The Exchange Reaction between Hydrogen Chloride and Aluminum Chloride

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Richardson and Benson[1] have observed that no exchange occurred between hydrogen chloride and aluminum chloride when they were allowed to stand in contact for 12 hours at room temperature. Equilibrium exchange occurred in a 76-hour run with a maximum temperature of 213°. These investigators used reagent grade aluminum chloride "further purified by fractionation in an all-Pyrex system pressured to 1.2 atm. with dry nitrogen."

The purpose of this note is to report experiments, using aluminum chloride synthesized *in situ* and Mallinckrodt commercial "Aluminum Chloride Anhydrous" resublimed in vacuum, in which we have observed exchange with hydrogen chloride at room temperature in times as short as five minutes. The results are summarized in Table I.

TABLE I

EXCHANGE OF CHLORINE BETWEEN HYDROGEN CHLORIDE AND ALUMINUM CHLORIDE

A. Cl^{36} initially in aluminum chloride: Volume of reaction flask: 1 liter in expt. 1 and 2; 190 ml. in expt. 3 and 4. a, b and c, etc., represent successive fresh samples of HCl exposed to a single aluminum chloride surface. The values in the last column show the % of the activity originally in the aluminum chloride which appeared in each sample of HCl. In expts. 3a and 3c, CH_2Cl_2 was substituted for HCl. All expts. were made at 25° unless otherwise indicated in parentheses in column I.

Exp. no.	Time, min.	HCl, cm. at 25°	HCl, equivalents Cl $\times 10^4$	$AlCl_3$, equivalents Cl $\times 10^4$	Exchange, %
1a	10	5	28	22	3
1b	60	20	110		7
1c (100°)	10	20	110		65
2	120	10	55	4.5	35.8
3a	5	3.7	7.5 (CH_2Cl_2)	2.2	1.4
3b	5	3.8	3.8		13.6
3c	5	3.8	7.6 (CH_2Cl_2)		0.3
3d	5	3.5	3.6		10.4
3e	5	7.5	7.6		6.8
3f	5	14.9	15.1		6.6
3g	60	3.8	3.9		5.2
3h	1200	3.8	3.1		5.1
4a (−80°)	5	3.7	3.7	1.8	2.3
4b (−80°)	10	3.7	3.7		0.7
4c (−80°)	5	7.4	7.5		0.4
4d	5	3.7	3.7		13.2
4e	10	3.7	3.7		9.5
4f	10	3.7	3.7		6.7

B. Cl^{36} initially in HCl: Volume of reaction flask 110 ml. In expt. 5 the $AlCl_3$ was prepared *in situ* from AgCl and Al as in expt. 1, 2, 3 and 4. In expt. 6 the $AlCl_3$ was Mallinckrodt "Aluminum Chloride Anhydrous" resublimed three times under vacuum. The values in the last column are for the cumulative total % decrease in activity of the HCl. a, b, c and d represent successive exposures of a single sample of HCl to a single aluminum chloride surface. Column 3 shows the amount of HCl in the sample as determined by pressure volume measurements after each exposure. In expt. 6 exposure **a** was made before a count was taken on the gas, so an unknown amount of activity in addition to that recorded in the last column was exchanged.

Exp. no.	Time, min.	HCl, cm. at 25°	HCl, equivalents Cl $\times 10^4$	$AlCl_3$, equivalents Cl $\times 10^4$	Exchange, %
5a	5	3.6	2.14	5	30
5b	5	3.5			38.8
5c	20	3.5			45
5d	115	3.4			50
6a	10	10.3	6.0	19	..
6b	10	10.3			12.5
6c	10	10.3			18
6d	90	10.2			25

Experimental

The techniques were similar to those described in detail earlier.[2,3]

For the first five experiments of Table I aluminum chloride was synthesized in a vacuum by heating aluminum with fused silver chloride. The product was sublimed onto the walls of the reaction chamber and the synthesis tubes were then removed by sealing. In the first four experiments the silver chloride contained Cl^{36} [4] and consequently the aluminum chloride was labeled. Hydrogen chloride which was not labeled was admitted to the reaction chamber and after standing for the desired time was frozen out in a side tube with the aid of liquid air. In expts. 1 and 2 the tube was sealed off from the system and the hydrogen chloride was dissolved in water and counted with a Geiger tube equipped with an annular jacket for holding solutions. After the aluminum chloride had been exposed to a series of gas samples the reaction chamber was removed and the solid was dissolved in the water and counted. The fraction of exchange was found by dividing the counting rate obtained from an individual hydrogen chloride sample by the sum of the counting rates of the dissolved aluminum chloride and all of the hydrogen chloride samples exposed to it. Experiments 3 and 4 were performed in the same manner as 1 and 2 except that the hydrogen chloride was counted as a gas in the annular jacket of a Geiger tube attached to the vacuum system. Experiments 5 and 6 used aluminum chloride which was not labeled and hydrogen chloride which was labeled. The latter was prepared in the vacuum system by treating a solution containing HCl^{36} with concentrated sulfuric acid, passing the gas through phosphorus pentoxide and subsequently mixing with inactive hydrogen chloride. The mixture was counted in the gas phase after each of several successive exposures to a single aluminum chloride sample. In all cases where counting rates of samples counted in the gas phase were to be compared with those counted in solution an experimentally determined conversion factor was used.

The hydrogen chloride (Matheson Co. "Anhydrous") used in these experiments was condensed directly from the tank into a liquid air trap on the vacuum system. The gas used for the exchange reactions was obtained by partial evaporation of the liquid hydrogen chloride, the vapor being passed through a four-inch packing of glass wool covered with phosphorus pentoxide.

Discussion

In addition to establishing the fact that the exchange reaction occurs at room temperature the data of Table I illustrate the following facts: (1) The rate of exchange varied from one experiment to another as would be expected from the fact that the relative amounts of reactants and also the surface to volume ratio of the aluminum chloride varied. (2) Relatively rapid exchange occurred at 100° where visible sublimation was observed (expt. 1c). This was presumably due to the exposure of fresh surface; *i.e.*, unexchanged surface was made available to the gas by a process which

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[1] R. L. Richardson and S. W. Benson, THIS JOURNAL, **73**, 5096 (1951).

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

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

[4] Item 17-P, U. S. A. E. C. Isotopes Division Catalog and Price List No. 4 (March 1951).

was faster than diffusion. (3) The rate of exchange of hydrogen chloride gas is faster than the rate of exchange of methylene chloride (expt. 3a, b, c, d) (other halogenated methanes which we have tested show much faster exchange, however). (4) Detectable exchange of hydrogen chloride gas with aluminum chloride occurs at −80° and the temperature coefficient of the exchange is low (expt. 4). (5) The exchange may be observed with vacuum sublimed commercially produced aluminum chloride (expt. 6) as well as with aluminum chloride synthesized *in situ* (expt. 1, 2, 3, 4, 5).

Because of the fact that negative results have been reported in an attempt to measure the exchange[1] we have sought tests which would be as conclusive as possible in demonstrating that the results which we have observed are not due to causes other than exchange. Thus, the fact that hydrogen chloride picks up more activity than methylene chloride, when exposed to the same aluminum chloride surface at the same pressure and transferred in the system in the same way, eliminates the possibility that bulk transfer of aluminum chloride to the counter or other physical effects are involved. Transfer of aluminum chloride as a spurious indication of exchange is also eliminated by the fact that exchange was observed when the activity was initially in the hydrogen chloride, and yet again by an analysis for aluminum in the hydrogen chloride fraction from expt. 2. The latter analysis showed aluminum equivalent to only 0.25% of the aluminum used in the reaction. In order to demonstrate the absence of radioactive hydrogen chloride which would have been produced by hydrolysis if water were present as an impurity in expt. 2 the aluminum chloride reactant was analyzed for aluminum and chlorine after the reaction. The ratio was found to be 0.256 in agreement with the calculated value of 0.2535 for $AlCl_3$.

The absence of exchange in the experiments of Richardson and Benson at room temperature may have been due to the method of preparation of their aluminum chloride. An example of the sensitivity of such surfaces to small differences in treatment is the fact that aluminum chloride prepared *in situ* by our method and subsequently exposed briefly in a "dry-box" to nitrogen which had been dried by passage through magnesium perchlorate always exchanged chlorine with carbon tetrachloride much less readily than aluminum chloride which had not been so exposed.[5] This presumably was due to small amounts of residual moisture in the dry-box atmosphere, since no effect on the reactivity was observed as a result of exposing a similar surface in a vacuum system to air dried by passing through a long train of phosphorus pentoxide.[2]

In order to determine whether aluminum chloride prepared by the *in situ* synthesis we have used has a greater ability to form a stable compound with hydrogen chloride than that investigated by other workers,[1,6] Mr. James Reavis of our laboratory has made adsorption measurements of the pressure–volume type. These show that there is no reaction at room temperature and 500 mm. pressure in excess of that which might be expected from slight physical adsorption.

It is impossible to state the mechanism of the exchange reported here on the basis of the facts available. The difficulty of obtaining identical aluminum chloride surfaces with which to test the influence of pressure and temperature of hydrogen chloride is a complicating factor in making quantitative studies. It seems clear from the work of Brown and Pearsall[6] and Richardson and Benson[1] and of more recent work in our laboratory, however, that the equilibrium concentration of $HAlCl_4$ must be extremely low.

It has been suggested[2] that the exchange between alkyl chlorides and solid aluminum chloride may be due to the fact that the aluminum chloride is an ionic crystal with localized spots of unsaturated charge on the surface which can adsorb molecules with permanent or induced dipoles by coulombic attraction. There is then the possibility that when the species leaves the surface it will do so with a different chlorine atom than came on. It may be that a process of this type is involved in the exchange of hydrogen chloride with aluminum chloride.

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[5] C. W. Herrmann, Ph.D. thesis, University of Wisconsin, 1949.

[6] H. C. Brown and H. Pearsall, THIS JOURNAL, 73, 4681 (1951).

Tritiation of Multiple Bonds—Synthesis of Tritiated Styrene

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Tritium labeled styrene has been prepared by the reduction of acetophenone with tritium and subsequent dehydration of the methylphenylcarbinol. The reduction was carried out at room temperature and atmospheric pressure over platinum oxide. Dehydration of the carbinol in the presence of *p*-toluenesulfonic acid[1] gave a 79% yield of styrene of specific activity 0.66 mc./mm.

An apparatus for tritiation has recently been described.[2] A simpler, more convenient apparatus of general application is reported here that permits efficient utilization of tritium. The significantly different reaction rates of tritium and protium make it essential to use a reduction mixture as rich in tritium as possible. By the Toeplering procedure outlined below the effects of the differences in diffusion rates of tritium and protium are avoided and a very efficient transfer of tritium from the low pressure ampoule to the hydrogenation vessel is accomplished. Tritium assay of benzoic acid obtained from the oxidation of the tritiated styrene indicates that 9% of the total tritium in the styrene was introduced by exchange with protium on the benzene ring.

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[1] Procedure developed by M. A. Leaffer of this Laboratory.

[2] D. L. Williams and A. R. Ronzio, THIS JOURNAL, 72, 5787 (1950).