[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Some Complexes of Oxygen Bases with Aluminum Chloride in Benzene

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The solubility of aluminum chloride has been determined in solutions of benzene containing various concentrations of water, methanol, ethyl ether, tetrahydrofuran, dioxane, diethyl ether of ethylene glycol, heptafluorodiethyl ether and perfluorodibutyl ether at 25°. The data indicate that methanol, ethyl ether and tetrahydrofuran form compounds of the type $R_2O \cdot AlCl_3$ and water forms $AlCl_2OH$. However, the bifunctional ethers solvate more than one unit of $AlCl_3$. Perfluorodibutyl ether does not form a compound with aluminum chloride. Heptafluorodiethyl ether forms tars and a highly colored solution.

The purpose of this paper is to present data on the solubility of aluminum chloride in solutions of benzene containing various concentrations of the oxygen bases: water, methanol, ethyl ether, tetrahydrofuran, dioxane, diethyl ether of ethylene glycol, heptafluorodiethyl ether ($CF_3CH_2OCF_2CF_2H$) and perfluorodibutyl ether. These data make it possible to discuss the equilibria

$$Al_2Cl_6(s) + 2R_2O \rightleftarrows 2R_2O \cdot AlCl_3 \qquad (1)$$

$$Al_2Cl_6(s) + R_2O \rightleftarrows R_2O \cdot AlCl_3 \cdot AlCl_3 \qquad (2)$$

$$Al_2Cl_6(s) + 2H_2O \rightleftarrows 2AlCl_2OH + 2HCl \qquad (3)$$

Reaction 1 represents the rupturing of both bridging bonds of the Al_2Cl_6 molecule whereas reaction 2 probably involves the breaking of only one bridge bond. Use of oxygen bases covering a wide range in basicity should give information as to which of the two equilibria occurs or give information about each one. Reaction 3 is the suggested reaction which probably results from reactions of type 1 or 2 followed by splitting out hydrogen chloride.

Experimental Part

General Procedure.—Highly purified benzene was added to a cylindrical solubility flask which contained a large excess of quadruply sublimed aluminum chloride. The mixture was magnetically stirred under nitrogen. After an initial solubility determination in the pure solvent, small amounts of a pure oxygen base were added to the solution. After each addition, the system was equilibrated at 25 ± 0.1°, and samples of the homogeneous solution were analyzed for aluminum content and acidity.[2]

The data are presented as millimoles of aluminum chloride (calculated as $AlCl_3$) dissolved per millimole of oxygen base added to the solution. Each series of oxygen base additions caused a linear increase in solubility of aluminum chloride. If we assume that the increase in solubility can be accounted for by equations 1 and 2, then the slopes m could be used to calculate equilibrium constants for reaction 1 or 2.

$$K_1 = \frac{(R_2O \cdot AlCl_3)}{(R_2O)^2} = \frac{m^2}{(1 - m)^2}$$

$$K_2 = \frac{(R_2O \cdot AlCl_3 \cdot AlCl_3)}{(R_2O)} = \frac{m/2}{1 - m/2}$$

Materials.—Anhydrous aluminum chloride (Baker and Adamson) was carefully sublimed four times under vacuum, then a fifth time into the solubility flask. High purity benzene was doubly distilled from a solution containing the blue ketyl formed by the reaction of potassium alloy with benzophenone.

Tetrahydrofuran and the diethyl ether of ethylene glycol were pretreated with activated alumina to remove peroxides.[3] Tetrahydrofuran and ethyl ether were refluxed over the blue ketyl. Methanol was refluxed over mercuric chloride and aluminum.[4] Commercial grade dioxane was refluxed with hydrochloric acid, separated and then distilled from sodium.[5]

All of the oxygen bases were refluxed in a nitrogen atmosphere, and in most cases the additions to the equilibrium flask were taken directly off of reflux as needed.

All work was done in an integrated all-glass system with no exposure to the air at any time during the process. Prior to each run the all-glass train was repeatedly flamed and pumped out to remove traces of absorbed water and oxygen.

Equilibrations, purifications and other manipulations involving aluminum chloride and the solvents were carried out under nitrogen. Linde high-purity nitrogen was purified by passing the gas through a Pyrex coil trap and a copper trap (40 ft. of tubing in a coil) both immersed in liquid nitrogen. Nitrogen purified in this manner could be bubbled for several hours through a benzene solution containing excess aluminum chloride without causing a detectable increase in the solubility of the chloride. Previous work[6,7] had shown that the solubility of aluminum chloride in benzene is very sensitive to water and oxygen contamination. The purity of the nitrogen (absence of oxygen and moisture) was confirmed by mass spectrometer analysis.

Results and Discussion

The solubility of aluminum chloride has been shown by these studies to be a linear function of the oxygen base added. In the case of methanol, ethyl ether and tetrahydrofuran the ratio of $AlCl_3$ units to moles of oxygen base added is essentially unity (Table I). This fact together with the high basicity of the oxygen in tetrahydrofuran[8] makes it reasonable to assume that for the cyclic ether, reaction 1 occurs (both bonds in the Al_2Cl_6 dimer are broken) and the reaction goes to completion. Since the results for methanol and ethyl ether are identical to those for tetrahydrofuran, reaction 1 is likewise proposed as the solubilizing mechanism. No hydrogen chloride could be detected when methanol was added to aluminum chloride in benzene. In these experiments with methanol, ethyl ether and tetrahydrofuran, the solutions remained water white. It appears that aluminum chloride is not a sufficiently differentiating acid to give a comparison of the base strengths of methanol, ether and tetrahydrofuran in benzene.

The Aluminum Chloride–Water–Benzene System.—The study of the aluminum chloride–water–benzene system is complicated by the formation of hydrogen chloride and tars. The data of Table II can be interpreted as evidence for reaction 3 going to completion. Evidence for reaction 3 is (1) the detection of hydrogen chloride in the vapors

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[1] Taken from the dissertation presented by James R. Bercaw to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree.

[2] L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945).

[3] W. Dazler and C. D. Bauer, *ibid.*, **18**, 52 (1946).

[4] H. Eisenberg and R. M. Fuoss, THIS JOURNAL, **75**, 2914 (1953).

[5] K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

[6] Lucille Amade, M.S. Thesis, The Ohio State University, 1950.

[7] L. D. Swan, Ph.D. Thesis, The Ohio State University, 1952.

[8] H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942).

TABLE I

SUMMARY OF DATA FOR THE SOLUBILIZATION OF ALUMINUM CHLORIDE IN BENZENE AT 25° BY THE ADDITION OF OXYGEN BASES

$[R_2O]$,[a] mmole/ 100 g. of benzene	$[AlCl_3]$, mmole/ 1000 g. of benzene	$[AlCl_3]/[R_2O]$ slope *m*	$[R_2O]$,[a] mmole/ 100 g. of benzene	$[AlCl_3]$, mmole/ 1000 g. of benzene	$[AlCl_3]/[R_2O]$ slope *m*
[MeOH]			[HFE]		
00	13.3	1.01	0	5.9	0.79
17.0	29.2		11.3	13.3	
30.8	45.2		22.5	23.8	
48.6	62.8		[DEC]		
$[Et_2O]$					
0	16.0	1.01	0	3.7	2.5
2.5	17.9		10.7	33.3	
18.7	34.8		16.5	44.4	
33.2	49.8		22.2	60.0	
[THF]			[DIOX]		
0	7.0	1.00	0	6.4	1.7
10.4	17.6		12.2	28.4	
22.7	30.0		17.9	34.7	
34.4	41.7		27.3	52.7	
[PFE]					
0	6.2	0			
3.7	6.5				
12.2	6.9				

[a] MeOH, methanol; Et_2O, ethyl ether; THF, tetrahydrofuran; PFE, perfluorodibutyl ether; HFE, heptafluoro diethyl ether, $CF_3CH_2OCF_2CF_2H$; DEC, diethyl "Cellosolve," $C_2H_5OCH_2CH_2OC_2H_5$; DIOX, dioxane.

over the solution, (2) the 1-to-1 ratio of H_2O to $AlCl_3$, and (3) the titrations of the acid present in solution which indicate that approximately 37 ± 10% of the HCl had been thrown out of solution in the process of equilibration. Once this reaction had come to equilibrium there was no further change in concentration of the products with time.

TABLE II

SOLUBILITY OF ALUMINUM CHLORIDE (AS $AlCl_3$) IN BENZENE AT 25° AS A FUNCTION OF WATER ADDITIONS

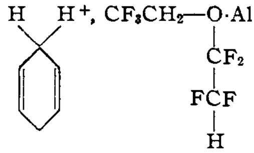
$[H_2O]$,[a] mmole/1000 g. of benzene	$[AlCl_3]$, mmole/1000 g. of benzene	$[H_2O]$,[a] mmole/1000 g. of benzene	$[AlCl_3]$, mmole/1000 g. of benzene
0	9.2	17.0	26.3
0*	8.0	19.8	29.3
2.8	11.9	22.7	32.3
5.4	14.8	25.6	35.4
8.0	17.5	27.0	37.5
10.5	20.3	31.2*	40.6
11.2*	21.0		

[a] Additions were made as benzene saturated with water except where designated by (*) in which case pure water was added.

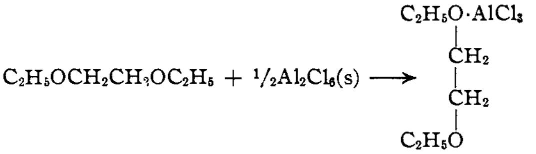
It is recognized that these data might also be explained by postulating a series of complex equilibria involving aluminum chloride, $AlCl_2OH$, HCl, water and benzene.

The Fluorinated Ethers.—The greatly reduced basicity of the fluorinated ethers should appear as we measure the solubility of aluminum chloride in solutions of these ethers for the reduced basicity should affect the tendency of a fluorinated ether to coördinate with aluminum chloride.

The data indicate that within the limits of the experimental error, perfluorodibutyl ether does not form a benzene-soluble complex with aluminum chloride. However, heptafluorodiethyl ether, $CF_3CH_2OCF_2CF_2H$, forms a highly colored (red-wine) ternary complex involving aluminum chloride and benzene. Tars were formed rapidly in the reaction mixture, but an equilibrium was established quickly. Tar formation has been reported by Henne and Newman[9] in the reaction of $CF_3C_6H_4COCH_3$ with CH_3COCl in the presence of aluminum chloride; furthermore, exchange of fluorine and chlorine occurred. The reactions that occurred on addition of heptafluorodiethyl ether are surprising and may be accounted for if we assume the formation of a weakly bound, active complex of the type

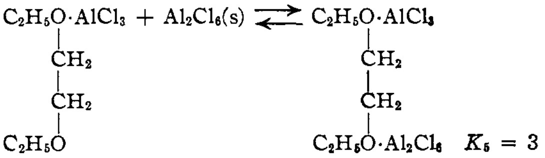


The Bifunctional Ethers.—Dimethyl "Cellosolve" ($CH_3OCH_2CH_2OCH_3$) was found to have a van't Hoff *i* factor of 1.76 in 100% sulfuric acid.[10] This might be interpreted to mean that the diether is a very weak base. The data of Table I indicate that each molecule of diethyl ether of ethylene glycol causes the solubilization of 2.5 molecules of aluminum chloride, calculated as $AlCl_3$. A possible explanation of this ratio incorporates (requires) two consecutive reactions.



$$C_2H_5OCH_2CH_2OC_2H_5 + {}^1/_2Al_2Cl_6(s) \longrightarrow \begin{array}{c} C_2H_5O\cdot AlCl_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ C_2H_5O \end{array} \qquad (4)$$

It is proposed that reaction 4 (analogous to reaction 1) goes to completion. The very weakly basic complex formed then equilibrates with additional Al_2Cl_6 according to equation 5.



$$\begin{array}{c} C_2H_5O\cdot AlCl_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ C_2H_5O \end{array} + Al_2Cl_6(s) \rightleftarrows \begin{array}{c} C_2H_5O\cdot AlCl_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ C_2H_5O\cdot Al_2Cl_6 \end{array} \quad K_5 = 3 \qquad (5)$$

It has been reported that only one of the oxygen atoms in dioxane forms a bond with boron trichloride[11] or with aluminum chloride in benzene.[12] From this information and the data of Table I, it is suggested that reaction 2 occurs between dioxane and aluminum chloride in benzene at 25°. In this case K_2 = 5.7 if only one oxygen atom participates in complex formation.

General Conclusions.—This work is in accord with previous contentions[13] that $AlCl_2OH$ is present in benzene solutions of aluminum chloride which contains small amounts of water.

Methanol, ethyl ether and tetrahydrofuran

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(9) A. L. Henne and M. S. Newman, THIS JOURNAL, **60**, 1697 (1938).

(10) V. J. Wottle, Ph.D. Thesis, The Ohio State University, 1951.

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(13) D. P. Stevenson and O. Beeck, THIS JOURNAL, **70**, 2890 (1948).

appear to be strong enough bases to rupture both bonds of Al_2Cl_6 and form strong colorless complexes of the type $R_2O \cdot AlCl_3$.

As might be expected, perfluorodibutyl ether forms no complex with aluminum chloride because of low basicity brought on by the presence of the fluorine atoms.

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[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Rate of Radioactive Exchange between Antimony(III) and Antimony(V) in Hydrochloric Acid Solution[1]

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By use of the known equilibrium and kinetic data on the Sb(V) system it is demonstrated that all of the exchange results can be interpreted on the assumption that $SbCl_6^-$ is the only species of Sb(V) that exchanges with Sb(III). The observed complexities of the exchange reaction result from the fact that under certain conditions the rate of formation of $SbCl_6^-$ is rate determining, while under other conditions the exchange process itself is rate determining. By performing the exchange reaction at conditions where chemical equilibrium does not exist, it is possible to show that the rate of exchange between $SbCl_6^-$ and Sb(III) decreases with increasing acidity. It is suggested that $SbCl_3$ is the exchangeable form of Sb(III), and some possible transition states are discussed.

The first work on the radioactive exchange between Sb(III) and Sb(V) in hydrochloric acid solution was that of Bonner.[2] The complexity of the system is apparent from the empirical rate law that he proposed: rate = $k[\mathrm{Sb(III)}]^{0.6} \times [\mathrm{Sb(V)}]^{1.1} \times [\mathrm{Cl}^-]^9[\mathrm{H}^+]^4$. Subsequently Cheek[3] has made a more extensive study of this system.

It will be demonstrated in this paper that most of the complexities of the system arise from the behavior of the Sb(V). Although a few new exchange experiments are reported, the primary purpose will be to correlate the known equilibrium[4] and kinetic[5] behavior of Sb(V) with the previous results of Bonner and Cheek.

It has been suggested[3] that possibly not all forms of Sb(V) are capable of exchanging with Sb(III), and that, as a result, the rate of formation of the exchangeable form might be the rate-determining step in the observed exchange. If this position were true it became most reasonable to assume that $SbCl_6^-$ was the exchangeable form. The data suggesting this assumption were: (1) the great increase in exchange rate with increasing acidity[2]; (2) the increasing equilibrium amounts of $SbCl_6^-$ at increasing acidity[4]; and (3) the slow rate of formation of $SbCl_6^-$, particularly at low acidities.[4] An additional argument is that $SbCl_6^-$ is the only form of Sb(V) reduced reversibly at the rotating platinum electrode,[5] and it is a general observation that reversible electrode reduction and radioactive exchange in these systems generally coincide.

Two preliminary exchange experiments were performed to test this hypothesis. In one experiment the Sb(V) added to the reaction mixture had been allowed to come to equilibrium in 6 *M* HCl, the acidity of the ultimate exchange mixture. In the second the Sb(V) came from a 12 *M* HCl solution, and hence was present entirely as $SbCl_6^-$. The experimental conditions for the exchange were then the same except for the form in which the Sb(V) was present. The first reaction had a half-time of 49 hours; the second a half-time of 12 min. This evidence clearly pointed to $SbCl_6^-$ as the exchangeable form of Sb(V).

Practically all exchange experiments of this type are performed in systems at chemical equilibrium, and this was the case in the work of Bonner and Cheek, and in the first of the two experiments just described. For acidities, like 6 *M* HCl, where the equilibrium amount of $SbCl_6^-$ is small, and the rate of formation of $SbCl_6^-$ slow, the rate of exchange is often determined by the rate of formation of $SbCl_6^-$, and hence such experiments do not give information about the exchange process itself.

To learn about the exchange process itself requires the experiment to be performed under non-equilibrium conditions, such as the second of the two experiments described above. It is true that there is a difficulty in that one must take into account the changing amount of $SbCl_6^-$; this difficulty will be considered when necessary.

Experimental

Reagents.—The radioactive tracer was the 60 day Sb^{124}, obtained from Carbide and Carbon Chemicals Co., Oak Ridge National Laboratory. It was obtained as the processed material, stated to be greater than 95% pure from a radiochemical point of view. It was further purified by reduction to Sb(III), extraction with isopropyl ether from hydrochloric acid solution to remove extractable impurities, oxidation to Sb(V), extraction of the Sb(V) into isopropyl ether, and back-extraction into water. Other reagents used in the exchange reaction were Baker and Adamson reagent grade $SbCl_3$ and $SbCl_5$, Baker Analyzed reagent hydrochloric acid, and Mallinckrodt analytical reagent LiCl.

Non-equilibrium Exchange Experiments.—A stock solution 0.0916 *M* in Sb(V), and containing the radioactive Sb^{124}, was prepared in concentrated HCl. A stock solution 0.104 *M* in Sb(III) was prepared in concentrated HCl. Two ml. of the Sb(III) stock solution was placed in a 10-ml. volumetric flask, and slightly less than six ml. of a hydrochloric acid solution added. The concentration of hydrochloric acid was such as to give approximately the final desired acidity. These solutions were thermostated at 25°. At what was considered zero time for the reaction 2 ml. of the Sb(V) stock solution was added, followed by hydrochloric acid until the volume was 10 ml. For expt. 4 the Sb(III) stock solution was 0.104 *M* in Sb(III), but it was in 2.4 *M* hydrochloric acid.

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[1] Presented in part at the Kansas City meeting of the American Chemical Society, March, 1954.

[2] N. A. Bonner, THIS JOURNAL, **71**, 3909 (1949).

[3] C. H. Cheek, Ph.D. thesis, Washington University, St. Louis, January, 1953.

[4] H. M. Neumann, THIS JOURNAL, **76**, 2611 (1954).

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