[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY AND THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Catalytic Halides. I. A Study of the Catalyst Couple, Aluminum Chloride–Hydrogen Chloride, and the Question of the Existence of $HAlCl_4$[1]

BY HERBERT C. BROWN[2] AND HOWARD PEARSALL[3]

In spite of considerable evidence to the contrary many authors have recently assumed that the catalytic activity of aluminum chloride plus hydrogen chloride is due to the formation of a stable substance, hydrogen tetrachloroaluminate, $HAlCl_4$, which presumably functions as an exceedingly strong acid. A careful examination of the hydrogen chloride–aluminum chloride system under a variety of conditions, including temperatures as low as −120°, yielded no evidence indicating any combination of the two acids. It is concluded that $HAlCl_4$ must be considered as a hypothetical acid whose salts are stable but which does not itself exist in detectable concentrations.

Introduction

Reactions brought about by metal halide catalysts are exceedingly important in chemistry. An enormous amount of time and effort has been devoted to the study of such reactions. Yet at present the precise manner in which these metal halides perform their catalytic function is still little understood. Several years ago a systematic investigation of the chemistry of the catalytic halides was undertaken in the hope that the information thus gained would contribute to a better understanding of their catalytic activity. The present paper reports the results of an early investigation in this program—an examination of the aluminum chloride–hydrogen chloride system.

The literature contains numerous references to observations that hydrogen chloride and aluminum chloride do not combine to form stable acids such as $HAlCl_4$.[4,5] In spite of this evidence the recent literature contains numerous references to the substance $HAlCl_4$ as the active catalytic species in mixtures of aluminum chloride and hydrogen chloride.[6] In some instances it has been postulated that the product, $HAlCl_4$, is so stable that elevated temperatures (~120°) are required to bring about appreciable dissociation into its components.[6c]

A careful examination of the system therefore appeared desirable in order to obtain a definitive answer to the question of the possible existence of a stable product, $HAlCl_4$, as the active catalyst in reactions brought about by the catalyst couple, aluminum chloride–hydrogen chloride.

Results and Discussion

All experiments were carried out in an all-glass high vacuum apparatus[7] in which the materials came in contact only with glass and mercury. All materials were rigorously purified.

Early experiments carried out at room temperature and at elevated temperatures soon demonstrated the lack of detectable combination of the two components. It was therefore decided to emphasize study of the system at low temperatures (−80 to −120°) where conditions should be particularly favorable for the formation of the product. However, even under these conditions the results fully confirm the conclusion reached by earlier workers[4] that hydrogen chloride and aluminum chloride do not combine in detectable amounts. A few typical experiments will be briefly outlined to indicate the basis for this conclusion.

(1) A sample of pure hydrogen chloride (5.80 mmoles; v.p. 124 mm. at −112.1°) was placed in a tube connected to a manometer. The pressure exerted by the gas was 664 ± 0.5 mm. at 21°. The hydrogen chloride was temporarily stored in another part of the vacuum apparatus and 0.79 g. (5.98 mmoles) of pure white aluminum chloride was sublimed into the tube and deposited in the form of a thin powdery coating on the glass surface. The hydrogen chloride was returned to the tube. The pressure now read 665 ± 0.5 mm. at 21°. Moreover, the pressure did not change over a period of 38 hours. Evidently under these conditions aluminum chloride does not combine with appreciable amounts of hydrogen chloride.

(2) The experiment was repeated at −80°. The pressure of hydrogen chloride in the tube was 586 ± 0.5 mm. before addition of aluminum chloride. After introduction of the aluminum chloride sample, the pressure observed was 586 ± 1.5 mm. over a period of 40 hours. (The larger experimental error in the latter reading is attributed to minor temperature variations over the long period of observation.) It is again evident that even at this low temperature no significant amount of hydrogen chloride combines with aluminum chloride.

(3) At −97° (a slush of liquid–solid methanol was used to maintain the temperature constant) over a period of 11 hours the sample showed vapor pressures of hydrogen chloride of 345–353 mm. A vapor tension thermometer (filled with hydrogen chloride) in the same bath showed pressures which varied between 346–350 mm. The average difference in the readings of the sample and the thermo-

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[4] R. Schwartz and G. Meyer, *Z. anorg. Chem.*, **166**, 190 (1927); G. Malquori, *Atti accad. Lincei*, [6] **7**, 740 (1928); M. C. Boswell and R. R. McLaughlin, *Canadian J. Research*, **1**, 400 (1929); V. Ipatieff, "Catalytic Reactions at High Pressures and High Temperatures," The Macmillan Company, New York, N. Y., 1936, p. 564.

[5] C. M. Fontana and R. J. Herold, THIS JOURNAL, **70**, 2881 (1948), have recently reported observations which point to the non-existence of the corresponding bromo compound, $HAlBr_4$, at room temperature.

[6] (a) C. A. Thomas, "Aluminum Chloride in Organic Chemistry," A. C. S. Monograph No. 87, Reinhold Publishing Corp., New York, N. Y., 1941, p. 74; (b) P. A. Leighton and J. D. Heldman, THIS JOURNAL, **65**, 2276 (1943); (c) T. M. Powell and E. Reid, *ibid.*, **67**, 1020 (1945); (d) H. Pines and R. C. Wackher, *ibid.*, **68**, 595, 599 (1946).

[7] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

meter was 1.2 mm., entirely random with respect to sign. Thus even liquid hydrogen chloride in contact with excess solid aluminum chloride over an extended period of time exhibits no evidence of combination.

(4) At −112.1° (liquid–solid slush of carbon disulfide) the pressure observed over a period of several hours was 124 mm. This agrees with the vapor pressure of pure hydrogen chloride at this temperature. Finally at −117° (liquid–solid slush of diethyl ether) the pressure of hydrogen chloride in the tube agreed with the pressure of the hydrogen chloride vapor tension thermometer over a nine-hour period. At these temperatures the hydrogen chloride could be quantitatively recovered by distillation within a matter of seconds. There was no evidence of absorption or retention of the gas by the solid aluminum chloride.

These representative experiments definitely establish that no appreciable combination of hydrogen chloride and aluminum chloride occurs under these conditions. However, it might be argued that these experiments do not eliminate the possibility that a stable substance $HAlCl_4$ exists but requires relatively vigorous conditions or a catalyst to bring about combination of the two components.

This possibility would be contrary to all of our experience with the behavior of Lewis acids and is further rendered improbable by the observation that at −80° aluminum chloride readily combines with ammonia, trimethylphosphine and similar bases. However, a number of experiments were carried out to examine this possibility. Three representative experiments with this objective are outlined.

(5) The sample of aluminum chloride was repeatedly vaporized, by heating, in the presence of the atmosphere of hydrogen chloride. Experiments 1–4 were repeated without change in the experimental results. At 150° the observed pressure, 45.0 mm., was equal to the sum of the partial pressures of the two components, aluminum chloride, 11.5 mm., and hydrogen chloride, 33.5 mm. Therefore, elevated temperatures do not bring about combination.

(6) It was considered that traces of water might be required to catalyze the combination. Small quantities of water were absorbed as vapor on the aluminum chloride maintained at −80°. The hydrogen chloride was then introduced and experiments 2–4 repeated. No absorption of hydrogen chloride was observed. Other experiments were carried out in which the partially hydrated aluminum chloride was heated at 100° until hydrogen chloride was no longer evolved and then tested with a measured quantity of gaseous hydrogen chloride under the conditions of experiments 1–4. Again no combination occurred.

(7) Since hydrogen chloride–aluminum chloride catalysts are usually used in the presence of hydrocarbons, a final attempt was made to induce combination in the presence of a suitable hydrocarbon. Neohexane was selected. It is readily available in pure form, remains liquid at −80° and is stable to the reagents. Three ml. (23.0 mmoles) of neohexane, purified by distillation from aluminum chloride at room temperature, and 1.745 mmoles of hydrogen chloride were placed in the reaction tube and the pressures developed at various temperatures noted, after equilibrium had been reached. The materials were temporarily removed, 0.446 g. of aluminum chloride (3.34 mmoles) introduced, and the experiment repeated. The results are summarized in Table I.

TABLE I

PRESSURES OBSERVED IN PRESENCE AND ABSENCE OF ALUMINUM CHLORIDE

Without $AlCl_3$		With $AlCl_3$	
Temp., °C.	Press., mm.	Temp., °C.	Press., mm.
0	436	0	434
−40	270	−39	268
−72	174	−73	174
−86	111	−87	113

Hydrogen chloride was recovered by distillation at −80°. A total of 1.758 mmoles (100.7%) was recovered, again pointing to no combination of the gas with aluminum chloride.

The experiments furnish convincing evidence that in the absence of any substance which can function as a base, aluminum chloride and hydrogen chloride do not combine to any appreciable extent. The possibility that trace quantities of $HAlCl_4$ may exist in equilibrium with hydrogen chloride and aluminum chloride cannot be excluded. However, the present experiments demonstrate that the extent of combination must be less than 0.2 mole per cent. at temperatures as low as −80°. Any possible concentrations at the usual temperatures at which Friedel–Crafts reactions are ordinarily carried out must therefore be vanishingly low.[8]

It is therefore highly improbable that free $HAlCl_4$ as such plays any significant role in Friedel–Crafts reactions any more than the free unsolvated proton plays any part in acid-catalyzed reactions in aqueous systems. **In the light of present evidence, the substance $HAlCl_4$ must be considered as a hypothetical acid whose salts are known but which does not itself exist.**

The precise manner in which the catalyst couple, hydrogen chloride–aluminum chloride, functions in Friedel–Crafts reactions will be the subject of subsequent papers in this series.

Experimental Details

Materials.—Hydrogen chloride was generated by adding C.P. concentrated hydrochloric acid to sulfuric acid. The gas was introduced into the high vacuum system and fractionated through a −118° U-tube into one cooled at −196°. The hydrogen chloride after a single fractionation was tensiometrically homogeneous—all fractions exhibited a constant vapor pressure of 124 mm.[9] at −112.1° (melting carbon disulfide).

Aluminum chloride (Baker and Adamson reagent-grade) was sublimed by gentle heating into a Pyrex manifold containing several small, fragile ampules, and connected at the far end to a pump. The bulbs were thereby filled with

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[8] The exchange between tagged aluminum chloride and hydrogen chloride

$$AlCl_3^* + HCl \rightleftharpoons AlCl_3 + HCl^*$$

at low temperatures offers a means of estimating the equilibrium concentration of $HAlCl_4$. Such a study was contemplated but it was shelved after we learned from Professor S. Benson of the University of Southern California that he was planning such an investigation.

[9] W. J. Giauque and R. Wiebe. THIS JOURNAL, **50**, 101 (1928).

sublimed aluminum chloride and sealed off *in vacuo*. One of these weighed ampules was placed in a side arm of the reaction tube and broken with a glass-enclosed magnetically operated hammer. The aluminum chloride was sublimed into place, the side arm sealed off and the fragments of the glass ampule collected and weighed. The technique was thoroughly tested both as to the quantitativeness of the transfer and the purity of the aluminum chloride samples.[10]

Action of Water on Aluminum Chloride.—A number of observations were made of the action of water on anhydrous aluminum chloride. Although the objective of the experiments, catalysis of the combination of hydrogen chloride and aluminum chloride, was not attained, the results are of considerable interest in their own right.

To a sample of 0.79 g. of aluminum chloride (5.98 mmoles) in the reaction tube, cooled to −80°, 0.132 mmole of gas-free water was added as vapor. The temperature was raised to 24°; the pressure in the tube rose to 9 mm. In the course of 70 min. the pressure rose slowly to 12 mm. The tube was heated at 100° for 5 hours. The final pressure observed was 25 mm. at 24°. The gas was pure hydrogen chloride, 1.40 moles per mole of water added. As mentioned previously the product did not absorb hydrogen chloride at low temperatures.

Additional water, 0.76 mmole, was added to the product of the previous experiment and the treatment repeated. An additional quantity of hydrogen chloride, 0.94 mmole, was recovered. This represents 1.23 moles per mole of water added.

Pines and Wackher[6d] had previously noted similar phenomena in the action of water on aluminum bromide: treatment with an equimolar quantity of water yielded 1.25 moles of hydrogen bromide per mole of water. Treatment with 2 moles and 3 moles of water, respectively, yielded only 1.06 and 0.85 moles of hydrogen bromide per mole of water. A satisfactory explanation of these observations would be desirable.

Aluminum Chloride, Hydrogen Chloride and Neohexane.—The neohexane (Phillips Petroleum Company, Research Grade) was introduced into the vacuum apparatus and placed over sublimed aluminum chloride for 15 minutes at 25°. The neohexane was distilled over sublimed aluminum chloride for 15 minutes at 25°. The neohexane was distilled away and placed on fresh aluminum chloride. After 15 minutes at room temperature there was observed only a very faint color formation.

Neohexane was measured as a liquid in a calibrated vessel of the high vacuum apparatus. A magnetically operated agitator was introduced to facilitate attainment of equilibrium with the hydrogen chloride. In spite of extended contact with aluminum chloride and hydrogen chloride at temperatures between 22 and −87°, no chemical interaction was noted. The individual components were quantitatively recovered in pure state; no color formation was observed.

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(10) Both aluminum and chlorine were determined by the method of Snyder, *Anal. Chem.*, **17**, 37 (1945).

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Studies of Metallated Dye Complexes. I. Copper(II) Complex with *o,o'*-Dihydroxyazobenzene[1]

BY HANS B. JONASSEN, MAE M. COOK AND JOHN S. WILSON

The complex compound formed between the dye *o,o'*-dihydroxyazobenzene and copper(II) ion has been investigated by spectrophotometric and conductometric methods. A previously postulated one to one copper(II) dye complex was verified. Experimental evidence is presented for the formation of a copper(II) dye–monohydroxy complex in the presence of potassium hydroxide. Further addition of the base seems to break up the complex forming the potassium salt of the dye and the copper hydroxy complex $Cu(OH)_5^{-3}$. The coördinatively unsaturated copper(II) dye complex seems to make possible the formation of a copper hydroxy complex anion without the precipitation of copper hydroxide.

Ortho-substituted azo dyes form stable lakes with most of the transition metals. Melting points indicated that in the lakes of ortho-hydroxy azo compounds, the metal ion displaced a hydrogen of the hydroxyl groups and that it coördinated to one of the nitrogen atoms of the azo group.[2]

Drew and Landquist[3] reported a one to one coördinatively unsaturated complex between *o,o'*-dihydroxyazobenzene and copper(II) ion based on analytical methods verified by the formation of monopyridine and monoquinoline compounds with the Cu(II)–dye complex.

An investigation was undertaken to verify the structure of the Cu(II)–dye complex and to study the behavior of this complex in the presence of excess potassium hydroxide.

A. Absorption Studies

Experimental.—Absorptions were determined between the wave lengths of 360 and 800 mμ with a Beckman spectrophotometer, model DU, using 1-cm. matched corex cells and standard solutions of 0.0002 *M* in 95% alcohol. *o,o'*-Dihydroxyazobenzene, prepared according to the literature, was recrystallized from methanol, m.p. 172–173°. C.P. Baker Analyzed $CuCl_2 \cdot 2H_2O$ was dried for 24 hours over partially dehydrated $CuSO_4 \cdot 5H_2O$.

Figure 1 shows the absorptions of the solutions of the dye and of the mixture of dye and copper salt. The absorption of the latter (0.0002 *M*), alone, was below 0.02 at all wave lengths measured.

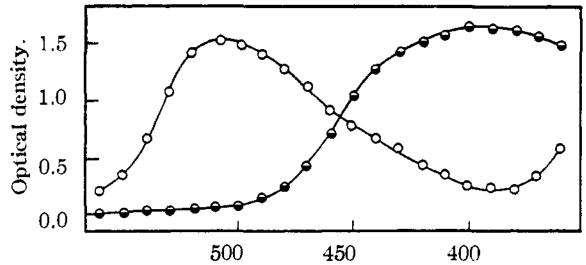

Fig. 1.—Absorption spectra of 0.0002 *M* *o,o'*-dihydroxyazobenzene, ◒; and 0.0001 *M* Cu(II)-*o,o'*-dihydroxyazobenzene, ○.

Using the continuous variation method as modified by Vosburgh and Cooper[4] the Cu(II)–dye complex solutions of 0.0002 *M* $CuCl_2 \cdot 2H_2O$ and 0.0002 *M* dye in 95% alcohol were mixed in varying proportions such that the total solute

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[1] Presented in part before the Physical and Inorganic Section of Southwide Chemical Conference, Atlanta, Georgia, October 16–18, 1950.

[2] M. Elkins and L. Hunter, *J. Chem. Soc.*, 1598 (1935).

[3] H. D. K. Drew and J. K. Landquist, *ibid.*, 292 (1938).

[4] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).