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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Isotopic Exchange between $SnCl_4$ and 2-Chlorobutane

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The homogeneous exchange of Cl^{36} between $SnCl_4$ and 2-chlorobutane occurs at a measurable rate in heptane solution at 140° and faster at 160°. In heptane at room temperature exchange was observed only in the presence of HCl and of the white solid which is formed when water is added to $SnCl_4$. The data on the homogeneous exchange appear to be most consistent with a mechanism involving formation of a rather stable ($SnCl_4 \cdot C_4H_9Cl$) complex.

Introduction

A number of isotopic exchange reactions between alkyl halides and Friedel–Crafts catalysts have been studied[1-6] because the interactions between these materials have played an important role in mechanisms postulated for Friedel–Crafts reactions. Recent work in this Laboratory[1] has shown that negligible exchange of Cl^{36} occurs between $SnCl_4$ and 2-chlorobutane in the vapor phase at 200° in 180 minutes. The present paper presents the results of investigations of the same exchange in condensed systems where measurable reaction has been observed.[7]

Experimental

Materials.—$SnCl_4$, HCl and 2-chlorobutane were purified and dried as in the earlier work,[1] and radioactive $SnCl_4$ was prepared by the exchange between HCl^{36} and liquid $SnCl_4$ as previously described.[1]

Phillips Petroleum Co. pure grade normal heptane was passed through a silica gel column, greatly reducing the absorption of the solvent in the ultraviolet so that the optical density in a one cm. cell was less than 0.1 at wave lengths above 2200 Å. This heptane was distilled through a P_2O_5–glass wool column into the vacuum system used to fill the reaction cells. Phillips Petroleum Co. pure grade butene-2 was passed into the vacuum system through a P_2O_5–glass wool column. Ethyl chloride, used as the solvent in some of the runs, was purified by bubbling through a column of concentrated H_2SO_4 and then passing through columns of NaOH pellets and P_2O_5 on glass wool.

Filling and Analysis of Reaction Tubes.—All of the runs were made in sealed Pyrex tubes filled on a vacuum system. In general the tubes had volumes of about 6 ml. and held 1–2 ml. of solution. $SnCl_4$ was metered out roughly by filling a known volume to the vapor pressure of $SnCl_4$ at some temperature below that of the room. More accurate values were obtained at the end of each experiment by titrations with NaOH and $AgNO_3$. The amounts of 2-chlorobutane were measured by pressure readings on a mercury manometer while the vapor was confined in a known volume. The volumes of solution were determined after the cells were broken open for analysis.

After a reaction tube had been exposed at the desired temperature for the desired time, it was broken open, water and heptane were added to give two phases each of 5 ml., and this two-phase system was shaken vigorously. During this procedure the heptane layer became very cloudy and then cleared up with the formation of white flakes of stannic hydroxide, most of which settled to the bottom of the water layer.

The water and heptane solutions from each run were placed separately in the annular jackets of glass-walled solution-type Geiger–Muller tubes and their radioactivities were counted. An empirical correction was applied in comparing activities from different tubes and with different solvents.

Solid Formed by Traces of Water.—A distinct cloudiness appeared when $SnCl_4$ was added to heptane in preparing the reaction tubes unless the $SnCl_4$ was dried by exposure to P_2O_5 in the vacuum system just before it was added. On standing for about half an hour the white solid responsible for the cloudiness settled out on the walls of the tube, leaving a clear solution. This behavior was a very sensitive test for small amounts of water and extreme care was necessary in degassing the walls of the vacuum system and in drying all the materials in order to obtain initially clear solutions.

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[1] R. A. Howald and J. E. Willard, THIS JOURNAL, **77**, 2046 (1955).

[2] C. H. Wallace and J. E. Willard, *ibid.*, **72**, 5275 (1950).

[3] M. Blau and J. E. Willard, *ibid.*, **73**, 442 (1951); **75**, 3330 (1953).

[4] F. Fairbrother, *J. Chem. Soc.*, 293 (1941).

[5] N. E. Brezhneva, S. Z. Roginskii and A. I. Shilinskii, *J. Phys. Chem. USSR.*, **10**, 368 (1937); *Acta Physicochim., USSR.*, **7**, 201 (1937).

[6] G. B. Kistiakowsky and J. R. Van Wazer, THIS JOURNAL **65**, 1829 (1943).

[7] Further details of these experiments may be found in the Ph.D. thesis of Reed A. Howald filed with the University of Wisconsin Library in 1955 and available from University Microfilms, Ann Arbor, Michigan.

Most of the cells reported here showed at least a trace of cloudiness; however even when the $SnCl_4$ was not freshly dried only small amounts of H_2O were present, as shown by the fact that the addition of 0.01 to 0.07 mole of H_2O per mole of $SnCl_4$ gave considerably larger amounts of white solid.

Results

Heterogeneous Isotopic Exchange between $SnCl_4$ and 2-Chlorobutane.—No exchange was observed between $SnCl_4$ and 2-chlorobutane at room temperature in heptane solution in times as long as two weeks. Considerable isotopic exchange was observed in similar reaction cells to which small amounts of both HCl and H_2O were added. These cells contained a white insoluble solid material similar to that described above. Negligible exchange occurred, however, in several reaction tubes filled with the clear supernatant liquid decanted away from this solid, under vacuum, thus demonstrating that this room temperature exchange reaction was heterogeneous. The rates of exchange showed considerable scatter, as would be expected due to variation in surface area, but in general increased with increasing amounts of either HCl or H_2O, provided that the other "promoter" was present at an appreciable concentration. A typical cell containing about 0.2, 0.1, 0.1 and 0.007 mmoles of butyl chloride, $SnCl_4$, HCl and H_2O, respectively, with one milliliter of heptane showed exchange with a half time of about 7 days. The role of H_2O in promoting the exchange is the formation of the white solid which is a hydrate or hydrolysis product of $SnCl_4$. The role of HCl is less clear: it may lead to the formation of a white solid of a somewhat different composition, or the surface exchange may occur only between HCl and 2-chlorobutane. The exchange between HCl and $SnCl_4$ is presumably very rapid in these cells.[1] An experimental test showed no exchange between HCl and 2-chlorobutane in heptane solution at room temperature in the absence of $SnCl_4$.

In a number of reaction tubes which contained HCl and butene-2, in addition to 2-chlorobutane and radioactive $SnCl_4$, in heptane solution at room temperature, an initial rise in organic activity unaccompanied by the corresponding decrease in specific activity of the inorganic chloride indicated addition of HCl to the olefin. This reaction was catalyzed by the presence of water.

The Exchange between $SnCl_4$ and 2-Chlorobutane at Elevated Temperatures.—The white solid formed by the reaction between $SnCl_4$ and H_2O is soluble in heptane at elevated temperatures, and with the amounts of H_2O used in this work clear colorless solutions were obtained at 140°. Visibly crystalline material was deposited when such solutions were cooled. Cells containing 2-chlorobutane, $SnCl_4$ and H_2O added to heptane, which gave no exchange at room temperature as no HCl was added, showed large amounts of isotopic exchange after being heated to 140°. The amounts of exchange were not reproducible, however, and showed much greater dependence on the number of times the tubes were heated and cooled than on the total time at 140°. Most of the observed exchange apparently was due to a heterogeneous reaction at elevated temperature before the white solid dissolved.

Some exchange at 140° still was observed, however, when no water was added and the $SnCl_4$ was freshly dried with P_2O_5. In these cells there was no appreciable difference in the rate of exchange on comparing one long exposure at 140° with another similar cell given 11 shorter exposures at 140°. The rate of exchange at 140° was too low for a convenient study of the kinetics, but 6 reaction tubes were used to determine the rate of exchange as a function of the $SnCl_4$ and 2-chlorobutane concentrations at 160°. The results are shown in Table I and Fig. 1. Comparison of the rates at 160° and at 140° gives a value of 25 ± 10 kcal./mole for the activation energy.

TABLE I

EXCHANGE BETWEEN $SnCl_4$ AND 2-CHLOROBUTANE IN HEPTANE SOLUTION AT 140 AND 160°

$[C_4H_9Cl]$, moles/l.	$[SnCl_4]$, moles/l.	Time, min.	% Exchange	$R \times 10^{8}$[a]
		At 140°		
0.179	0.024	2620	7.5	1.7
.179	.024	15585	17.9	1.0
.179	.024	10255[b]	13.9	1.1
		At 160°		
0.468	0.065	18680	71.3	18.6
.497	.0535	6720	34.5	15.5
.184	.0185	10020	36.8	4.0
.144	.014	9870	29.2	2.5
.066	.0125	12930	37.5	1.7
.063	.0082	25410	43.3	0.8

[a] R is the rate of isotopic exchange in moles $liter^{-1}$ $sec.^{-1}$.
[b] This cell was heated to 140° 11 different times for a total exposure of about 10255 minutes.

The organic material from two of the runs at 160° was distilled with added 2-chlorobutane (b.p. 68°) and *t*-butyl chloride (b.p. 52°) carriers. Counting of the successive fractions showed that less than 1% of the organically bound radioactivity was present as tertiary butyl chloride, at least 90% was present as 2-chlorobutane, and approximately 8% was in the form of materials with higher boiling points than that of heptane (98°).

Exchange between $SnCl_4$ and 2-Chlorobutane in Other Solvents.—A number of cells were filled with ethyl chloride as the solvent, since the products of the reaction between $SnCl_4$ and H_2O are appreciably soluble in ethyl chloride[8] and it is a satisfactory solvent for the $SnCl_4$ catalyzed polymerization of isobutene. In general the runs in ethyl chloride solution showed negligible isotopic exchange after times up to four weeks at room temperature, but a few reaction tubes which were allowed to stand for over six months gave definite evidence for a very slow exchange. A similar very slow exchange was observed in one reaction tube in which *m*-xylene was used as the solvent. The addition of enough water to precipitate a white solid from the ethyl chloride did not favor the exchange, and an excess of ethyl alcohol completely inhibited it.

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(8) R. G. W. Norrish and K. E. Russell, *Trans. Faraday Soc.*, **48**, 91 (1952); *Nature*, **160**, 543 (1947).

Discussion

The results of this work indicate quite clearly that at elevated temperatures isotopic exchange between $SnCl_4$ and 2-chlorobutane will occur homogeneously in solution and that certain solid surfaces will give heterogeneous exchange at lower temperatures and presumably with a lower activation energy. Previous studies on isotopic exchange between alkyl chlorides and Friedel–Crafts catalysts have shown exchange with solid $AlCl_3$.[2,3] In such studies it is very difficult to avoid conclusively the presence of solid surfaces of the inorganic chlorides or their hydrolysis products. The data available for $AlCl_3$ in very dilute solution[2] and in the gas phase[2] indicate that a solid surface is necessary for the exchange between $AlCl_3$ and CCl_4.

Many of the data in the literature on the corresponding exchange reactions of bromides do not distinguish between homogeneous and heterogeneous processes, but there is good evidence for the occurrence of homogeneous exchange between $SnBr_4$ and *t*-butyl bromide[4] and between $AlBr_3$ and ethyl bromide in nitrobenzene[4] and in CS_2.[5]

Simple second-order kinetics and an activation energy of 11 ± 2 kcal./mole have been reported[5] for the exchange between $AlBr_3$ and ethyl bromide in CS_2 solution. This activation energy is considerably higher than that of 4.6 kcal./mole reported[6] for the heterogeneous exchange between gaseous methyl bromide and solid $AlBr_3$, but there are no data available for a quantitative comparison between homogeneous and heterogeneous exchange reactions with the same pair of bromides.

The lack of homogeneous exchange between $SnCl_4$ and 2-chlorobutane in heptane solution at room temperature is in agreement with the failure of $SnCl_4$ to catalyze the racemization of 2-chlorobutane.[9]

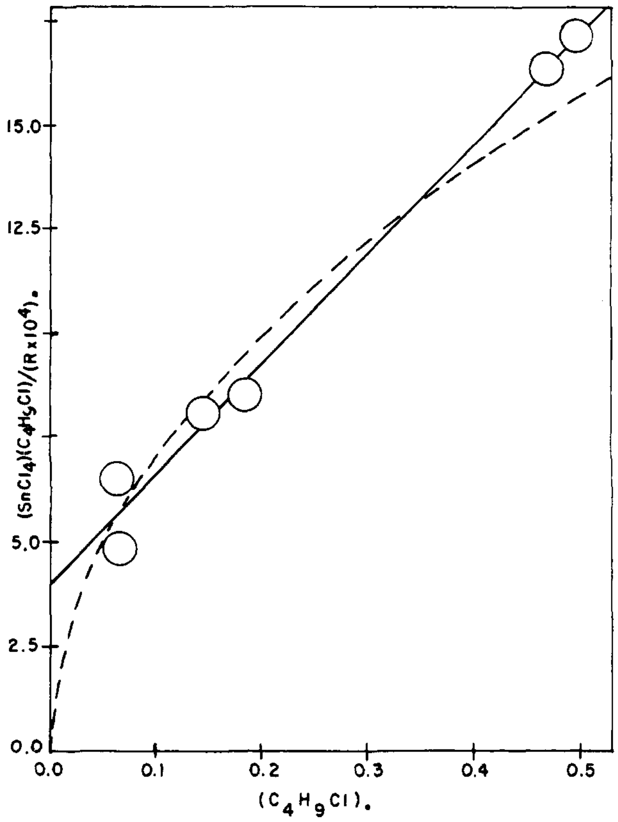

Fig. 1.—Isotopic exchange between $SnCl_4$ and 2-chlorobutane in heptane solution at 160°. Curves represent suggested rate laws described in the discussion.

The kinetic data on the exchange between $SnCl_4$ and 2-chlorobutane in heptane at 160° do not fit a simple second order expression (this would give a horizontal line in Fig. 1), but a good fit is given by an expression of the form

$$R = k_{3/2}(SnCl_4)(C_4H_9Cl)^{1/2};\ k_{3/2} = 4.5 \pm 0.6 \times 10^{-6}\ l.^{1/2}\ moles^{-1/2}\ sec.^{-1}$$

which gives the parabola shown by the dotted line shown in Fig. 1. The less than first-order dependence of the rate on the concentration of 2-chlorobutane implies that either the activated complex contains a dissociation product of 2-chlorobutane (*i. e.*, HCl) or that a sufficient fraction of the $SnCl_4$ was combined in a reactive complex with 2-chlorobutane so that the concentration of the complex was not proportionally increased as the concentration of 2-chlorobutane was increased. The first of these alternatives is unlikely since the exchange of HCl with $SnCl_4$ is not likely to be slow enough to be rate determining. The simplest complex which could explain the rate data is $SnCl_4 \cdot C_4H_9Cl$. Then letting "*a*" and "*b*" represent the total concentrations of $SnCl_4$ and 2-chlorobutane, respectively, the equilibrium constant for the dissociation of the complex can be represented by $K = (a - x) \cdot (b - x)/x \approx (a - x)b/x$, where x is the concentration of the complex and, since the concentration of 2-chlorobutane was in all cases at least 5 times the concentration of $SnCl_4$, x can be neglected with respect to b as a first approximation. If the rate of exchange is proportional to the concentration of the complex, one obtains $R = k_1x = k_1ab/(K + b)$. If this equation correctly represents the rate of exchange, a plot of ab/R *vs.* the concentration of 2-chlorobutane should give a straight line. Such a plot is shown in Fig. 1, and the straight line in this figure, which was obtained from a least squares fit of the data, gives if anything a better fit than the parabola which represents $^1/_2$ power dependence of the rate on the 2-chlorobutane concentration. The least squares fit gives a value of 0.150 mole per liter for K and k equal to $3.8 \pm 0.5 \times 10^{-6}$ sec.$^{-1}$, but other combinations with K between 0.1 and 0.2 and k varying between 3.3 and 4.3 × 10^{-6} give almost equally good fits.

An appreciable concentration of a complex such as $SnCl_4 \cdot 2C_4H_9Cl$ would give an additional term in b^2 in the denominator of the rate expression, which would give a positive curvature in a plot such as Fig. 1. This is not apparent over the concentration range which was covered.

This interpretation of the kinetics postulates a surprisingly stable complex between $SnCl_4$ and 2-chlorobutane. At the highest concentrations used in this work about 75% of the $SnCl_4$ must be present as the complex at 160°. If the complex has an exothermic heat of formation it must be still more stable at room temperature. There is consid-

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(9) K. Bodendorf and H. Bohme, *Ann.*, **516**, 1 (1935); H. Bohme and O. Siering, *Ber.*, **71**, 2372 (1938).

erable evidence in the literature on the formation of complexes between alkyl halides and Friedel-Crafts catalysts from measurements of conductivity,[10,11] dielectric polarization,[12] vapor pressures,[13] and spectra,[14] and solid complexes of $GaCl_3$ and $AlBr_3$ with methyl halides have been isolated.[13] The kinetics for the propylation of benzene with $GaCl_3$ in CS_2 solution can be interpreted in terms of a complex between $GaCl_3$ and propyl chloride which is almost as stable as that between $GaCl_3$ and benzene.[15] On the basis of these other studies, and the fact that where they have been determined[13,14] the heats of formation of these complexes are quite small, it is at least not unreasonable to postulate a fairly stable complex between $SnCl_4$ and 2-chlorobutane even at 160°.

An extrapolation of the data to 200° gives a value of about 10^{-4} sec.$^{-1}$ for k_1. This can also be expressed in terms of a second-order rate constant using the concentrations of uncomplexed $SnCl_4$ and 2-chlorobutane, *i.e.*, $k_2 = k_1/K = 10^{-3}$ l.-moles^{-1} sec.$^{-1}$ where $R = k_2(SnCl_4)(C_4H_9Cl)$. The previous data on the lack of exchange between $SnCl_4$ and 2-chlorobutane in the vapor phase in 180 minutes at 200°[1] are only accurate enough to show that the second order rate constant is less than 2×10^{-3} l. moles^{-1} sec.$^{-1}$. Thus, although it is unlikely on other grounds, the available data do not exclude the possibility of a homogeneous vapor phase exchange between $SnCl_4$ and 2-chlorobutane at elevated temperatures with a rate constant of the same order of magnitude as that in heptane solution.

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(10) E. Wertyporoch and T. Firla, *Z. physik. Chem.*, **162**, 398 (1934).

(11) R. E. Van Dyke and H. E. Crawford, THIS JOURNAL, **73**, 2018 (1951).

(12) F. Fairbrother, *J. Chem. Soc.*, 503 (1945).

(13) H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953); H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6279 (1953).

(14) J. W. Bayles, A. G. Evans and J. R. Jones, *J. Chem. Soc.*, 206 (1955).

(15) H. Ulich and G. Heyne, *Z. Elektrochem.*, **41**, 509 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Disulfur Monoxide. I. Its Identification as the Major Constituent in Schenk's "Sulfur Monoxide"

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The product of an electric discharge through sulfur and SO_2 has been reported by several workers to be a mixture of SO and S_2O_2 in the gas phase. On the basis of mass spectrographic, stoichiometric and gas effusiometric measurements it is shown that this material is a mixture of SO_2 and disulfur monoxide, S_2O. The presence of any S_2O_2 in this product is highly improbable, though it is possible that a small amount of SO may be present in the mixture. The properties previously attributed to the presence of SO or S_2O_2 in the discharge product are shown to be due to S_2O.

In a series of papers Schenk[1] discussed the preparation and properties of a lower oxide of sulfur which he characterized as "sulfur monoxide." This new oxide can be prepared in purest form by passing a high voltage discharge through a mixture of sulfur vapor and SO_2 at a total pressure of a few mm. of mercury. Schenk also reported that his "sulfur monoxide" could be identified as a product from the combustion of sulfur at low oxygen pressures, the thermal decomposition of $SOCl_2$ and $SOBr_2$ and from their reaction with certain metals. The gaseous "sulfur monoxide" is stable in a clean glass system for several hours at a pressure of a few mm. of mercury, but it decomposes rapidly at pressures greater than 30 mm. When this lower oxide is condensed in a low temperature trap an orange-red solid is obtained. This solid decomposes into sulfur and SO_2 when warmed to room temperature.

Schenk initially characterized this oxide as sulfur monoxide from the fact that it has an intense ultraviolet absorption spectrum in the same region as the well established emission spectrum of SO. In addition Schenk found that what he believed to be the pure oxide had a sulfur to oxygen ratio of 1:1. Kondrat'eva and Kondrat'ev[2] present stoichiometric evidence that the formula of Schenk's "sulfur monoxide" is S_2O_2. In addition they show that the ultraviolet absorption spectrum of "sulfur monoxide" does not correspond to the SO emission spectrum. Jones[3] re-examined the ultraviolet spectrum under high resolution and concluded that "sulfur monoxide" was probably S_2O_2 with a structure similar to that of SO_3.

During an investigation of the microwave spectrum it became clear that neither SO or S_2O_2 could fit the observed spectrum. The stoichiometry of "sulfur monoxide" also became uncertain in light of the work of Rao.[4] While investigating the properties of "sulfur monoxide," Rao observed that when the low pressure combustion products of sulfur were passed through CCl_4 a deep yellow colored solution resulted. When the CCl_4 solution was purified by a stream of oxygen Rao found that the

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(1) First paper, P. W. Schenk, *Z. anorg. allgem. Chem.*, **211**, 150 (1933); for a review see P. W. Schenk, *Chem. Z.*, **67**, 273 (1943) or E. Maxted, "Modern Advances in Inorganic Chemistry," Oxford, 1947.

(2) E. Kondrat'eva and V. Kondrat'ev, *J. Phys. Chem., U.S.S.R.*, **14**, 1528 (1940).

(3) A. V. Jones, *J. Chem. Phys.*, **18**, 1263 (1950).

(4) B. S. Rao, *Ind. Acad. Sci.*, **10**, 491 (1939).