tetrachloride in water were calculated from the data of Clifford,[2] Rosenbaum and Walton[3] and Gross and Saylor.[4]

Figure 1 shows the solubility curves of the systems carbon tetrachloride–acid–water at 25° for butyric and isobutyric acids. The curve for *n*-butyric acid was taken from the data of Smith and Berman.[1] Figure 2 shows the diagrams for similar systems using *n*-valeric acid, isovaleric acid, methylethylacetic acid, and trimethylacetic acid. Again the curve for *n*-valeric acid was taken from the data of Smith and Berman.[1]

An examination of these curves shows that in all cases the mutual solubility area is decreased by substitution of a branched chain acid for a normal acid. The curves for isovaleric acid and methylethylacetic acid indicate that a methyl group substituted in the alpha position is more effective in decreasing the mutual solubility area than a methyl group substituted in the beta position.

Summary

The solubility curves at 25° of the systems CCl_4–RCOOH–H_2O have been studied for the following acids: isobutyric, isovaleric, methylethylacetic, and trimethylacetic. The curves show that the mutual solubility area decreases with increased chain branching.

BETHLEHEM, PENNA. RECEIVED MAY 13, 1938

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(2) Clifford, *Ind. Eng. Chem.*, **13**, 631 (1921).

(3) Rosenbaum and Walton, THIS JOURNAL, **52**, 3568 (1930).

(4) Gross and Saylor, *ibid.*, **53**, 1744 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Action of Aluminum Chloride on Fluorinated Compounds

BY ALBERT L. HENNE AND MELVIN S. NEWMAN

In an effort to establish the orientation effect of a CF_3 group by the synthesis of $CF_3C_6H_4$-$COCH_3$, benzotrifluoride was allowed to react with acetyl chloride and aluminum chloride. Instead of the expected products, the reaction gave benzotrichloride and aluminum fluoride in excellent yield and purity. In the absence of acetyl chloride, the reaction was not clean-cut and produced a large amount of tar; only a small quantity of benzotrichloride was isolated. In neither reaction was there a copious evolution of hydrogen halide; in the first case only hydrogen chloride came off, while in the second case a small amount of hydrogen fluoride was present in the hydrogen chloride.

From these results, it is concluded that the principal reaction is an exchange of halogen atoms between the organic fluoride and the inorganic chloride. In the presence of acetyl chloride, a complex presumably is formed between this compound and the aluminum chloride, and the exchange of halogen atoms is smooth because it occurs between the complex and the organic fluoride. In the absence of acetyl chloride, the exchange occurs directly and the benzotrichloride produced is subjected to the action of free aluminum chloride. This is known to cause tar formation.[1] The fact that some hydrogen fluoride comes off indicates that either benzotrifluoride or the intermediate benzofluorochloride is also involved in the condensation.

The replacement of organically bound fluorine by chlorine in the presence of aluminum chloride suggests a reason for the repeated failures[2] to effect Friedel–Crafts condensations between organic fluorides and chlorinated ethylenes or benzene.[3] The reactions involving only aliphatic compounds always gave tarry materials, which were abandoned. The reactions involving benzene were tried with the following fluorides: CCl_2FCCl_2F, CCl_2FCClF_2, $CClF_2CClF_2$, $CHClF_2$ and CCl_2F_2. In the last two cases, the fluorinated compound was passed as a gas through benzene containing aluminum chloride. In the other cases, aluminum chloride was dropped in small portions into a cooled solution of the fluoride in an excess of benzene. In general, a vigorous but controllable reaction started at once but soon stopped; it was started again every time a portion of aluminum chloride was added. The gas evolved was mostly hydrogen chloride which contained only a very small amount of hydrogen fluoride. After completion of the reaction, and decomposition with water in the usual way, the

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(1) Wohl and Wertyporoch, *Ann.*, **481**, 30 (1930).

(2) Henne and Leicester, THIS JOURNAL, **60**, 864 (1938).

(3) The use of metalloid fluorides instead of aluminum chloride is now under investigation.

products were tarry, somewhat elastic masses which were either fluorine-free, or almost so. From these masses, only fluorine-free substances were isolated by extraction with benzene, chloroform or dioxane, followed by precipitation with alcohol, ether or acetic acid. These substances had molecular magnitudes of about one thousand. The aluminum salt separated from the aqueous portion invariably tested very strongly for fluorine.

Even in the absence of benzene, the effect of aluminum chloride on stable aliphatic fluorides is apparent after a relatively short period of heating. After forty-eight hours of refluxing over aluminum chloride, CCl_2FCClF_2 generated a small quantity of CCl_3CClF_2, which was isolated, and some higher boiling material which no longer contained any fluorine. In a similar experiment with $CHCl_2$-$CClF_2$ the fluorine was more easily removed, hydrogen fluoride was evolved slowly and steadily and tar formation was more pronounced. In both cases, the aluminum salt tested positively for fluorine.

It is fitting to recall an old experiment[4] which was performed in order to establish the structure of $CHCl_2CHF_2$. This derivative was exposed to the action of chlorine in sunlight, in the presence of aluminum chloride, and from 60 g. of product only 4 g. of impure CCl_3CClF_2 was isolated, while the remainder was predominantly hexachloroethane. More recent work[5] has established that chlorination in sunlight follows a perfectly normal course if the aluminum salt is omitted, and pure CCl_3CClF_2 is obtained quantitatively from $CHCl_2CHF_2$. In the older experiment, the mechanism of the reaction was not well understood. It is probable that an exchange of halogens between the organic fluoride and the aluminum salt took place first, and that the small amount of CCl_3-CF_2Cl obtained owed its formation to the fortuitous fact that an insufficient quantity of aluminum chloride was present to take care of all the organic fluorine.

From this series of experiments it is concluded that it would be futile to use aluminum chloride to effect condensations between a fluorinated derivative and either an aliphatic or an aromatic compound.

Experimental

Benzotrichloride from Benzotrifluoride.—To a solution of 78 g. (1 mole) of acetyl chloride in 540 g. (450 cc.) of benzotrifluoride was added 140 g. (1.05 mole) of powdered anhydrous aluminum chloride over a period of one-half hour, the reaction flask being cooled to prevent the temperature from rising above 40°. A greenish solid seemed to form on the surface of the aluminum chloride at first. After the mixture had been stirred at 30–40° for one hour and then slowly heated to 70° during another hour, the solid gradually dissolved to give a deep red solution. During this latter period a slow steady stream of hydrogen chloride was evolved. A test for hydrogen fluoride was negative and the glass apparatus was not etched during the reaction. After stirring for two hours more at 65–70° the mixture was cooled, poured on ice (very little heat evolved) and steam distilled. By observing the distillate a crude separation of benzotrifluoride and benzotrichloride was effected. Upon fractional distillation there was obtained 135 g. (0.69 mole) of pure benzotrichloride, f. p. −4.4°, b. p. (10 mm.) 89.0–89.5°, $d^{20}{}_4$ 1.3741, $n^{20}{}_D$ 1.55789, *MR* calcd. 45.54, found 45.67. *Anal.* Calcd. for $C_7H_5Cl_3$: C, 43.01; H, 2.58; Cl, 54.41. Found: C, 43.02; H, 2.62; Cl, 53.02, 53.07. In addition, about 20 g. (0.165 mole) of benzoic acid was isolated, which resulted from hydrolysis of the benzotrichloride during steam distillation (benzotrifluoride is not hydrolyzed[2] under similar conditions). Thus the total yield based on the aluminum chloride amounted to 86%. The analysis of the aluminum salt proved it to be aluminum fluoride slightly contaminated by chloride.

Summary

The condensation of fluorinated substances with aliphatic or aromatic compounds cannot be obtained with aluminum chloride, because an exchange of halogen atoms takes place between the organic fluoride and the aluminum salt. A particularly clean-cut exchange was observed when benzotrifluoride reacted with a mixture of aluminum chloride and acetyl chloride. Benzotrichloride of unusual purity was thus obtained in good yield.

COLUMBUS, OHIO RECEIVED MAY 7, 1938

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[4] Swarts, Mémoire couronne, *Acad. roy. soc. Belg.*, **61**, 68-70 (1901).

[5] Henne and others THIS JOURNAL, **58**, 402, 404, 888 (1936); **59**, 1201, 2434 (1937)