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The toluene-aluminum chloride-hydrogen chloride complex

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THE TOLUENE-ALUMINUM CHLORIDE-HYDROGEN CHLORIDE COMPLEX

by

William Spencer Cassedy UC 1966

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

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This Thesis

Submitted by

William S. Cassidy

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

William B. Martin, Jr

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Historical Background

Introduction

In Friedel-Crafts reactions aluminum chloride is a heterogeneous catalyst.Some Friedel-Crafts catalysts employ hydrogen chloride with the aluminum chloride. Mr. Poccia,whose work under the National Science Foundation Research Associate Fellowship at Union College in the summer of 1965 dealt mainly with the study of such Friedel-Crafts catalysts, found that xylene, toluene and even benzene formed a dark, homogeneous, moderately dense liquid when dry hydrogen chloride was bubbled into a heterogeneous mixture of the arene and aluminum chloride. It was the aim of this project to:

1- Develope analytical techniques to determine the relative amounts of the aluminum chloride, hydrogen chloride, and toluene in the dark liquid catalyst.

2- Determine the change in the relative amounts of aluminum chloride, hydrogen chloride, and toluene with time as the addition of hydrogen chloride was discontinued and the reaction mixture was left standing, protected from moisture by a drying tube.

Literature Research

Research on the Complex

Olah (1) discusses briefly some of the characteristics of these arene-aluminum chloride-hydrogen chloride complexes. He cites work in which a mixture of aluminum chloride, toluene, and dry hydrogen chloride will yield a homogeneous red oil which forms several ternary complexes of toluene, aluminum chloride, and hydrogen chloride in the respective ratios 2:1:6 , 2:1:4 , 1:1:2 , and 1:1:3 . Mr. Olah points out that a change in the pressure of the dry hydrogen chloride gas affects the formula of the ternary complex produced. The reaction

$$Al_2Cl_6 + HCl + C_6H_5CH_3 \longrightarrow Al_2Cl_7^- + C_6H_5CH_3H^+$$

takes place at low hydrogen chloride pressures, followed at higher hydrogen chloride pressures by the equilibrium

$$Al_2Cl_7^- + HCl + ArH \longrightarrow 2AlCl_4^- + ArH^+$$

Research on the Quantitative Analysis of Aluminum Ion

A titration with a water solution of the disodium salt of ethylenediaminetetraacetic acid (EDTA) was used to determine the aluminum ion concentration in the water extract of the ternary complex. Welcher (2) gave the appropriate procedure for such a titration, an accurate analysis which could be performed in the presence of hydrogen ions and chloride ions.

Research on the Quantitative Analysis of Chloride Ion

Since titrations are generally less time consuming than gravimetric analyses, an EDTA titration of chloride ion was tried using the procedure described by Welcher (3). Unfortunately, this analysis failed because it was difficult to determine a stable end point due, presumably, to the instability of either (or both) the indicator or the tetracyanonickelate ion. Other simpler chloride titrations, such as Mohr's method, could not be used because of the interference of the aluminum ions with the indicators,* and so a gravimetric analysis was used. This simple analysis, which consisted of the precipitating, washing, drying, and weighing of the chloride as silver chloride, was carried out without literature research.

Research on the Quantitative Analysis of Toluene

A quantitative ultraviolet spectrophotometric analysis of the toluene was performed on a Perkin Elmer Model 262 Ultraviolet-Visable Spectrophotometer. The extinction coefficient and wavelength of maximum absorption for toluene was found in Orchin, Milton, and Friedel (4).

* Private communication from Dr. E. K. Bacon, Union College.

Experimental Procedure

Preparation of the Catalyst

The catalyst was prepared by bubbling dry hydrogen chloride gas through a mixture of about 50 grams of aluminum chloride and 200 milliliters of toluene until all of the aluminum chloride was dissolved, leaving the dark brown catalyst layer on the bottom and a toluene layer above. Ten 3 milliliter aliquots of the catalyst layer were drawn off as quickly as possible and placed separately into 10 glass stopper bottles, each of which contained 50.00 milliliters of water. These samples were then shaken immediately to avoid the loss of HCl gas and were numbered from one to ten.

About two months later the catalyst layer was once again prepared in the same way as before; at intervals of 30 seconds, 2 minutes, 5 minutes, 60 minutes, 2 hours, 24 hours, and 48 hours after the bubbling of dry hydrogen chloride had been discontinued, 3 milliliter aliquots of the catalyst layer were drawn off, placed in 50 milliliters of water and shaken. These 7 samples were numbered from 11 to 17 respectively and analyzed for relative amounts of aluminum ion, chloride ion, and toluene.

EDTA Titration of Aluminum Ion (2)

A hematoxylin solution was prepared by dissolving 0.5 grams of hematoxylin in 20 milliliters of 0.05 N HCl, neutralizing to a color change with sodium hydroxide, and diluting to 100 milliliters with ethyl alcohol. 10 milliliters of a 0.0500 M solution of the disodium salt of EDTA was added to each of 17 erlenmeyer flasks along with 0.5 milliliters of the indicator solution of the hematoxylin, 2 milliliters of 2 M acetic acid, and 10 milliliters of 40 % ammonium acetate solution and heated to boiling. Each of these 17 solutions was then titrated with portions of the water layers of samples 1 through 17 with the temperature maintained at about 80± 5°C by partial immersion of the erlenmeyer flask in a beaker of hot water which was heated by a flame. The data were recorded, and the number of moles of aluminum ion in each solution was then calculated.

Gravimetric Analysis of Chloride Ion

Since samples 1 through 3 were used for the unsuccessfull EDTA titration of the chloride ion, only samples 4 through 17 were used for the gravimetric analysis. Thus, to each of the 10 milliliter aliquots of samples 4 through 17 was added 25 milliliters of a .1 N solution of $AgNO_3$. Each precipitate was then filtered by suction into a previously weighed gooch crucible with only filter paper as the filtering surface, washed with approximately ten 10 milliliter portions of distilled water, dried overnight in an oven estimated to be at a temperature of 110 to 115° C, cooled, and weighed. The number of moles of chloride ion in samples 4 through 17 was then calculated.

Ultraviolet Spectrophometric Analysis ofToluene

Toluene in each of samples 4 through 6 and 11 through 17 was extracted with several 20 milliliter portions of Eastman Kodak yellow label practical cyclohexane, and each was diluted to 100.00 milliliters. Each of these solutions was then diluted 10 fold from 5.00 milliliters to 50.00 milliliters with fresh cyclohexane. Portions of these 10 samples were then placed in the 1.00 centimeter quartz cell of the Perkin Elmer 202 Ultraviolet Spectrophotometer and the absorbance of each of these portions was measured against the pure solvent. The number of moles of toluene in samples 4 through 6 and 11 through 17 was then calculated from the data obtained.

Experimental Results

EDTA Titration of Aluminum Ion

Table 1

Sample #	Ml .0500 M EDTA	Ml Aqueous Solution Containing Al^{+++}	Moles Al^{+++} in Catalyst
3	10.00	4.20	.00595
4	10.00	4.49	.00556
5	10.00	4.29	.00583
6	10.00	4.65	.00538
7	10.00	4.32	.00578
8	10.00	4.11	.00608
9	10.00	4.40	.00568
10	10.00	4.23	.00590
11	10.00	4.34	.00576
12	10.00	4.00	.00625
13	10.00	4.50	.00555
14	10.00	4.32	.00578
15	10.00	4.30	.00581
16	10.00	4.07	.00614
17	10.00	4.22	.00592

From the reference (5) it is apparent that 1 mole of EDTA complexes 1 mole of Al^{+++}. 10 milliliters of .05 M EDTA is .5 millimoles of EDTA or .0005 moles, and thus Al^{+++} in the given volume of titrant will represent .0005 moles of Al^{+++}, or again .5 millimoles of Al^{+++}. Thus in sample 3, for example, .0005 moles of Al^{+++} were found in 4.20 milliliters. In 50 milliliters there would be (50.00) (.0005) / 4.20 moles of Al^{+++} in the sample, representing, presumably, all of the Al^{+++} in the 3 milliliters of original catalyst.

Gravimetric Analysis of Chloride Ion

Table 2

#	Wt of Crucible	Wt of Crucible Plus Contents	Wt of AgCl	Moles Cl^- in 10 Ml Aliquot	Moles Cl^- in 50 Ml
4	19.8239	20.4009	.5770	.00404	.0202
5	19.8234	20.4242	.6008	.00420	.0210
6	18.9723	19.5255	.5532	.00387	.0194
7	19.9825	20.5749	.5924	.00414	.0207
8	19.2742	19.9404	.6662	.00466	.0233
10	19.2744	19.9178	.6434	.00449	.0225
11	19.2742	19.9244	.6502	.00455	.0228
12	19.8234	20.4235	.6001	.00420	.0210
13	18.9720	19.5954	.6234	.00436	.0218
14	19.9825	20.4132	.4307	.00301	.0151
15	19.9721	20.4442	.4721	.00330	.0165
16	19.8237	20.3249	.5012	.00350	.0175
17	19.8241	20.2771	.4530	.00317	.0159

"Wt" in table 2 stands for the weight in grams.

Table 3

#	Moles Al^{+++}	Moles Cl^- in AlCl	Total Moles Cl^-	Moles HCl
4	.00556	.0167	.0202	.0035
5	.00583	.0175	.0210	.0035
6	.00538	.0161	.0194	.0033
7	.00578	.0173	.0207	.0034
8	.00608	.0182	.0233	.0051
10	.00590	.0177	.0225	.0048
11	.00576	.0173	.0228	.0055
12	.00625	.0188	.0210	.0022

Table 3 (cont.)

#	Moles Al^{+++}	Moles Cl^- in AlCl	Total Moles Cl^-	Moles HCl
13	.00555	.0167	.0218	.0051
14	.00578	.0173	.0151	(-.0022)
15	.00581	.0174	.0165	(-.0009)
16	.00614	.0184	.0175	(-.0009)
17	.00592	.0178	.0159	(-.0019)

All quantities in table 3 are expressed in moles per 3 milliliters of the catalyst.

Ultraviolet Spectrophometric Analysis of Toluene

Table 4

#	Absorbance	Moles of Toluene
4	.763	.00271
5	.800	.00284
6	.729	.00259
11	.820	.00291
12	.750	.00266
13	.770	.00273
14	.900	.00319
15	.877	.00311
16	.704	.00250
17	.810	.00287

The following equation shows how the number of moles of toluene in the 3 milliliter aliquot of the catalyst was determined:

$$C = A / be$$

c = moles of toluene in 3 milliliters of the catalyst

A = absorbance of an aliquot of the solution (measured)

b = path length = 1.00 centimeters (fixed)

e = absorbtivity = 282 (fixed, from literature (4))

Both e and A were measured at a wavelength of 2625 A^o, the wavelength of maximum absorbance of toluene.

Conclusion

Discussion of Results

The average mole ratio for toluene, aluminum chloride, and hydrogen chloride was calculated as .00271 : .00578 : .0039 or 1 : 2.2 : 1.4 , respectively. These average ratios were based on samples 4, 5, and 6 for toluene, 4 through 10 for aluminum chloride, and 4 through 8 and 10 for hydrogen chloride. No elimination of data was attempted. The following results were obtained for samples 11 through 17 :

Table 5

#	Time	Mole Ratio of $C_6H_5CH_3$ - $AlCl_3$ - HCl
11	30 sec	.00291 : .00576 : .0055 = 1 : 2.0 : 1.4
12	2 min	.00266 : .00625 : .0022 = 1 : 2.4 : 0.8
13	5 min	.00273 : .00555 : .0051 = 1 : 2.0 : 1.9
14	60 min	.00319 : .00578 :-.0022 = 1 : 1,8 : ?
15	2 hrs	.00311 : .00581 :-.0009 = 1 : 1.9 : ?
16	24 hrs	.00250 : .00614 :-.0009 = 1 : 2.4 : ?
17	48 hrs	.00287 : .00592 :-.0019 = 1 : 2.0 : ?

From the experimental data obtained, it appears that the mole ratio of toluene, aluminum chloride, and hydrogen chloride in the ternary complex is approximately 4 : 9 : 6 , which doesn't agree with any of Olah's ratios (1) ; according to his ratios, the ratio of hydrogen chloride to aluminum chloride should have been much greater. Thus, according to Olah, the amount of aluminum chloride calculated in this research was too large and (or) the amount of hydrogen chloride calculated in this research was too small ; this conclusion is further strengthened by the fact that no moles of hydrogen chloride were left (by calculating the data) for samples 14 through 17, indicating that the amount of aluminum chloride calculated was too large or that hydrogen chloride had volatilized and some moisture may have decomposed the aluminum chloride, with the subsequent loss of more hydrogen chloride.

From the results of the analyses of samples 11 through 17 it seems quite possible that, in relation to time upon standing, this complex is fairly stable in regard to the relative amounts of aluminum chloride and toluene but seems to be unstable in regard to the relative amount of hydrogen chloride, which appears to decrease with time. According to the experimental results, this complex seemed to be stable for at least five minutes (and probably longer) after the hydrogen chloride bubbling had been discontinued. It is suspected that such behavior is due to the fact that the hydrogen chloride gas still remains with the solution for a while "preserving", in a sense, the stability of the complex. No conclusions as to the structure of this complex can be ascertained from the experimental data; in fact, it is difficult to make even a good guess at its structure. The poor reproducibility of measurements from the hydrogen chloride analysis indicates that either better techniques or a new method of analysis must be performed.

Error Analysis

The moles of toluene, aluminum chloride, and hydrogen chloride in 3 milliliters of the catalyst were found to have a maximum deviation from the average that indicated a 5% error in the toluene analysis, a 6% error in the aluminum chloride analysis, and a 30% error in the hydrogen chloride analysis. The following sources of error in the experimentation were noted:

(1) The usual sources of error in gravimetric, volumetric, and spectrophometric analyses.

(2) The loss of toluene through evaporating on standing in a stoppered hydrolysis bottle. (This could be high)

(3) The presence of unanalyzed toluene in the 2 ten milliliter aqueous aliquots taken from each sample.

(4) Failure to redry and reweigh the chloride samples an appropriate number of times.

(5) Assumption that the hydrochloric acid in the hematoxylin solution was neutralized correctly by sodium hydroxide through a color change.

(6) Loss of hydrogen chloride through volatilization. (major source)

(7) Possible contamination of the catalyst layer with toluene from the toluene layer.

(8) Decomposition of the catalyst layer from the presence of water vapor.

(9) Variation in pressure of the hydrogen chloride gas.

(10) Variation in the temperature of the catalyst as it was being generated.

(11) Possible distortion of the toluene spectrum due to small amounts of protonated toluene.

(12) Failure to obtain a reference spectrum of the pure solvent for the calculation of the absorbance of the toluene solution. This could be large (perhaps 5%)

(13) Possible inferior quality of the hematoxylin, the grade and purity of which was unknown.

(14) Possible inferior quality of the toluene, the grade and purity of which was unknown.

(15) Possible variation in the temperature of the drying oven.

(1) Olah, George Andrew, Friedel Crafts and Related Reactions, pp. 735-6, John Wiley & Sons, London, 1963.

(2) Welcher, Frank J. , The Analytical Uses of Ethylenediaminetetraacetic Acid, p. 165, D. Van Nostrand, London, 1957.

(3) Welcher, Frank J. , ibid. p. 255.

(4) Friedel, Robert A. , Orchin, Milton, Ultraviolet Spectra of Aromatic Compounds, COMPOUND # 8, John Wiley & Sons, London, 1951.

(5) Welcher, Frank J. , ibid. , p. 12