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

The Exchange Reaction between Aluminum Chloride and Carbon Tetrachloride[1]

BY CAROL HERRMANN WALLACE AND JOHN E. WILLARD

Introduction

Aluminum chloride has been widely used as a catalyst in many reactions of the Friedel–Crafts type[2] and it has been postulated[3] that in some of these the initial step in the mechanism is a reaction of the type $RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$. If such a reaction, and the reverse step, can occur it must lead to exchange between the chlorine of the aluminum chloride and that of the organic chloride. In agreement with this prediction Fairbrother[4] has found that the chlorine in acetyl chloride will exchange with that in aluminum chloride and, further, that radioactive hydrogen chloride is liberated when the acylation of benzene is catalyzed by aluminum chloride containing radioactive chlorine. These observations are consistent with the postulated mechanism but might also be accounted for by other mechanisms.

In order to learn more about the mechanism of exchange of the chlorine in aluminum chloride with organic chlorides we have investigated its reaction with carbon tetrachloride. Carbon tetrachloride was chosen because it avoids side reactions such as the production of hydrogen chloride. The investigations were carried out with the reactants in a vacuum system, with aluminum chloride prepared *in situ* and with purified, degassed carbon tetrachloride.

For the purpose of this discussion the formula $AlCl_3$ will be used as a formal designation of aluminum chloride. It has been shown by X-ray diffraction studies[5] on a single crystal that aluminum chloride exists as an ionic lattice in the solid state and by electron diffraction measurements[6] that it exists as the dimer Al_2Cl_6 in the vapor phase up to 400°. There is evidence that it may exist as the monomer[7] in some solvents and as the dimer in others.[8] There is no information available on its formula in carbon tetrachloride solution.

Experimental

Radioactive Aluminum Chloride.—The aluminum chloride used in this work was prepared by the reaction $3AgCl + Al \rightarrow 3Ag + AlCl_3$ in an evacuated system. The silver chloride was prepared by addition of Mallinckrodt Analytical Reagent silver nitrate to solutions of hydrochloric acid containing Cl^{36} with a specific activity of 0.3 mc./g.[9] It was heated with an excess of Baker and Adamson 30 mesh aluminum metal (cleaned by immersing in aqueous hydrochloric acid, rinsing in water and drying) until at about 450° a rapid production of aluminum chloride occurred. When moisture was occluded in the silver chloride its presence could be determined after the synthesis by freezing out and counting the equivalent amount of radioactive hydrogen chloride which was formed by hydrolysis of the aluminum chloride. Such tests showed that silver chloride which had been dried by heating at 160° for four hours retained occluded moisture equivalent to about 1% of its weight but that silver chloride which was fused on the vacuum system before reaction was completely dry. Aluminum chloride prepared from the two types of silver chloride gave equivalent results. Unless otherwise indicated aluminum chloride prepared *in situ* was used because it was more reactive than material synthesized in a similar manner but transferred from ampoules to the vacuum system in a dry-box in which only ordinary care had been taken to dry the gas.

Carbon Tetrachloride.—The carbon tetrachloride was Mallinckrodt Analytical Reagent "low sulfur" grade further purified by: (1) illuminating for 40 hours with a 1000-watt bulb at 6 inches while saturated with chlorine gas; (2) washing with sodium carbonate solution; (3) washing with water; (4) drying over phosphorus pentoxide. It was distilled from fresh phosphorus pentoxide through a 15-inch Vigreux column, just prior to use, the center cut at the boiling point being used. After introduction to the vacuum system it was degassed and distilled through phosphorus pentoxide.

Preparation and Separation of Reaction Mixtures.—In a typical experiment aluminum was added to silver chloride, which had been fused under vacuum, by jarring the tubing shown at B of Fig. 1. The mixture was heated, and the resultant aluminum chloride was sublimed into E which was cooled with liquid air. Tubes B were then sealed off. Purified carbon tetrachloride, degassed by

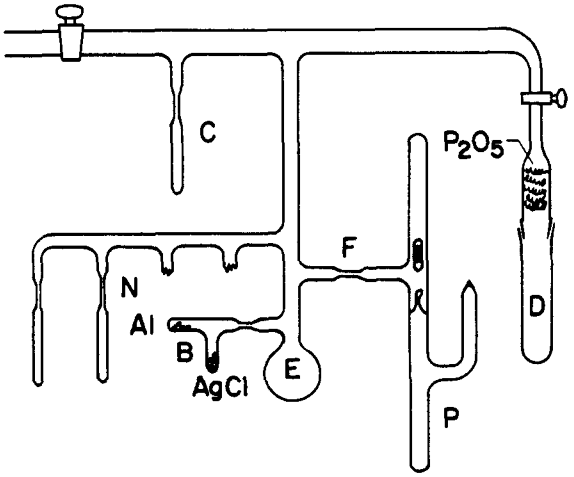

Fig. 1.—Vacuum system for preparing $AlCl_3$–CCl_4 reaction mixtures.

---

[1] Presented before the Division of Physical and Inorganic Chemistry at the September 1949 meeting of the American Chemical Society at Atlantic City, N. J.

[2] (a) N. O. Calloway, *Chem. Rev.*, **17**, 327 (1935). (b) A. E. Remick, "Electronic Interpretation of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., p. 477, 1949; (c) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941.

[3] H. Meerwein, *Ann.*, **455**, 227 (1927).

[4] F. Fairbrother, *J. Chem. Soc.*, 503 (1937).

[5] J. A. A. Ketelaar, C. H. MacGillavry and P. A. Renes, *Rec. trav. chim.*, **66**, 501 (1947).

[6] K. J. Palmer and Norman Elliott, THIS JOURNAL, **60**, 1852 (1938).

[7] T. J. Lane, P. A. McCusker and B. Columba Curran, *ibid.*, **64**, 2076 (1942).

[8] J. A. A. Ketelaar, *Z. Krist.*, **90**, 237 (1935).

[9] Item S-6, U. S. Atomic Energy Commission Isotopes Catalogue (Aug. 1949).

three cycles of freezing, evacuation and thawing was distilled from D onto the aluminum chloride, and E, together with the manifold of sampling tubes N, was sealed off from the system and thermostated at the desired temperature. Samples were taken by distilling carbon tetrachloride from E into one of the tubes N, freezing the liquid at both E and the tube with liquid air and sealing off the tube. The sample was washed with water before counting to remove any traces of aluminum chloride which might have been carried over in spray.

Small accurately known amounts of water vapor were, in some cases, added to the aluminum chloride before addition of carbon tetrachloride by opening the break-seal to a tube of water vapor P. About ten minutes after admission of the water the tube C was cooled with liquid air and the hydrogen chloride produced by reaction of the moisture with the aluminum chloride was removed from the system and counted. When there was no other source of moisture, the number of moles of hydrogen chloride removed was equal to the moles of water added, indicating that the water reacted rapidly and quantitatively with the aluminum chloride in preference to reacting with the glass walls of the system.

In all the work reported here the vacuum system was degassed by evacuating while flaming to temperatures just below the softening point of the glass. Final pressures were about 1 micron. Silicone "high vacuum" stopcock grease was used.

The total amount of aluminum chloride initially present in an experiment was calculated from the summation of the counts of radiochlorine recovered in all the organic and aqueous samples and residues, corrected for the difference in counting yield in the two media. At equilibrium distribution of the radioactive chlorine $>99.9\%$ of the activity would have been in the carbon tetrachloride in all experiments reported here, since the mole fraction of aluminum chloride relative to carbon tetrachloride was always less than 10^{-3}. Therefore the counting rate per ml. in the first carbon tetrachloride sample divided by the counting rate per ml. which would have been observed if all of the activity had transferred to the organic liquid was equal to the fraction of equilibrium distribution of radioactivity which had been achieved. For succeeding samples, account was taken of the fact that activity had been removed from the system when the earlier samples were taken and that the volume of carbon tetrachloride into which further activity was exchanging from the aluminum chloride became less with each sample removed.

Measurement of Radioactivity.—Radioactive aluminum chloride and carbon tetrachloride were separated by washing with water, and the water and carbon tetrachloride layers were counted with a Technical Associates No. TA-BIJ glass walled Geiger–Mueller counting tube which had an annular jacket of 10-ml. capacity to hold the solution around the sensitive portion of the tube. The counting efficiency for the 0.64 Mev. beta particles from Cl^{36} dissolved in water was about 3%. The relative counting efficiency in carbon tetrachloride solution was 82% of that in water.

In order to calculate the total quantity of aluminum chloride present in each experiment the specific counting rate of the chlorine in counts $min.^{-1}$ $mg.^{-1}$ was determined by accurately weighing about 10 mg. of the radioactive AgCl, dissolving it in aqueous ammonia solution and counting it in the solution tube. It is believed that the values for weights of aluminum chloride deduced from counting rates are accurate to within 5%.

Results and Interpretation

Products of the Reaction.—When radioactive *solid* aluminum chloride at "concentrations" *greater than 10^{-3} m./l.* was heated for two hours or more in a sealed tube at 100° with a large mole excess of carbon tetrachloride and the mixture was then washed with water, essentially all of the radioactive chlorine was nearly always found in the organic fraction. This was true for aluminum chloride which had been prepared in the absence of all moisture and also for that which had been exposed to some moisture. A fractional distillation with carriers indicated that all of the radioactive chlorine was present as CCl_4. Since no activity was found in the aqueous extract it appears that all of the chlorine atoms of either dry or partially hydroxylated aluminum chloride can enter into the exchange reaction.

The Reaction as a Function of Temperature.—Table I gives data from two experiments which show the type of results which were repeatedly obtained when purified carbon tetrachloride, dried by distillation through phosphorus pentoxide, was distilled in vacuum onto dry aluminum chloride cooled with liquid air, and samples were then distilled off both as soon as the mixture had been rapidly melted (−21°) and at later times after the mixture had stood at higher temperatures.

TABLE I

EXCHANGE REACTION BETWEEN ALUMINUM CHLORIDE AND CARBON TETRACHLORIDE

Temp., °C.	Total time elapsed	Total % exchange
3.3×10^{-3} mole $AlCl_3$ per liter of CCl_4		
−9	10 min.	16
−10	2.0 hr.	16
0	6.5	22
26	9.5	33
51	26	100
6.0×10^{-3} mole $AlCl_3$ per liter of CCl_4		
−21	5 min.	15
0	1 hr.	19
28	1.5	49
28	2.0	49
28	2.5	49
28	3.0	49
45	12	75

It seems reasonable to explain the fact that a limiting value of transfer of radioactivity is reached at each temperature by the hypothesis that the solubility of aluminum chloride at the lower temperature is so low that only a relatively thin layer of the aluminum chloride particles has opportunity to enter into the solubility equilibrium and that complete recrystallization of the particles is very slow. If this is the situation the transfer of radioactivity will be limited to the aluminum chloride in this outer layer. When the radioactive chlorine in this layer has been replaced by inactive chlorine the exchange reaction will continue but no further transfer of radioactivity will be observed since the remaining radioactive chlorine on the inside of the particles does not have access to the carbon tetrachloride. At a higher temperature, on the basis of this hypothesis, a greater transfer of radioactivity will be observed before the reaction appears to stop, because the solubility of the aluminum chloride is higher and a greater depth of surface is turned over in the solubility equilibrium. It seems probable that variations in the amount of activity exchanged at a given temperature for different runs are due to variations in the particle size, and hence the surface to volume ratio of the aluminum chloride in the different experiments.

The Effect of Moisture on the Exchange Reaction.—Exposure of the aluminum chloride surface to water equal to 10 mole % of the aluminum chloride, when the latter is present at a "concentration" of about 5 × 10^{-3} m./l., seems to have no effect in decreasing the rate of the exchange reaction (Expt. (1), Table II). Exposure to somewhat larger amounts of moisture stops the exchange reaction at the lower temperatures studied (Expt. (2), Table II) and decreases the rate at the higher temperatures studied (Figs. 2 and 3).

TABLE II

EXCHANGE REACTION BETWEEN CARBON TETRACHLORIDE AND ALUMINUM CHLORIDE TO WHICH WATER HAD BEEN ADDED

Temp., °C.	Total elapsed time	Total % exchange
Expt. (1)	Mole $AlCl_3$, 1.2 × 10^{-4} (4.5 × 10^{-3} m./l.) Mole H_2O added, 1.5 × 10^{-5} Mole HCl removed, 1.5 × 10^{-5}	
−21	5 min.	11
0	1.0 hr.	22
25	1.5	50
25	2.0	53
25	2.5	52
44	3.0	73
100	6	100
Expt. (2)	Mole $AlCl_3$, 1.6 × 10^{-4} (5.3 × 10^{-3} m./l.) Mole H_2O added, 2.6 × 10^{-5} Mole HCl removed, 2.5 × 10^{-5}	
−21	5 min.	0
0	1.0 hr.	0
28	1.5	0
55	2.0	7.5
55	3.0	15

The silver chloride used in Expt. (1) of Table II was fused under vacuum prior to synthesis of the aluminum chloride so it is believed that the only water which came in contact with the latter was the 1.5 × 10^{-5} mole which was added. Since the value given for moles of aluminum chloride is for the amount calculated by counting the radiochlorine in the aqueous extract at the end of the experiment, the total moles of aluminum was that equivalent to this chlorine (1.2 × 10^{-4} mole) plus that which was hydroxylated, as indicated by the hydrogen chloride collected (1/3 × 1.5 × 10^{-5} = 5 × 10^{-6} mole) or a total of 1.25 × 10^{-4} mole, and the ratio of hydroxyl groups to chlorine atoms was 0.05/1.20 = 1/24. Within the limits of accuracy of this work this amount of water did not have any effect on the exchange reaction.

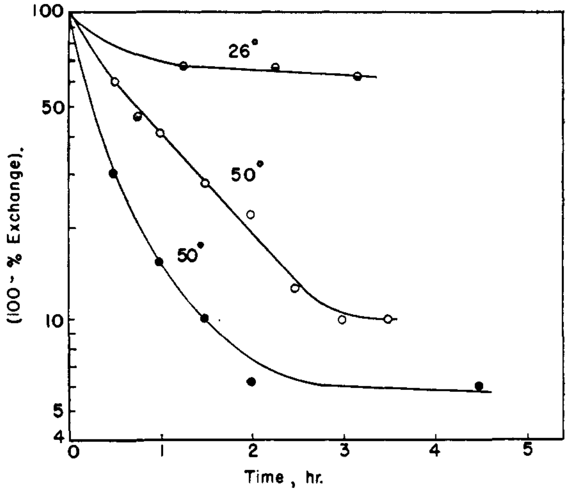

Fig. 2.—Exchange of slightly hydroxylated $AlCl_3$ with CCl_4 as a function of time: the curves refer to runs with three different samples of $AlCl_3$, each of which was exposed to some moisture during transfer in a dry-box.

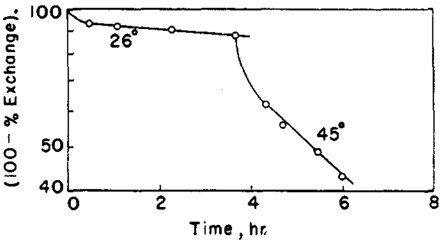

Fig. 3.—Exchange of slightly hydroxylated $AlCl_3$ with CCl_4 as a function of time: reaction of a single sample of $AlCl_3$ at two temperatures.

The silver chloride used in Expt. (2) of Table II was not fused before synthesis of the aluminum chloride and therefore contained a small indeterminate amount of moisture. It may be estimated from other experiments however that the aluminum chloride did not contain more than one hydroxyl group per 8 chlorine atoms. It should be emphasized that the *average* ratio of hydroxyl to chlorine in the reactant is, at best, only an approximate criterion of whether reaction will occur at low temperatures because the exchange reaction occurs only with the outer layers of the aluminum chloride particles. The ratio of hydroxyl to chlorine in these layers, after water is added to the particles, is undoubtedly much higher than the average ratio throughout the particle. The decrease in reactivity following addition of a given mole ratio of water may be expected to be less when the particle size of the aluminum chloride is low than when it is high because in the former case the surface to mass ratio is larger and hence the depth of the hydroxylated skin on the particles is less.

One possible explanation of results of the type illustrated in Expt. (2), Table II and in Figs. 2 and 3 is as follows: (a) an aluminum hydroxide surface layer completely protects the aluminum chloride from reaction at the lowest temperature; (b) at higher temperatures the pure aluminum hydroxide film is partially dissolved, or is partially eroded away by the increasing tendency for underlying aluminum chloride to dissolve, and chlorine exchange occurs; (c) as exchange occurs the transfer of radioactivity slows down and nearly stops as the result of deposition of non-radioactive aluminum chloride on the surface.

A comparison of the rates of the reaction at 26° and those at 50° in Fig. 2 has only qualitative significance since it was not possible to reproduce quantitatively either the total amount of aluminum chloride used in successive experiments or the surface area per mg. In two experiments with all conditions identical except the surface area the one with the larger surface area would be expected to react the faster. On the other hand, in two experiments with the same surface area of aluminum chloride but different quantities the one with the smaller quantity would be expected to show the greater fractional transfer of its radioactivity to carbon tetrachloride per unit time since a given *fractional* transfer in the latter case represents a smaller *quantity* transfer than in the former.

Effect of Changing the Aluminum Chloride Surface by Sublimation.—Sublimation of aluminum chloride which had been exposed to moisture might be expected to replace the surface which had been partially hydroxylated with non-hydroxylated aluminum chloride from the interior of the particles and thus make it more reactive in the exchange reaction. This prediction was tested as follows. The rate of transfer of radioactivity to liquid carbon tetrachloride from aluminum chloride which had been briefly exposed to slightly moist air was determined at 30°. The carbon tetrachloride was then cooled to 0° to stop further exchange and was distilled at this temperature into an auxiliary reservoir surrounded with liquid air. While the carbon tetrachloride was thus separated the aluminum chloride was partially sublimed from one part of the initial reservoir to another. This treatment may have increased the total surface area as well as exposing aluminum chloride which was less hydroxylated and turning over the inactive aluminum chloride which had been formed by exchange. Following the sublimation the carbon tetrachloride was poured back onto the aluminum chloride and the exchange reaction at 30° again followed. The results shown in Fig. 4 indicate a much faster reaction after the sublimation than before.

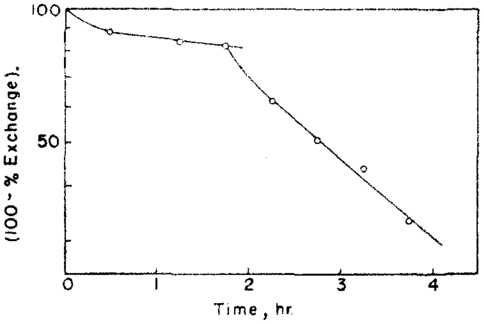

Fig. 4.—Effect of sublimation of slightly hydroxylated $AlCl_3$ on the rate of exchange with CCl_4 at 30°.

Absence of Effect of Air on the Exchange Reaction.—A single experiment in which 9 mg. of aluminum chloride was prepared *in situ* on the vacuum line and then exposed for 15 min. to air dried with phosphorus pentoxide, after which the air was pumped out and carbon tetrachloride distilled in through phosphorus pentoxide, showed that exposure of aluminum chloride to dry air does not decrease its reactivity in the exchange reaction.

Effect of "Concentration" of Aluminum Chloride on the Extent of Reaction.—Although 97–100% exchange occurred when tubes containing aluminum chloride at "concentrations" of 10^{-3} to 10^{-1} m./l. in carbon tetrachloride were heated for two hours at 100°, "concentrations" of 10^{-4} m./l. and below gave only 1 to 10% exchange. Intermediate "concentrations" gave values ranging from 20 to 85%.

Such a drop in exchange with decreasing ratio of aluminum chloride to carbon tetrachloride might result if: (1) small, approximately constant, amounts of aluminum chloride were adsorbed on the walls of the reaction vessel in such a way as to prevent their entering into the exchange reaction; (2) small, approximately constant, amounts of water or some other impurity capable of reacting with aluminum chloride remained in the carbon tetrachloride after the purification and drying procedures; (3) the exchange reaction occurred only on the surface of the solid salt and therefore failed to occur when the amount of salt was sufficiently low to go completely into solution rapidly.

Five experiments in which sufficient Pyrex glass wool was present in the reaction vessel to increase the surface 15- to 22-fold showed that the glass surface was not responsible for the observed "concentration" effect.

Three experiments in which the carbon tetrachloride had no contact with phosphorus pentoxide but anhydrous calcium sulfate was substituted as the drying agent in the preparatory distillation and magnesium perchlorate was used for the gas phase drying on the vacuum system showed a drop in exchange at low concentrations indistinguishable from that obtained when phosphorus pentoxide was used. Three experiments in which carbon tetrachloride which had been distilled through phosphorus pentoxide in the usual manner was allowed to stand with resublimed inactive aluminum chloride gave similar results. Mr. Monte Blau of our laboratory has tested the dryness of carbon tetrachloride distilled through phosphorus pentoxide by measuring the pressure of hydrogen generated by heating such carbon tetrachloride at 100° for 15 hr. with calcium hydride. The test showed that it contained less than 3×10^{-5} m./l. of water. These experiments all lead to the conclusion that the drop in percentage exchange at low concentrations is not due to water or other impurities in the carbon tetrachloride. They lend weight to the hypothesis that the exchange reaction can occur only in the presence of a solid aluminum chloride surface.

This hypothesis assumes that at "concentrations" of 10^{-3} m./l. and greater the solubility[10] of aluminum chloride in carbon tetrachloride at 100° is exceeded and so a solid surface is present throughout the reaction period. At concentrations slightly below 10^{-3} m./l. the aluminum chloride all dissolves at 100° but during the process of heating to 100° and completion of the dissolution appreciable exchange occurs on the dissolving surface. At still lower concentrations the time required for dissolution is sufficiently small so that relatively little exchange occurs. Since the surface of the aluminum chloride and its time of dissolution are not reproducibly controlled there is considerable fluctuation in the exchange values in the intermediate "concentration" region.

Test of Reaction in the Gas Phase.—If the hypothesis that exchange between aluminum chloride and liquid carbon tetrachloride occurs only on the solid aluminum chloride is valid, it seems improbable that a homogeneous gas phase exchange would occur. The gas phase reaction was tested by allowing aluminum chloride vapor at a few tenths of a mm. pressure to mix with carbon tetrachloride vapor at about 180 mm. pressure by opening a break seal between liter bulbs of the two vapors while the bulbs were thermostated in an oven at 140°. After standing for several hours at the reaction temperature the reactants were quickly frozen out with liquid air and the solid so obtained was placed in water so that the aluminum chloride would be extracted as rapidly as it thawed. Four experiments were conducted. Two gave essentially no exchange and two nearly complete exchange. It seems reasonable to conclude that a homogeneous gas phase reaction does not occur up to 140°. It is highly unlikely that any inhibitor could have been present which would completely inhibit the homogeneous reaction in two of the experiments but relatively probable that a little solid hydroxylated aluminum chloride or some other catalyst could have been present in those experiments where reaction occurred.[11]

The Exchange of Chlorine between Aluminum Chloride and Chloroform at Low Temperature.—When it was found that aluminum chloride would exchange rapidly with carbon tetrachloride at the lowest temperature at which tests could be made (its melting point of −21°) a similar experiment was carried out with chloroform which melts at −63° (Table III). The fact that the extent of exchange at each temperature was greater than in the case of carbon tetrachloride suggests that the aluminum chloride may be considerably more soluble in chloroform than in carbon tetrachloride. The chloroform used was Merck Reagent Grade which had been distilled from phosphorus pentoxide.

TABLE III

EXCHANGE REACTION BETWEEN ALUMINUM CHLORIDE AND CHLOROFORM

Temp., °C.	Total time elapsed, hr.	Total % exchange
About 10^{-3} mole $AlCl_3$ per liter of $CHCl_3$		
−63	15 min.	42
−15	1	54
25	2	94
25	4	94
55–90	13	100

When chloroform from this experiment was distilled with added inactive carbon tetrachloride as carrier and successive fractions were counted to determine the distribution of the radiochlorine it was found that not more than 20% of the activity was present as carbon tetrachloride.

The Exchange Reaction with Other Organic Chlorides.—In exploratory tests early in the work of this paper samples of aluminum chloride containing radioactive chlorine were mixed with several of the butyl and amyl chlorides, the mixtures were distilled and the fractions taken near the boiling points of the parent organic compounds were counted to estimate the percentage exchange of the aluminum chloride with the compound. In all cases the aluminum chloride had experienced contact with moist air and in all cases there was some hydrogen chloride evolved and a yellow-orange color appeared in the distillation mixture. The "concentration" of aluminum chloride was of the order of 0.1 m./l. in each case. The results given in Table IV suggest that this type of exchange may be a convenient method of preparing a variety of labeled organic chlorides. It is probable that considerable isomerization occurred under the conditions of these tests and that this could be demonstrated in similar tests in which a second distillation was made with inactive portions of the isomers added as carriers.

---

[10] There is no satisfactory determination of the solubility of aluminum chloride in carbon tetrachloride described in the literature. Such a determination is difficult to make because of the very low solubility, the sensitivity to hydrolysis, the inapplicability of radiotracers, and the difficulty of solute separation.

[11] Since this work was completed it has been shown that gaseous carbon tetrachloride exchanges chlorine rapidly with solid aluminum chloride at 25° (Blau and Willard, THIS JOURNAL, in press).

TABLE IV

EXCHANGE BETWEEN ALUMINUM CHLORIDE AND BUTYL AND AMYL CHLORIDES

Alkyl chloride	Temp. of dist., °C.	Exchange, %
n-Butyl	76–77	95
s-Butyl	68–69	90
t-Butyl	50–52	90
n-Amyl	100–105	70

An analogous exchange of bromine between aluminum bromide and alkyl bromides and of iodine between aluminum iodide and alkyl iodides has been reported by earlier workers.[12]

Discussion of Mechanism

On the basis of the information thus far available it is impossible to assign a unique mechanism to the reaction of exchange of chlorine between aluminum chloride and carbon tetrachloride. It is perhaps particularly worthwhile to speculate about such mechanisms in this case, however, because the commonly accepted carbonium ion mechanism[3,4] for Friedel–Crafts type reactions does not seem consistent with the observations. Such a mechanism would seek to explain the exchange by the reversible reaction $CCl_4 + AlCl_3 \leftrightarrows CCl_3^+ + AlCl_4^-$. If heats of solvation, which are probably very low in the non-polar solvent carbon tetrachloride, are neglected, it may be estimated that the heat of the reaction as written must be endothermic by about 200 kcal. mole^{-1} minus the heat of the reaction $AlCl_3 + Cl^- \rightarrow AlCl_4^-$. Since it may be estimated from the available data that the activation energy of the over-all reaction is less than 19 kcal. mole^{-1} and since the endothermic heat of reaction cannot be greater than the activation energy the simple carbonium ion mechanism would require that the energy of binding of Cl^- to $AlCl_3$ to form $AlCl_4^-$ be of the order of 200 kcal. mole^{-1} which is an impossibly high value. The heat of the over-all reaction may be estimated by summing the estimated heats of the following hypothetical intermediate reaction steps.

(1) $CCl_4 \longrightarrow CCl_3 + Cl$; ~ -65 kcal./mole
(2) $Cl + e^- \longrightarrow Cl^-$; $+86$
(3) $CCl_3 \longrightarrow CCl_3^+ + e^-$; ~ -230
(4) $AlCl_3 + Cl^- \longrightarrow AlCl_4^-$; $\geqq (+209)$ − (over-all activ. energy)

An upper limit of the activation energy of the exchange reaction may be estimated from the data on the basis of the relation, no. of molecules reacted/no. of collisions = $e^{-E/RT}$, which assumes that every collision in which the energy of activation is available results in reaction. For this purpose the assumption was made that all of the aluminum chloride was in solution. Since, in fact, only a small fraction was dissolved, this assumption yields a higher value of E than the correct one. A minimum value for the number of molecules reacted per unit time was estimated by noting from the data of Tables I and II that all of the aluminum chloride which was free to react at all in the solid samples had reacted completely in five minutes. From this observation it can be concluded that a quarter to a half of all of the atoms available for reaction, and possibly much more, must have reacted at the end of one minute. If the lower limit thus set is too low the value of E obtained is again high. These estimates gave the results

$$\frac{5 \times 10^{21}\ \text{sec.}^{-1}\ (\text{moles of } AlCl_3)^{-1}}{6 \times 10^{38}\ \text{sec.}^{-1}\ (\text{moles of } AlCl_3)^{-1}} = e^{-E/RT};\ E = 19\ \text{kcal. mole}^{-1}$$

Because of the assumptions made it seems probable that the activation energy of the exchange is lower, and possibly very much lower than 19 kcal./mole.

In contrast with hypotheses involving formation of soluble ionic complexes an hypothesis that the exchange occurs as a result of adsorption of induced carbon tetrachloride dipoles on the ionic aluminum chloride lattice seems consistent with the available facts. According to such an hypothesis a center of charge on the ionic lattice may cause polarization of a carbon tetrachloride molecule which is then adsorbed on the surface of the lattice by electrostatic attraction. When the molecule is desorbed there is a possibility that it may leave one of its original chlorine atoms behind in exchange for one of those of the aluminum chloride. Such a process might be expected to have a very low activation energy and to proceed rapidly even at very low temperatures.

If a surface mechanism is responsible for the exchange reaction studied here it seems possible that it may also be responsible for Friedel–Crafts reactions of carbon tetrachloride and other reactions catalyzed in the presence of solid ionic inorganic halides. Friedel–Crafts reactions in systems where the inorganic catalyst is soluble must occur through a mechanism involving soluble molecular or ionic complexes.

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

Summary

1. The chlorine in solid aluminum chloride will exchange readily with that in liquid carbon tetrachloride.

2. The exchange with carbon tetrachloride and also with chloroform occurs rapidly even at the melting points of the compounds (−21 and −63°) if the aluminum chloride has never been exposed to moisture.

3. Partial hydroxylation of the aluminum chloride by exposure to moisture completely inhibits the exchange at low temperatures and decreases the rate at higher temperatures.

---

[12] Brejneva, Roginsky and Schilinsky, *Acta Physicochimica U. R. S. S.*, **5**, 549 (1936).

4. Except at elevated temperatures exchange is incomplete, indicating that recrystallization of the aluminum chloride particles is a very slow process.

5. Whereas complete exchange occurs at 100° in two hours at ratios of aluminum chloride to carbon tetrachloride greater than 10^{-3} m./l. relatively little or no exchange occurs at lower ratios. This observation suggests that exchange can occur only when an aluminum chloride surface is present.

6. Mixtures of gaseous aluminum chloride and carbon tetrachloride can be maintained at 140° for nine hours with no exchange.

7. The characteristics of the exchange between aluminum chloride and carbon tetrachloride cannot be explained by the carbonium ion type of mechanism commonly used to rationalize Friedel–Crafts reactions.

8. Butyl and amyl chlorides exchange chlorine easily with aluminum chloride and this exchange appears to be a convenient general method for tagging organic chlorides with Cl^{36}.

9. Silver chloride precipitated from water consistently retains about 1% by weight of occluded water even after heating in vacuum at 160° for several hours.

10. As little as 10^{-5} mole of water may be quantitatively detected in a vacuum system by collecting and counting the radioactive hydrogen chloride formed by hydrolysis of radioactive aluminum chloride.

MADISON, WISCONSIN RECEIVED MARCH 30, 1950

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric and Molecular Behavior of 1,3-Dipalmitin, 1,3-Distearin, Tripalmitin, Tristearin and Tetradecyl Palmitate[1]

BY ROBERT W. CROWE[2] AND CHARLES P. SMYTH

The polymorphic behavior of 1-monopalmitin and 1-monostearin has recently been investigated in this Laboratory[3] by dielectric constant measurements, the results of which have been correlated with the X-ray diffraction and thermal studies of Malkin and Shurbagy[4] and the more recent X-ray and dilatometer investigations of Lutton and Jackson.[5] It was found that the α-forms of these compounds possess molecular freedom, probably about their long molecular axes, as suggested by Malkin. Moreover, these α-forms showed an abnormally high conductivity suggesting a proton transfer mechanism enhanced by rotation of the hydrocarbon chains, similar to that occurring in the α-forms of the long-chain alcohols.[6] This similarity in behavior was not surprising in view of the fact that members of both series are highly hydrogen bonded and consist of long chains with hydroxyl groups at one end. It therefore appeared worthwhile to carry out a similar investigation on the corresponding 1,3-diglycerides with one hydroxyl group unesterified and triglycerides, in which hydrogen bonding does not exist. Members of both of these series have been reported to possess "multiple melting points." In this investigation, therefore, dielectric constant measurements were made on 1,3-dipalmitin, 1,3-distearin, tripalmitin and tristearin over a considerable temperature and frequency range. The various polymorphic forms were isolated by varying the previous thermal treatment of the samples. Similar measurements were made on a sample of tetradecyl palmitate, the results of which have been used for comparison purposes.

Preparation and Purification of Materials

Purified samples of the four glycerides investigated were kindly given to us by the Procter and Gamble Company of Ivorydale, Ohio. Since, as in the case of the monoglycerides, they were considered to be of at least 99% purity no attempt was made to purify them further. Moisture was removed before measurement by keeping the solvent-crystallized samples for several hours in a vacuum desiccator. The melting points as observed here are compared with recent literature values in Table I.

Tetradecyl palmitate was synthesized[7] by adding to 0.1 mole of tetradecyl alcohol, dissolved in a large excess of dry pyridine, an equimolar portion of palmitoyl chloride, prepared by the reaction of thionyl chloride with palmitic acid. After the reaction was complete, 100 ml. of benzene was added to the mixture and the pyridine removed by several washings with distilled water. The unreacted palmitic acid was removed by shaking the benzene solution several times with dilute sodium carbonate solution. Finally, the solution was evaporated to approximately half its original volume and about 50 ml. of methanol

---

[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] Procter and Gamble Fellow in Chemistry, 1949–1950, this article is based upon a thesis to be submitted by R. W. Crowe in partial fulfillment of the requirements for the degree of Ph.D. at Princeton University.

[3] Crowe and Smyth, THIS JOURNAL, **72**, 4427 (1950).

[4] Malkin and Shurbagy, *J. Chem. Soc.*, 1628 (1936).

[5] Lutton and Jackson, THIS JOURNAL, **70**, 2445 (1948).

[6] Hoffman and Smyth, *ibid.*, **71**, 431 (1949).

[7] Prepared by Mr. D. A. Pitt.