M ² -hr)
10	0.444	20.6	1.146	0.52 ^{b)}	7.24	7.6
8	0.665	20.6	1.146	0.47 ^{b)}	5.25	7.0
9	1.372	20.6	1.146	c)	6.39	c)
13	3.85	20.6	1.146	c)	4.81	c)
11	6.65	20.6	1.146	c)	6.57	c)
12	22.6	20.6	1.146	0.14 ^{d)}	4.20	3.4
21	0.927	9.65	8.04	0.20 ^{d)}	7.0	7.7
22	1.181	6.14	10.21	0.11 ^{d)}	10.3	7.6
26	0.336	0.815	13.60	0.065 ^{d)}	21.0	21.0

a) Experiment numbers of Masters and Norris (24).

b) Dielectric constant of pure sulfur dioxide used in these calculations.

c) Not calculated.

d) Assumed dielectric constants additive on a mole fraction basis.

it would seem that (49) should be replaced by an expression containing the degree of dissociation

$$k_3 = \frac{K_1(\alpha k_f + (1-\alpha) k_p)}{K_1(\text{SO}_2) + 1} \quad (52)$$

i.e., k_1 has been replaced by $(\alpha k_f + (1-\alpha) k_p)$, where k_f and k_p refer to the rate constants for the free ions (Cl^-) and the ion-pairs ($\text{Me}_4\text{N}^+\text{Cl}^-$), respectively.

Values of the degree of dissociation, α , calculated as above, and the experimental rate constants, k_3 (obs), are presented in Table XIV for several exchange experiments where tetramethylammonium chloride was the catalyst. The dissociation constant, K_d , and the degree of dissociation were calculated from the Bjerrum equation (27, p. 393-397) (see also Appendix B) assuming that, in excess sulfur dioxide, the dielectric constant of the solvent was the same as in pure sulfur dioxide, no account being taken of the thionyl chloride present. In the experiments where thionyl chloride was a major solution species, it was assumed that the dielectric constants of sulfur dioxide and thionyl chloride were additive on a mole fraction basis.

Taking the degree of dissociation and the rate constant from any three experiments and using equation (52) one may solve for the values of K_1 , k_f and k_p .

Values of these three constants, adjusted by trial to fit all the points in Table XIV reasonably well, are $K_1 = 0.8$, $k_f = 0.3$ and $k_p = 0.02$. The values of k_3 , calculated from equation (52) using these constants are shown in the right-hand column of Table XIV. It is seen that, indeed, these calculated values for k_3 are in reasonable agreement with the observed values. Discrepancies between the calculated and observed values may be attributed partly to scatter in the experimental data and partly to the approximations made in the calculations of the values of the ion pair dissociation constant and the degree of dissociation.

It is most interesting to find this agreement between calculated and observed values of k_3 . Thus we find a more satisfactory explanation for the observed increase in exchange rate on going from excess sulfur dioxide to excess thionyl chloride than is offered by equation (49). It further is of real interest to find the degree of dissociation of the ion pairs, α , having quite the significant values shown in Table XIV. Such an observation would appear to invalidate Masters and Norris' assumption that ion pairs represented the only important kinetic entity in the solutions. An additional final point of some interest is the observation that k_f is fifteen times

as large as k_p . In their work on radiobromine exchange between tetramethylammonium bromide and p-nitrobenzyl bromide, Lichtin and Rao (19) found a similar effect, their rate constant for free bromide ions being significantly larger than those for ion pairs.

If the foregoing analysis is correct, then the general mechanism suggested for base-catalyzed exchange may well also be applicable here. It would be very interesting to see this confirmed (or not, as the case may be) by a careful, detailed study of the exchange rate as a function of ionic chloride concentration at one concentration of sulfur dioxide and thionyl chloride, for various ionophores.

Finally, it is pertinent to consider the question: What is the effect of non-equilibrium behavior of the exchange solutions on the rate? Experiments 25, 45 and 46 were designed to test for this effect by equilibrating triethylamine with either sulfur dioxide (Experiment 45) or thionyl chloride (Experiments 25 and 46) before initiation of the exchange reaction (see Section III, D). Reference to Table XI shows that the rate constants for these experiments are, within experimental error, indistinguishable from the rate constants of the experiments run under the usual experimental conditions at comparable concentrations. As another point, it was

noted earlier that whenever it was done (this actually in the majority of runs) the rate calculated from the change in specific activity of thionyl chloride was the same, within experimental error, as the rate calculated from the change in specific activity of sulfur dioxide. Further, the McKay plots were typically good straight lines (see, for instance, Figure 4, the McKay plot for Experiment 25), typical of simple exchange systems. Finally, the fact that all of the rate data, over a wide range of concentration of reactants, form a unified picture by a simple kinetic treatment which ignores the non-equilibrium behavior of the exchange solutions, would lead one to believe that such non-equilibrium behavior has too small an effect on the exchange rate to be noticed from the kinetic measurements.

These experiments show that the nonionic base, triethylamine, catalyzes the exchange in a manner quite analogous to the ionic chloride bases (if one takes into account ion pairing in the latter). Thus, the experimental activation energies associated with the exchange catalyzed by these two type materials, are essentially the same, while the entropies of activation are quite similar. The kinetics of the exchange catalyzed by either ionic chlorides or the amine can be accounted for nicely by one mechanism (again, taking into account ion

pairing with the ionic materials), in which triethylamine acts directly as a base without any necessary pre-formation of chloride ions in the solutions. This is quite different than would be expected on the basis of the "solvent systems" concept of acids and bases, as propounded, for instance, by Spandau and Brunneck. Thus these experiments, like those of Johnson, Norris and Huston (16) and those of Herber and Norris (13), show the weakness of the "solvent systems" concept of acid-base behavior. It would seem, then, that some more general acid-base concept, such as that of Lewis, should be used in order to explain the chemistry in solutions such as were here investigated.

B. Acetone Experiments

In the acetone experiments, as in those with triethylamine, the quantities of reactants have been converted to molar concentrations assuming additivity of volumes. The data pertaining to these experiments are presented in Table XV. Since relatively large concentrations of acetone were required to attain conveniently measurable rates, it was not possible to vary the concentration of any one reactant independently of the other two. Therefore, a somewhat different approach than with triethylamine was used in deducing the rate law. First,

it was assumed, as before, that the rate law was of the form

$$\text{Rate} = k(\text{SO}_2)^a(\text{SOCl}_2)^b(\text{Me}_2\text{CO})^c \quad (53)$$

Then, since in the previous examples of the exchange catalyzed by a base, it had been found that $a = b = 1$, it was assumed, at least tentatively, that this held true here also. If so, a plot of $\log \frac{\text{Rate}}{(\text{SO}_2)(\text{SOCl}_2)}$ as a function of $\log (\text{Me}_2\text{CO})$ should yield a straight line of slope c . Figure 13 shows such a plot for all of the acetone experiments at 0°C and it is seen that a line of slope two fits the points reasonably well. This means that a plot of $\log \frac{\text{Rate}}{(\text{SOCl}_2)(\text{Me}_2\text{CO})^2}$ versus $\log (\text{SO}_2)$ should be linear and have a slope of one ($a = 1$) for consistency with the assumption that the order is first in sulfur dioxide and a plot of $\log \frac{\text{Rate}}{(\text{SO}_2)(\text{Me}_2\text{CO})^2}$ versus $\log (\text{SOCl}_2)$ would similarly yield a straight line of slope one ($b = 1$). Figures 14 and 15 show such plots with lines of slope one drawn through the points. The fit is seen to be satisfactory.

On the basis of these plots, the proposed rate law is

TABLE XV

Exchange Experiments with Acetone

Exp	(SO ₂)	(SOCl ₂)	(Me ₂ CO)	Rate x 10 ⁴ ^{a)}	k ₄ x 10 ⁴
	(M/l)	(M/l)	(M/l)	(M/l-hr)	(l ³ /M ³ -hr)
Temperature 25°C					
IV	18.0	1.14	1.01	1000	50.2
V	1.92	12.23	0.149	(14.8)	(28.2) ^{b)}
					Ave. 39.2
Temperature 0°C					
VIIA	0.810	12.86	0.747	4.7	0.809
VIIIB	0.829	12.84	0.754	8.04	1.33
VIII	1.40	12.29	0.928	22.5	1.52
IX ^{c)}	1.41	12.26	0.926	25.8	1.74
XIA	3.69	11.24	0.539	10.4	0.863
XIB	3.70	11.28	0.499	10.7	1.03
XIIA	8.58	8.58	0.124	(2.28)	(2.01) ^{b)}
XIIB	8.58	8.58	0.124	(4.22)	(3.73) ^{b)}
XVI	13.98	3.10	2.10	218	1.14
XVII	15.15	3.37	1.14	74.1	1.12
XVIII	12.97	2.88	2.92	382	1.20
XIX	17.32	1.86	1.29	119	1.15
XX	17.45	1.88	1.52	98.3	1.30
					Ave. 1.46

a) Based on F_{SOCl₂}.b) Estimated error, ±50%.

c) Run designed to test for effect of non-equilibrium conditions. See Run Procedures.

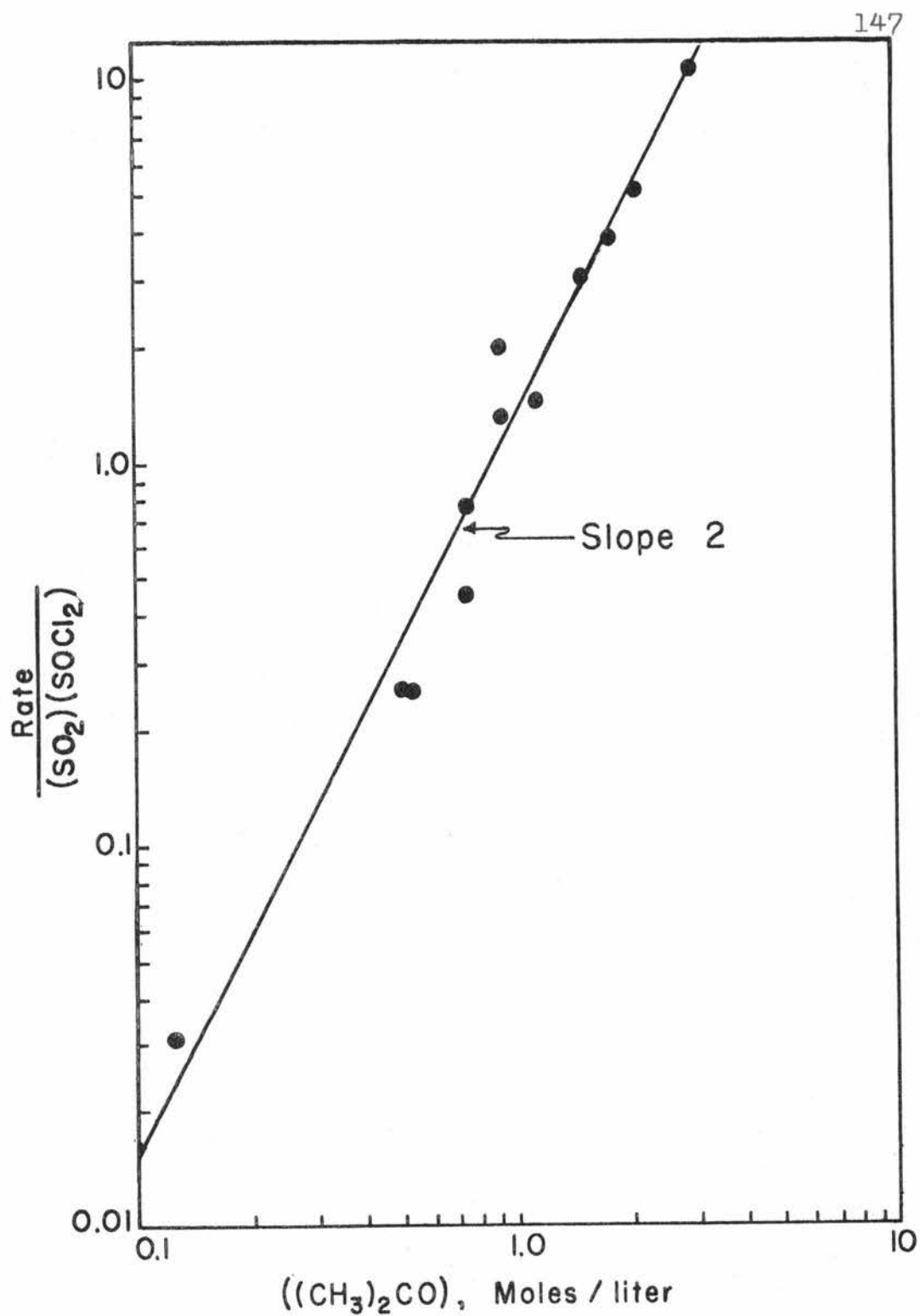


FIGURE 13. The Rate Dependence on Acetone Concentration.

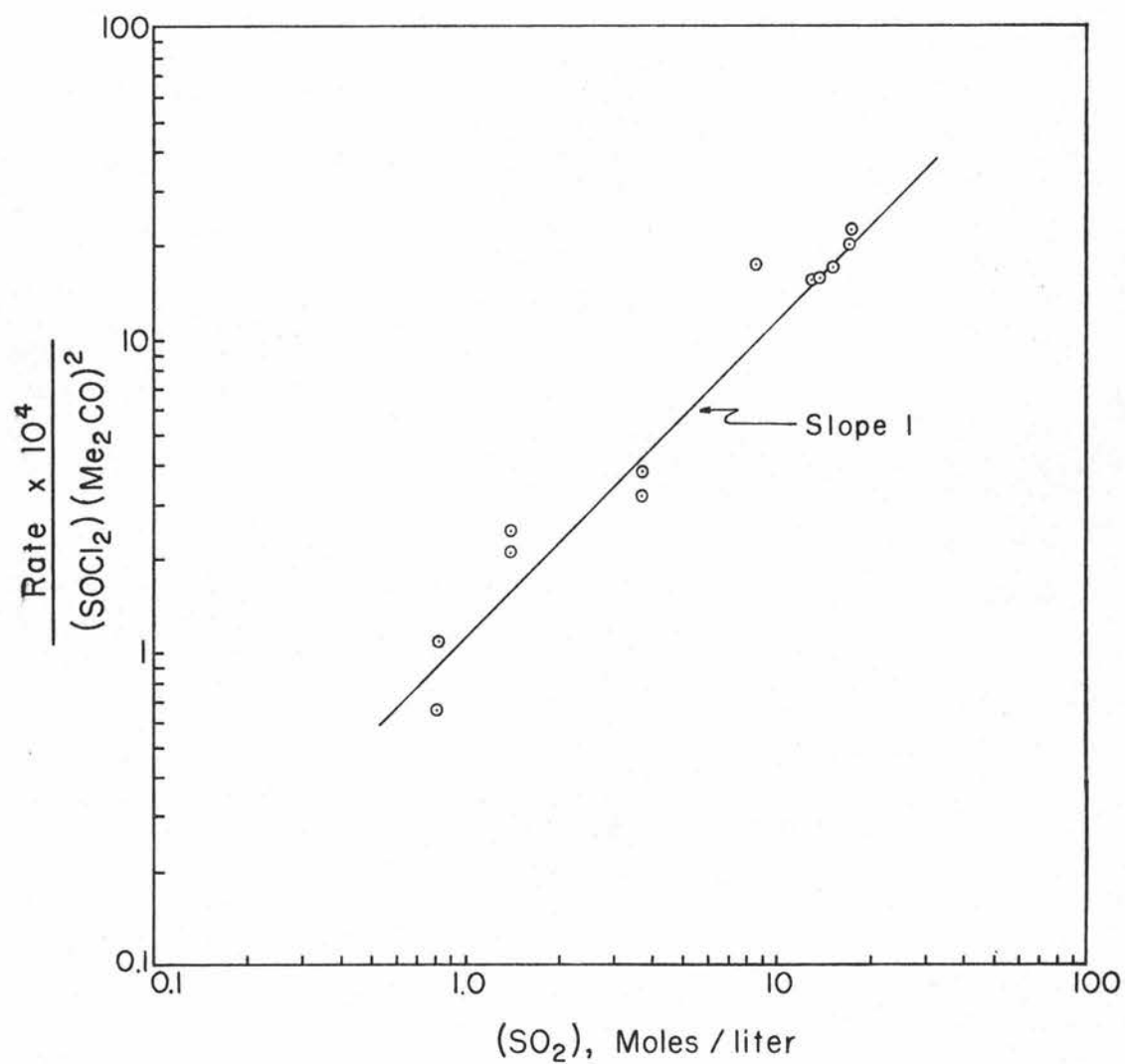


FIGURE I4. The Rate Dependence on SO_2 Concentration.

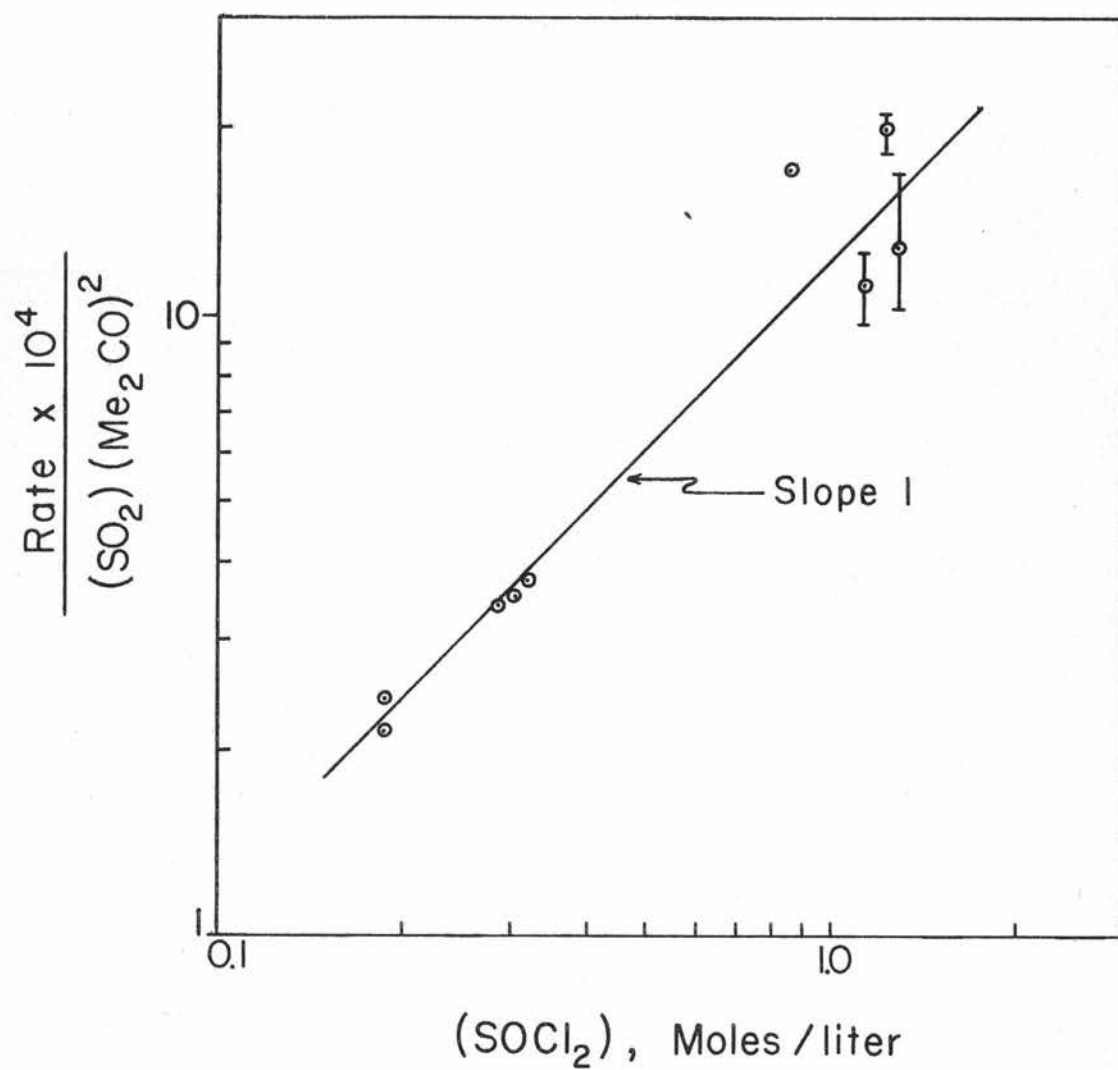


FIGURE 15. The Rate Dependence on SOCl_2 Concentration.

$$\text{Rate} = k_4(\text{SO}_2)(\text{SOCl}_2)(\text{Me}_2\text{CO})^2 \quad (54)$$

The last column of Table XV gives the values of the fourth order rate constant, k_4 .

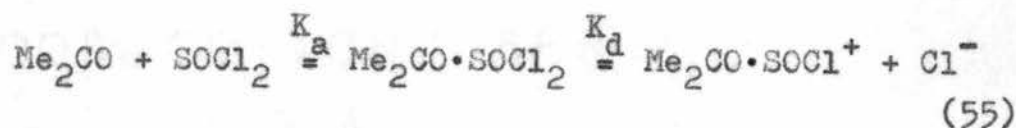
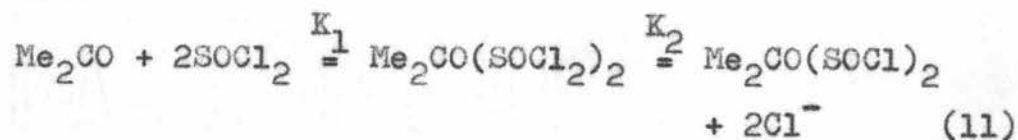
Considering first the experiments at 0°: the scatter in the k_4 figures is rather large, values ranging from 0.809 to 3.73 liters³/mole³-hour. Even leaving out Experiments XIIA and XIIB where the error is known to be large due to the small fraction exchange, the value of k_4 varies by more than a factor of two. Even replicate runs, however, e.g., XIA and XIB or VIIA and VIIB show variations as high as $\pm 45\%$; furthermore, there appears to be no trend in k_4 with concentration of any reactant. Hence there appears no immediate reason to believe, despite the scatter, that k_4 is not a constant. In excess sulfur dioxide the average value of k_4 is 1.18×10^{-4} liters³/mole³-hour; in excess thionyl chloride, 1.22×10^{-4} liters³/mole³-hour.

At 25° there were only two runs: one in excess thionyl chloride and one in excess sulfur dioxide and it is seen that k_4 in the former is somewhat more than one-half k_4 in the latter. It seems likely that this may be connected with difficulties in the running of Experiment V, where the radiochemical balance was poor and thus errors of uncertain size have been introduced.

Hence it has been assumed that the value of k_4 is independent, at 25° just as at 0°, of which substance, thionyl chloride or sulfur dioxide, is in excess.

The energy of activation has been calculated, as before, using here the average value of k_4 at 0° (ignoring Experiments XIIIA and XIIB; 1.2×10^{-4} liters³/mole³-hour), and the value of k_4 for Experiment IV. This results in $E_{\text{exp}} = 24$ Kcal/mole with an estimated error of approximately ± 1 Kcal/mole. Using this value for k_4 , A, the frequency factor, is calculated to be 5.3×10^{11} liters³/mole³-sec. The value of ΔS^\ddagger , the entropy of activation, calculated as before, is -12.6 cal/degree-mole.

These results are in sharp contrast to what might possibly have been expected. Earlier it was observed that acetone dissolved in thionyl chloride yields weakly conducting solutions. It has been postulated (32, 33) that some such equilibria as shown in equations (11) or (55)



must account for such conducting solutions. Assuming

the species formed in (55) to be the catalyst, it is of interest to compare the strength of the catalysis in the present case quantitatively with that previously observed with ionic chlorides as catalyst. Comparing the exchange rate of solutions 0.5 molar in catalyst and 3.0 molar in thionyl chloride in excess sulfur dioxide at 0°, one would expect with tetramethylammonium chloride a rate of 1.65 moles/liter-hour and with acetone 0.002 moles/liter-hour. Clearly, acetone is a far less effective catalyst than tetramethylammonium chloride. Further, as a rate law for an exchange derived from (55), by analogy with the results with tetramethylammonium chloride, one would write

$$\text{Rate} = k_3(\text{SO}_2)(\text{SOCl}_2)(\text{Me}_2\text{CO} \cdot \text{SOCl}_2) \quad (56)$$

Combining equation (55) with (56) (and assuming K_a or K_d small, as would be reasonable in view of the weak catalysis effect) yields

$$\text{Rate} = k_4(\text{SO}_2)(\text{SOCl}_2)^2(\text{Me}_2\text{CO}) \quad (57)$$

On the basis of (57) it follows that the chloride ion concentration in the exchange solutions produced by equation (55) must be slight indeed. Because of the very weak basicity of acetone, such a situation might be understandable, and hence the low rate in itself does

not rule out equilibria such as (55). The actual form of the observed rate law, namely first order in sulfur dioxide and thionyl chloride and second order in acetone, is, however, in conflict with (57) and suggests that some altogether different process than anything akin to equation (55) is of primary significance for the exchange, and presumably, for other chemical processes in such solutions. Any effect from equilibrium (55) would appear to be quite effectively swamped.

One might speculate that the formation of the polymer previously described is somehow connected with the exchange reaction. It would seem a possibility that a reversible equilibrium exists involving the formation of a complex from two acetones and one thionyl chloride molecule. This material we might assume to be the exchange active species, undergoing bimolecular exchange with a sulfur dioxide molecule before again dissociating. At the same time, this complex might well represent the first step in the polymerization process, and, as an alternative to redissociation, might undergo rearrangement, elimination and further polymerization reactions. Evidence pointing in this direction is that the half-time of polymer formation⁵ seems to be very roughly of the

⁵These values were deduced, very roughly, from the weight

same order of magnitude as the exchange half-times.

Alternatively, the exchange may proceed by a path quite independent of the polymerization reaction. The polymerization might be pictured as proceeding via addition of thionyl chloride across the double bond of the enol form of acetone, forming thereby a sulfinic acid chloride ($\text{ClOSCH}_2\text{COCH}_3$) which could further react with enol-acetone to form a sulfoxide ($\text{CH}_3\text{COCH}_2\text{SOCH}_2\text{COCH}_3$). Such sulfoxides may be cleaved in acid solution, i.e. in thionyl chloride (17) to yield such materials as mercaptans and ketoaldehydes; alternatively, they may be chlorinated in the presence of thionyl chloride (4). Further, sulfoxides are known to disproportionate to form mercaptans and sulfones. The exchange might then be pictured as going by coordination of a thionyl chloride molecule (as a Lewis acid) to two acetone carbonyls (keto form), forming an ionic substance which could undergo exchange with sulfur dioxide molecules in a rate-determining bimolecular process. Although one would not wish to press the point without further data, it may be noted, parenthetically, that curvature observed in the McKay plot in Run XVIII (the only case where such was

of residue produced in several experiments (Appendix A). These were then compared with the half-times for the exchange, calculated from the slope of the McKay plot.

observed) may well indicate that the exchange pathway is independent of the polymerization pathway. Such a consideration, then, would support the immediately preceding alternative interpretation of the results over that first discussed.

In the absence of any real knowledge of the products of the reaction between thionyl chloride and acetone, speculation such as the foregoing tends to be rather sterile. Hence it does not seem feasible to carry the discussion further at this point. The principal conclusion to be reached here is that the system is far more complex than would have been predicted on the basis of Spandau and Brunneck's observations.

Before terminating this discussion, the occurrence of non-equilibrium processes in the solution requires some comment. In only one experiment, Experiment XVIII, was a definite non-linearity in the McKay plot discernible. In this experiment acetone concentration was substantially higher than in the other experiments and in fact was essentially equal to that of the thionyl chloride. Hence the polymerization reaction was here sufficiently rapid to remove progressively quite appreciable amounts of both acetone and thionyl chloride, thus modifying the concentrations of these materials available for the exchange to an extent much greater than in the

other experiments. On the basis of such concentration changes the curvature in the McKay plot is readily understandable. Such an effect follows immediately from the rate equation for a simple exchange reaction

$$-\frac{d(S^*O_2)}{dt} = (\text{Rate})(k)(A_{SO_2} - A_{SOCl_2}) \quad (58)$$

(k is the proportionality constant that converts relative activity to absolute activity). In a stable system the exchange rate ("Rate" in (58)) is a constant and the linearity of the McKay plot depends on this fact. In the present non-stable system, however, the progressive change in thionyl chloride and/or acetone concentration would certainly affect the exchange rate (cf. the empirical rate law, equation (54)), and so would lead to the observed curvature. On this basis, it is clear that the exchange rate at zero time would correspond to a "true" rate related to the initial reactant concentrations. Hence, in Experiment XVIII the slope of the McKay plot at zero time was used to calculate the rate.

In all experiments other than XVIII, it was not possible to distinguish the McKay plots from straight lines, a fact indicating the minor importance for the kinetics of the exchange of any non-equilibrium effects in the systems. Hence in these instances the slopes of

the straight lines were used to calculate the rates. In further support of this procedure, one may look at the results of Experiment IX, where thionyl chloride and acetone were allowed to interact for sixty hours at room temperature before the sulfur dioxide was added and the exchange reaction initiated. The results again lead one to the conclusion that non-equilibrium behavior in these solutions is relatively unimportant in the exchange rate calculation in most cases, for here the value of k_4 was found to be indistinguishable, within experimental error, from the value of k_4 in experiments run under the usual conditions. These points plus the fact that the kinetic treatment given leads to a reasonably consistent set of kinetic data, whether the sulfur dioxide or the thionyl chloride is initially active, leads to the conclusion that this simple stable system treatment is satisfactory.

C. Mixed Catalysts Experiments

The results of the experiments with mixtures of the basic and acid catalysts, triethylamine and antimony pentachloride, appear in Table XVI. The concentrations are based on the amounts of reactants as mixed, no account being taken of any complex formation.

In order to establish how mixing these two catalysts affects the rate of the exchange reaction, the

TABLE XVI

Mixed Catalyst Experiments at 0°C

Exp	SO ₂	S*OCl ₂	SbCl ₅	Et ₃ N	Rate x 10 ²	Rate Expected x 10 ²	
	(M/l)	(M/l)	(M/l)	(M/l)	(M/l-hr)	(Moles/liter-hour)	
						SbCl ₅ ^{a)}	Et ₃ N ^{b)}
1a ^{c)}	13	2.9	1.7	0	2.45		
2a ^{c)}	12	1.4	0.84	0.22	2.16	1.84	8.8
3a ^{c)} -1	10	2.2	1.3	1.7	14.5 ^{d)}	1.20	89.0
-2	9.6	2.2	1.3	1.9	--- ^{e)}	1.09	95.5
-3	11	2.4	1.3	1.1	0.232 ^{d)}	1.49	69.1
-4	12	2.6	1.5	0.81	0.524 ^{d)}	1.63	60.1
5a	14	3.09	0.662	0.553	0.160	0.909	55.0
6a	14.5	3.22	0.686	0.287	0.842	1.00	31.9
7a-A	15.0	3.33	0.712	0.0428	1.32	1.08	5.09
7a-B	14.9	3.31	0.706	0.0793	1.42	1.07	8.67
8a ^{f)}	13.8	3.06	0.652	0.629	0.147	0.899	63.2
9a-A	14.9	3.33	0.713	0	1.22	1.18	0
-B ^{g)}	13.5	3.01	0.642	0.687	4.68	0.861	66.4

(Continued on next page)

TABLE XVI - (Cont'd.)

Exp	SO ₂	S*OCl ₂	SbCl ₅	Et ₃ N	Rate x 10 ²	Rate Expected x 10 ²	
	(M/l)	(M/l)	(M/l)	(M/l)	(M/l-hr)	(Moles/liter-hour)	
						SbCl ₅ ^{a)}	Et ₃ N ^{b)}
9a-C ^{c)}	12.4	2.75	0.586	1.27	62.3	0.705	103
-D ^{g)}	9.66	2.15	0.458	2.61	121	0.393	129

a) Calculated on the basis of (SbCl₅), ignoring any complex formation:

$$\text{Rate} = 1.48 \times 10^{-3} (\text{SO}_2) (\text{SbCl}_5 \cdot \text{SOCl}_2); 0.8 = \frac{[\text{SbCl}_5 \cdot \text{SOCl}_2]}{[\text{SOCl}_2] [\text{SbCl}_5]}.$$

b) Calculated on the basis of (Et₃N), ignoring any complex formation:

$$\text{Rate} = 2.34 \times 10^{-2} (\text{SO}_2) (\text{SOCl}_2) (\text{Et}_3\text{N}).$$

c) In experiments 1, 2 and 3, the stock solution was made up incorrectly, thus uncertainty in the amount of SbCl₅ present is about $\pm 30\%$. SOCl₂ was estimated from radiochemical balance to be $\pm 10\%$ of stated value.

d) Rate estimated from one bomb. Estimated error $\pm 50\%$.

e) F = 1 within sampling time (40 hours) -- expected F = .999 from amount of Et₃N excess. See footnote, Table II.

f) Very slight white precipitate.

g) Solutions opaque with copious precipitate.

ratio of the rate observed to that expected on the basis of antimony pentachloride catalysis in the absence of triethylamine has been plotted in Figure 16 as a function of the catalyst ratio, i.e., the concentration of triethylamine divided by the sum of the concentration of triethylamine and antimony pentachloride (Experiments 5a to 9a) (circles). In the same figure is shown the ratio of the rate observed to that expected on the basis of triethylamine catalysis if no antimony pentachloride were present as a function of the catalyst ratio (squares). The rate expected for antimony pentachloride in the absence of amine was calculated on the basis of the work of Burge and Norris (7), using the rate law

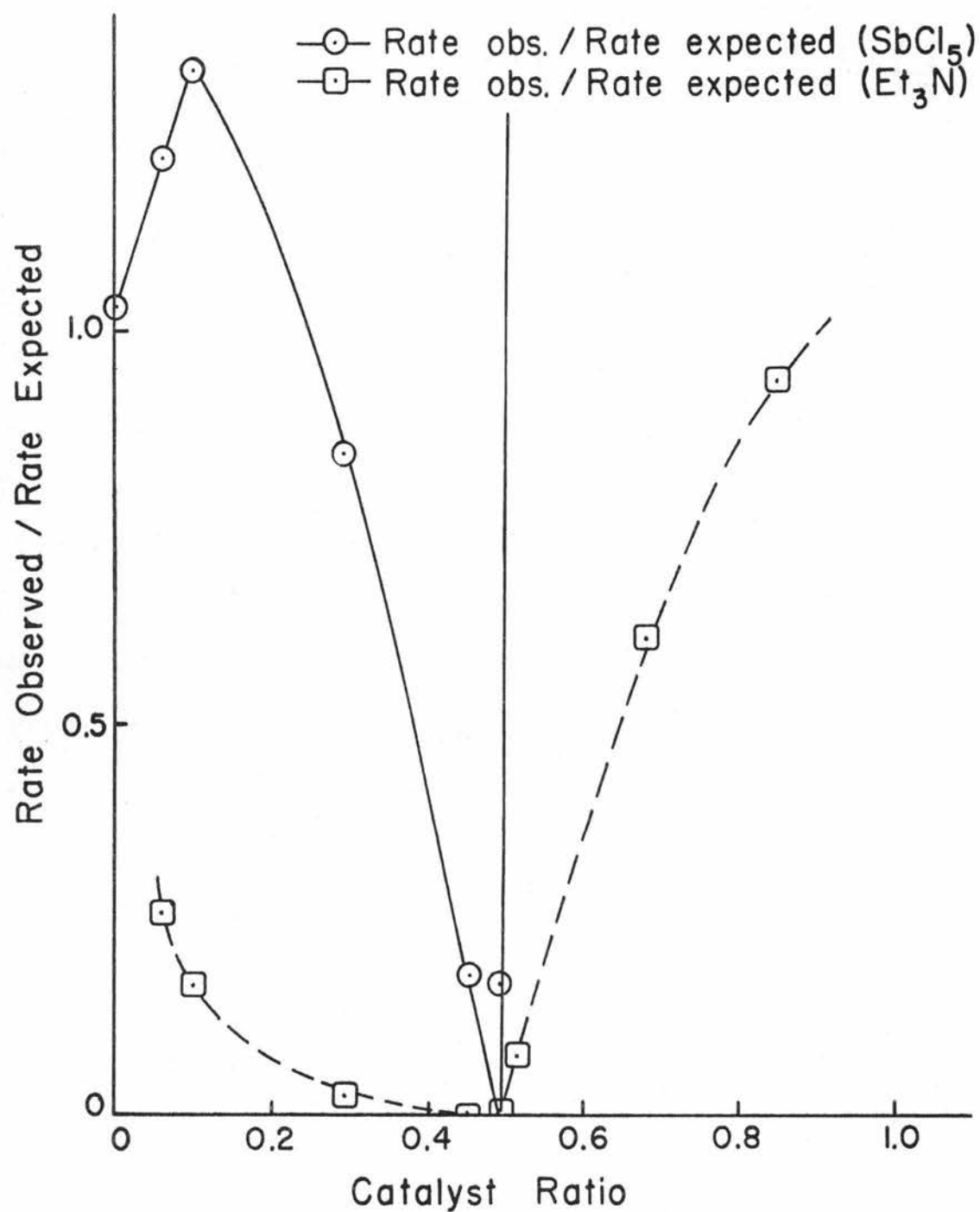
$$\text{Rate} = 1.48 \times 10^{-3} (\text{SO}_2)(\text{SbCl}_5 \cdot \text{SOCl}_2) \text{ moles/liter-hour} \quad (60)$$

where the equilibrium constant for association of thionyl chloride and antimony pentachloride is 0.8 moles/liter-hour. The rate expected if antimony pentachloride had been an inert additive and triethylamine were the catalyst was based on the present work. Here

$$\text{Rate} = 2.38 \times 10^{-2} (\text{SO}_2)(\text{SOCl}_2)(\text{Et}_3\text{N}) \quad (61)$$

Figure 16 clearly indicates that acid catalysis is inhibited by the addition of base, reaching a minimum at

FIGURE 16. Plot of Rate Ratio vs. Catalyst Ratio.



a 1:1 molar ratio, after passing through a maximum upon addition of small amounts of triethylamine. Further addition of base, beyond the 1:1 molar ratio, brings about a sharp increase in rate. Conversely, it is evident that addition of antimony pentachloride to exchange mixtures containing triethylamine strongly inhibits the basic catalysis. In other words, for a catalyst ratio, $\frac{(\text{Et}_3\text{N})}{(\text{Et}_3\text{N}) + (\text{SbCl}_5)}$, less than 0.5, antimony pentachloride may be considered the catalyst, while in experiments at higher catalyst ratio, triethylamine is the effective material. This hypothesis is further tested in Figures 17 and 18.

The set of points in Figure 17 represent the rates observed for Experiments 5a through 8a plotted as a function of the difference between the concentrations of the catalyst species. The solid line represents the rate expected for the excess antimony pentachloride, that in excess of triethylamine, based on the data of Burge and Norris. In Figure 18, the rate observed is plotted as a function of excess triethylamine, the solid line indicating the rate expected for the excess triethylamine based on equation (61). In either case, the agreement is good that the "excess" catalyst is the catalytic species and that it behaves in a manner analogous to that

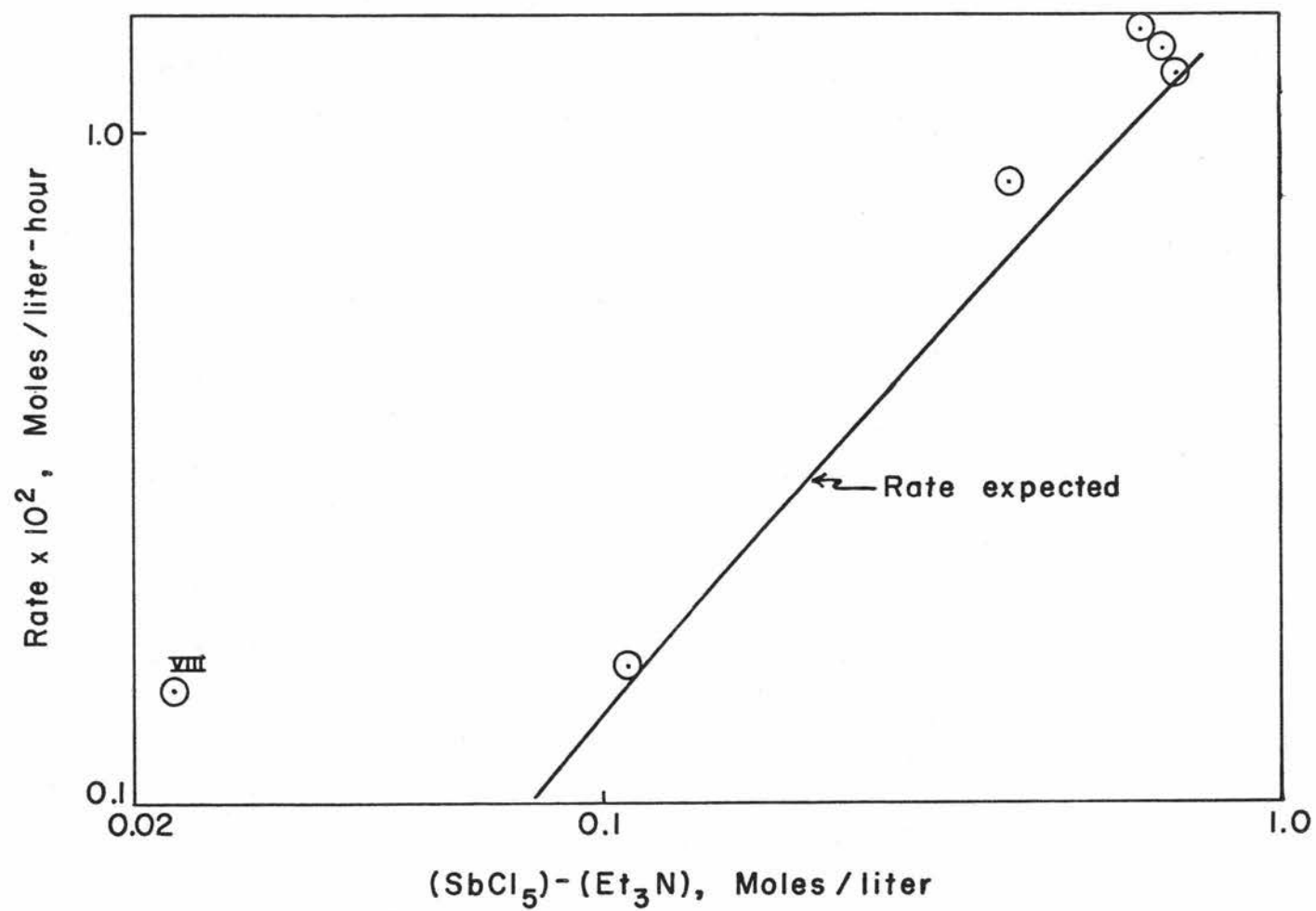


FIGURE 17. Rate vs. Excess Antimony Pentachloride.

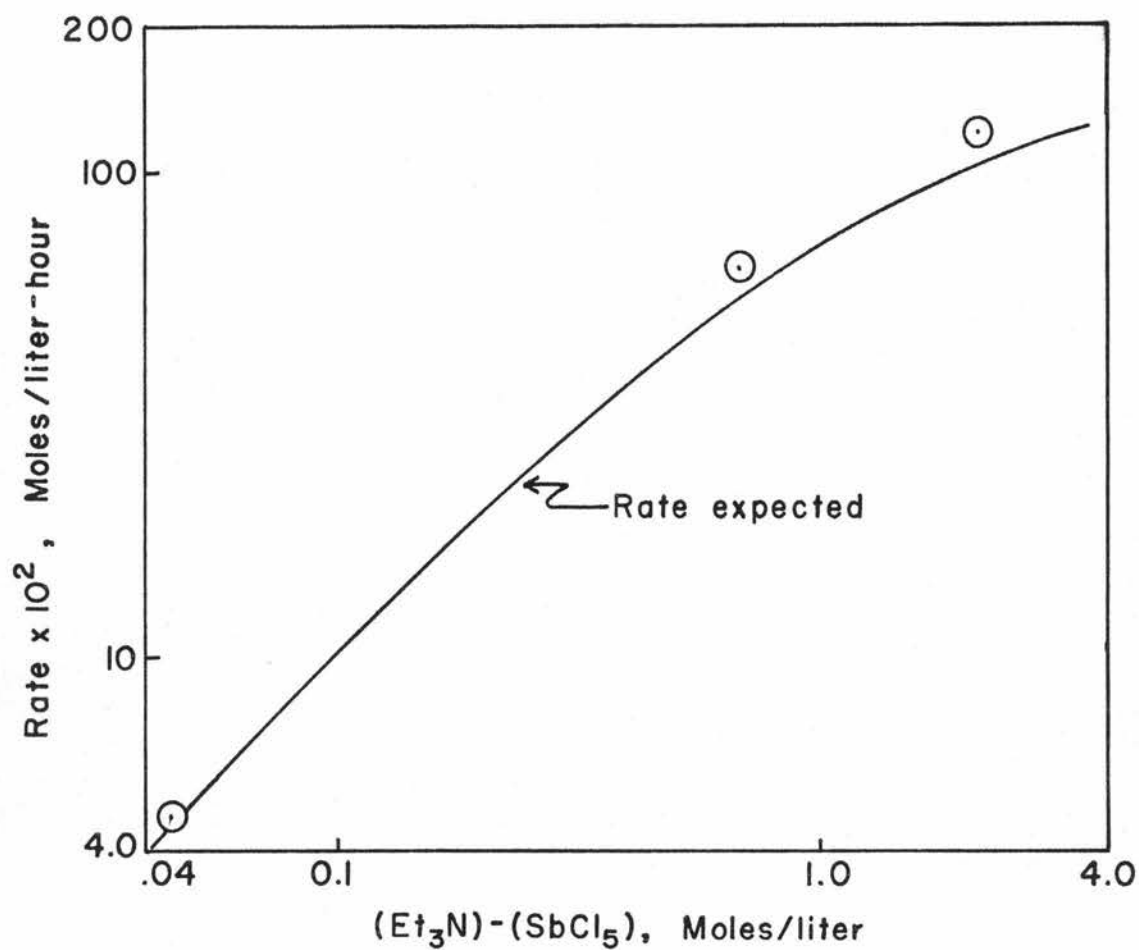


FIGURE 18. Rate vs. Excess Triethylamine.

of the one catalyst in the absence of the other. This is all the more remarkable in the excess triethylamine experiments, where there was a copious amount of precipitate in all cases, the presence of which evidently exerts no interfering effect.

The point labeled VIII in Figure 17 requires some comment. This point represents an experiment (Run 8a) where the concentrations of triethylamine and antimony pentachloride were about the same. Only a small error in our knowledge of the concentration of either the amine or antimony pentachloride would cause a large error in the difference of the two concentrations. The high rate value shown by VIII could, on the other hand, mean that the complex that is presumably formed dissociates to yield enough free amine to account for the high rate. On such a basis, one can calculate a value for the dissociation of the complex, assuming that no error in establishing the concentration of either catalyst was made, where

$$K = \frac{(\text{SbCl}_5)(\text{Et}_3\text{N})}{(\text{SbCl}_5 \cdot \text{Et}_3\text{N})} \quad (62)$$

The rate observed corresponds to a concentration of $\text{Et}_3\text{N} = 0.00147$ moles/liter. This leads to an upper limit value for K of 3×10^{-5} moles/liter. It is

interesting, though not necessarily meaningful to note that this figure is comparable to an upper limit of 5×10^{-5} moles/liter calculated similarly by Burge and Norris for the hexachloroantimonate complex (7).

A most striking observation in this work is that in all the experiments there is a positive deviation from the expected rate. It might be argued, since these experiments were carried out differently from the bulk of the experiments with the individual catalysts, most notably in that in these experiments the antimony pentachloride and labeled thionyl chloride were dosed by pipetting from a stock solution in the glove box, that some systematic error has been introduced. That this is not so is indicated by the good agreement between Experiment 9a-A and the rate data of Burge and Norris (6). From their rate law, equation (60), one calculates as the expected rate, 0.0118 moles/liter-hour, which is to be compared to the observed rate, 0.0122 moles/liter-hour. Relative to the positive deviations here observed, it should also be mentioned that Burge and Norris noted just such positive deviations from the expected rate in their study of the mixed catalysts antimony pentachloride and tetramethylammonium chloride (7). The reason for such a positive deviation is, at this point, obscure, but clearly merits further scrutiny.

Experiments 1a to 3a, in view of their very qualitative nature, will not be treated quantitatively. Qualitatively it may be seen, however, from Table XV that the rates observed for the mixed catalyst experiments in these cases are, in fact, less than would be expected were inhibition not occurring.

While there is good evidence in these experiments that some complex is formed between triethylamine and antimony pentachloride, it is not clear from the results of the kinetic experiments whether this is a simple addition complex between the two, or whether, as Spandau and Brunneck postulated (32), some such species as $(\text{Et}_3\text{N} \cdot \text{SOCl}) \cdot \text{SbCl}_6$ is formed. If thionyl chloride is involved in such a complex, it must be in rapid equilibrium with the free or unbound thionyl chloride, for otherwise, the calculated infinite time exchange would be different from that observed. That such a rapid equilibrium could be established, especially in those cases where some of the complex is in the form of a crystalline precipitate, seems highly doubtful. In view of the further fact that antimony pentachloride and triethylamine react in the absence of a solvent to form a crystalline compound that is qualitatively like the precipitate observed in the exchange solutions, leads one to believe that the complex here formed is not a hexachloroantimonate, but

rather a simple addition compound.

To pursue the last point somewhat further, it is clear that if the thionyl chloride is indeed involved in such a complex, this fact should be reflected in the rate law. In the present experiments, run at a constant but low ratio of antimony pentachloride to thionyl chloride, it has been possible to treat the data by either equation (60) or (61) using for the amount of thionyl chloride, the amount dosed, and not taking into account any thionyl chloride which might be involved in such a complex. (If this were taken into account, it may be noted that there would actually be an increase in the positive deviation of the observed rate in the present experiments from that expected.) It would seem that exchange experiments in which the concentrations of antimony pentachloride, thionyl chloride and triethylamine are about equal would show whether or not thionyl chloride is involved in such a complex, since the concentration of thionyl chloride appearing in equation (61), for instance (where triethylamine is at higher concentration than antimony pentachloride), is the concentration of thionyl chloride not involved in any complex. Thus, in such an instance, a rate much lower than would be expected on the basis of "excess" triethylamine and the dosed thionyl chloride would be evidence for the formation of a complex involving

thionyl chloride.

In summary, the mixed catalyst experiments have provided a good demonstration of the reality and kinetic significance, in liquid sulfur dioxide solutions, of complex formation between triethylamine and antimony pentachloride, these experiments nicely complimenting the earlier related type of study of Burge and Norris (7).

VI. SUMMARY

(1) The rate of sulfur-35 exchange between liquid sulfur dioxide and thionyl chloride catalyzed by the non-ionic bases triethylamine and acetone, has been investigated. For the former catalyst, the rate law

$$\text{Rate} = k_3(\text{SO}_2)(\text{SOCl}_2)(\text{Et}_3\text{N})$$

is followed fairly closely over a wide concentration range of reactants. There is, however, a real, consistent increase in k_3 in going from solutions rich in sulfur dioxide to solutions containing excess thionyl chloride. The rate constant is found to be $3.42 \times 10^6 e^{-14,600/RT}$ liter² mole⁻² sec⁻¹, in excess sulfur dioxide solutions, and $2.08 \times 10^6 e^{-13,500/RT}$ liter² mole⁻² sec⁻¹, in solutions containing excess thionyl chloride.

It has been found, for this catalyst, that the rate law

$$\text{Rate} = k_1[\text{SOCl}_2][\text{SO}_2 \cdot \text{Et}_3\text{N}] + k_2[\text{SO}_2][\text{SOCl}_2 \cdot \text{Et}_3\text{N}]$$

$$K_1 = \frac{[\text{SO}_2 \cdot \text{Et}_3\text{N}]}{[\text{SO}_2][\text{Et}_3\text{N}]}$$

$$K_2 = \frac{[\text{SOCl}_2 \cdot \text{Et}_3\text{N}]}{[\text{SOCl}_2][\text{Et}_3\text{N}]}$$

is obeyed closely over a wide range of reactant concentrations. Here, $(k_1 + \frac{K_2}{K_1} k_2) = 4.9 \text{ liter mole}^{-1} \text{ hour}^{-1}$ and $K_2/K_1 = 0.3$ at 25° . (Square brackets in these expressions refer to equilibrium concentrations in contrast to dosed concentrations denoted by the parentheses above and below.)

(2) Acetone has been found to exert only a weak catalytic effect on the exchange reaction, the rate law

$$\text{Rate} = k_4(\text{SOCl}_2)(\text{SO}_2)(\text{Me}_2\text{CO})^2$$

being obeyed over the range of concentrations employed. Here, there is no readily apparent variation of k_4 with any reactant concentration. In this rate law, k_4 was found to be $5.3 \times 10^{11} e^{-24,000/RT} \text{ liter}^3 \text{ mole}^{-3} \text{ sec}^{-1}$.

On the basis of the "solvent systems" concept of acid-base behavior, it would be expected that either of these catalysts, in order to exhibit their known basic properties, would react with thionyl chloride in the exchange solutions to produce chloride ion. This chloride, then, would be pictured as the active catalyst. In neither rate law is such behavior evident. On the contrary, the rate law in either instance implies that the active catalyst is the amine or ketone molecule as such.

(3) A brief investigation of this same exchange

catalyzed by mixtures of antimony pentachloride and triethylamine has shown the reality and kinetic significance of a 1:1 molar complex formed between the two catalysts. This complex, which exerts little, if any, catalytic effect on the rate of exchange, is believed to be a simple molecular addition compound, which probably does not involve thionyl chloride, contrary to the postulates of Spandau and Brunneck (32, 33).

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APPENDIX

APPENDIX A

Analysis of "Residues" from Several Exchange Experiments
in the Presence of Acetone at 0°

Exp. No.	Composition	Wt. Res.	S	Cl	Cl/S	Specific Act.		F ^{a)}	Time
	(millimoles)	(mg)	(wt. %)	(wt. %)		(cpm/mg)			(hr)
						Res.	SOCl ₂		
7B ^{b)}	$\left\{ \begin{array}{l} \text{SO}_2 \quad 4.45 \\ \text{SOCl}_2 \quad 70.6 \\ \text{Me}_2\text{CO} \quad 4.10 \\ \text{A}^\circ \text{SOCl}_2 \quad \text{c) } = 0 \end{array} \right\}$	215.5	21	47.3	2.04	1	10.9	0.180	254.6
16 ^{d)}	$\left\{ \begin{array}{l} \text{SO}_2 \quad 18.0 \\ \text{SOCl}_2 \quad 4.00 \\ \text{Me}_2\text{CO} \quad 2.69 \end{array} \right\}$	$\left\{ \begin{array}{l} 50.4 \\ 142.7 \\ 207.3 \end{array} \right\}$	$\left\{ \begin{array}{l} 13 \\ 9.5 \\ 12.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 16 \\ 14 \\ 20 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.10 \\ 1.34 \\ 1.53 \\ 1.46 \end{array} \right\}$	$\left\{ \begin{array}{l} 601 \\ 630 \\ 620 \\ 580 \end{array} \right\}$	$\left\{ \begin{array}{l} 646 \\ 638 \\ 639 \\ 607 \\ 517 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.043 \\ 0.057 \\ 0.056 \\ 0.124 \\ 0.174 \end{array} \right\}$	$\left\{ \begin{array}{l} 1 \\ 3 \\ 5 \\ 7 \\ 23.1 \end{array} \right\}$
	$\text{A}^\circ \text{SOCl}_2 = 670$								
17 ^{d)}	$\left\{ \begin{array}{l} \text{SO}_2 \quad 18.0 \\ \text{SOCl}_2 \quad 4.00 \end{array} \right\}$	$\left\{ \begin{array}{l} 96.4 \\ 196.7 \\ 220.8 \end{array} \right\}$	$\left\{ \begin{array}{l} 10 \\ 9.5 \\ \text{e) } \end{array} \right\}$	$\left\{ \begin{array}{l} 19 \\ 20 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.79 \end{array} \right\}$	$\left\{ \begin{array}{l} 548 \\ 532 \\ 528 \end{array} \right\}$	$\left\{ \begin{array}{l} 518 \\ 485 \\ 489 \end{array} \right\}$	$\left\{ \begin{array}{l} 0.104 \\ 0.176 \\ 0.180 \end{array} \right\}$	$\left\{ \begin{array}{l} 24.2 \\ 49 \\ 75 \end{array} \right\}$

(Continued on next page)

(Cont'd.)

Exp. No.	Composition (millimoles)	Wt. Res. (mg)	S (wt. %)	Cl (wt. %)	Cl/S	Specific Act. (cpm/mg)		F ^{a)}	Time (hr)
						Res.	SOCl ₂		
17 ^{d)}	4 { Me ₂ CO 1.36 }	147.3 ^{e)}	12	24	1.71	524	455	0.230	95
	5 { Me ₂ CO 1.36 }	121.2 ^{e)}	14	27	1.80	505	453	0.235	123.3
	A ^o SOCl ₂ = 560								
18 ^{d)}	1 { SO ₂ 18.0 }	175.0	19			541	510	0.119	9.6
	2 { SO ₂ 18.0 }					500	364	0.479	15
	3 { SOCl ₂ 4.00 }	208.1 ^{e)}	19	34	1.57	544	350	0.550	20
	4 { SOCl ₂ 4.00 }	262.9	17	29	1.59	517	162	0.864	24.44
	5 { Me ₂ CO 4.07 }	145.9	20	19	0.87	543	582	0.026	5
	6 { Me ₂ CO 4.07 }	248.1 ^{e)}	16	28	1.56	494	112	0.956	35
	A ^o SOCl ₂ = 603								
19 ^{d)}	1 { SO ₂ 6.93 }	17.4				424	426	0.005	16
	2 { SO ₂ 6.93 }	24.9				422	354	0.194	35
	3 { SOCl ₂ 0.742 }	24.6					342	0.199	48
	4 { Me ₂ CO 0.516 }	28.3				374	322	0.274	64.5
	5 { Me ₂ CO 0.516 }	31.0				372	259	0.420	86
	A ^o SOCl ₂ = 427								

(Continued on next page)

(Cont'd.)

Exp. No.	Composition	Wt. Res.	S	Cl	Cl/S	Specific Act.		F ^{a)}	Time
	(millimoles)	(mg)	(wt. %)	(wt. %)		(cpm/mg)			(hr)
						Res.	SOCl ₂		
20 ^{d,f)} 1	SO ₂ 6.90	20.4				314	381	0.053	16
3	SOCl ₂ 0.742	32.8				321	277	0.305	66.5
4		29.7				332	235	0.400	94
5	Me ₂ CO 0.487								
	A ^o SOCl ₂ = 401								

- a) Calculated from change in specific activity of SOCl₂ (see Calculations section under Results and Discussion).
- b) Procedure II, SO₂ initially active.
- c) A^o SOCl₂ refers to initial specific activity of SOCl₂.
- d) SOCl₂ initially active.
- e) Part of sample lost.
- f) Run in absence of light.

APPENDIX B

Calculation of K_d

In assessing the effect of ion-pairing on the kinetics of the ionic chloride-catalyzed exchange, it was necessary to calculate the equilibrium constant for the dissociation of the ion-pairs to form free ions. For this purpose, the Bjerrum equation was used (see, for instance, reference 27, p. 393-397). This equation for uni-univalent salts is

$$\frac{1}{K_d} \approx \frac{4\pi N}{1000} \times \left(\frac{e^2}{DkT} \right)^3 Q_b$$

where N is Avogadro's number

e is the electronic charge

D is the dielectric constant

\bar{k} is the Boltzman constant

T is the absolute temperature

and

$$Q_b = \int_2^{\infty} x^{-4} e^x dx$$

where x is $-\frac{e^2}{DkTr}$ for uni-univalent salts

r is the distance between two ions of unlike charge

and q is the distance of closest approach parameter

and for uni-univalent salts is equal to $\frac{e^2}{DkTa}$ where a is approximately the sum of the crystallographic radii of the ions involved.

According to this treatment, any two ions of unlike charge whose separation has a distance lying between the sum of the crystallographic radii of the ions and the critical Bjerrum distance, q^0 , are considered to be ion-pairs.

The value of K_d calculated in this way for tetramethylammonium chloride in pure liquid sulfur dioxide agrees quite well with the experimentally determined value, 8.6×10^{-4} as compared to 9.4×10^{-4} ,¹ respectively. Several values of K_d calculated in this way are given in Table XVII. For these calculations, it has been assumed that the dielectric constants for mixtures of thionyl chloride and sulfur dioxide are additive on a mole basis.

¹Norman N. Lichtin, private communication.

TABLE XVII
 Calculated Values of K_d
 for Ionic Catalysts
 in Exchange Solutions at 0°

Solvent		Catalyst	K_d
(mole fraction)			
SO ₂	SOCl ₂		
1		RbCl	9.5×10^{-5}
1		Me ₄ NCl	8.6×10^{-4} a)
	1	Me ₄ NCl	6.0×10^{-6}
0.55	0.45	Me ₄ NCl	1.7×10^{-5}
0.40	0.60	Me ₄ NCl	8.3×10^{-5}
0.16	0.84	Me ₄ NCl	2.2×10^{-5}
0.056	0.944	Me ₄ NCl	8.3×10^{-6}

a) This is in good agreement with the measured value,
 9.4×10^{-4} .