Solutions of Aluminum Chloride as Vigorous Catalysts

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The most refractory Friedel-Crafts type reactions—namely, the alkylation of isoparaffins with ethylene and the isomerization of normal paraffins including butane—can be catalyzed with solutions of aluminum chloride in organic solvents containing a molar excess of the solute. These catalysts seem even more vigorous than solid aluminum chloride because the induction period is avoided.

ALUMINUM chloride has been used as a catalyst under many different conditions to accomplish a wide variety of reactions. When used as a solid for refractory reactions with hydrocarbon or chlorohydrocarbon reagents alone, there is often an "incubation period" or induction period of 20 minutes to several hours (*2*, page 28; *14*; *18*, page 461; *19*), during which the only reaction is at the surface of the solid. After small amounts of cracked products have formed a liquid complex with the aluminum chloride, the renewable surface thus generated permits a vigorous and sometimes uncontrollable reaction—i.e., one accompanied by undesirable side reactions. In order to diminish side reactions the reagents have been diluted with carbon disulfide or relatively inert hydrocarbons or chlorohydrocarbons (*7*, *18*); or the catalyst has been dissolved in certain solvents such as nitrobenzene (*7*, page 769; *8*; *18*, pages 873–4), sulfur dioxide (*15*), or nitroparaffins (*16*). This procedure is satisfactory for mild catalysis, which is sufficient for alkylation of nonhydrocarbons or aromatic hydrocarbons and for propylation of isoparaffins. But when a vigorous catalyst is required, such as for ethylation of isobutane, or isomerization of normal paraffins, especially butane, it has been considered inadequate (*16*).

The concentrations of aluminum chloride employed previously have been 2 to 13% in sulfur dioxide (*15*), 20 to 25% in nitrobenzene (*8*), and up to 50% in nitroparaffins (*16*). Even members of the last group of solutions have less than 1 mole of aluminum chloride per mole of solvent, and might be considered dilute. It seems probable that the molar ratio is important, and that 1 mole of solvent partially deactivates 1 mole of the catalyst (*12*). This is suggested also by the observation (*7*, page 723) that for Friedel-Crafts reactions of reagents containing oxygen the number of moles of aluminum chloride required exceeds slightly an integer which in many cases is the number of oxygen atoms in the reagent molecule.

The concentration of aluminum chloride in nitrobenzene at room temperature is limited to 30 mole % by the solubility, as shown in Figure 1. These data and those for aluminum chloride with several nitroaromatics are due to Menshutkin (*10*). Each solvent forms an equimolar complex with aluminum chloride, melting above 90° C. With still higher concentrations of aluminum chloride, 60 to 64 mole %, a eutectic is formed which is liquid at 60° C. in the two systems plotted. These two concentrated solutions have been tested in this investigation for catalytic activity and found to be extremely active, even more so than solid aluminum chloride, probably because they are liquid and have rapidly renewable surfaces.

The solvents mentioned have certain disadvantages. Benzophenone is a solid (melting point, 48° C.) and is rather expensive. The nitroaromatics are so activated by the aluminum chloride that they become explosive. One violent explosion on a small scale was observed by the author while using nitrobenzene with excess aluminum chloride at about 90° C.

In a recent article (*16*) Schmerling made the statement, "aluminum chloride is highly soluble in ethers, ketones, and alcohols, but the resulting solutions are catalytically inactive, at least for the alkylation of hydrocarbons." This is true for solutions of moderate concentrations; but in view of the following observations the statement may be misleading with respect to solutions approaching saturation. It has been shown that solutions of aluminum chloride in ethyl and isopropyl ethers, ethyl and isopropyl acetates, acetone, benzophenone, nitrobenzene, and sulfur dioxide are all extremely vigorous catalysts, both for alkylation (*4*), and for isomerization of normal paraffins (*5*), provided aluminum chloride is present in molar excess. Schmerling also observed that equimolar complexes with some of these solvents have a fair catalytic activity (*16*, *17*).

The solutions in the aliphatic solvents are liquid at room temperature. Some approximate solubilities are given in Table I. The diagrams may be similar to Figure 1 but at much lower temperatures, since the complexes do not crystallize much above room temperature. The solutions are nonviscous liquids, very hygroscopic, and react with water with the vigor of chlorosulfonic acid. They are colorless when pure, except those in acetone which are yellow or orange. Acetone forms a crystalline complex, apparently $AlCl_3.2Me_2CO$ (53.5% $AlCl_3$), but at slightly higher concentrations of aluminum chloride the solutions are liquid at 0° C. Ethyl ether forms an equimolar complex melting at 33° C. The eutectic melts about 28° C. Ethyl acetate

TABLE I. SOLUBILITY OF ALUMINUM CHLORIDE AT 25° C.

Solvent	Solubility, Wt. %
Acetone	70
Ethyl ether	69 (d, 1.292)
Ethyl acetate	71.6 (d, 1.411)
Methyl ether	76 (b. p., 100° C.)
Sulfur dioxide	80? (extremely viscous)

TABLE II. ALKYLATION OF ISOBUTANE

[One hour at room temperature using 27 g. aluminum chloride (0.2 mole) and 125 g. isobutane]

Solvent	Amount, G.	Mole per Mole $AlCl_3$	Olefin	Pressure, Lb.	Alkylate, G.
None	..	0	Ethylene	175	None
Acetone	6	0.52	Ethylene	175	160
Sulfur dioxide	7	0.54	Ethylene	175	165
Ethyl acetate	6	0.34	Ethylene	175	160
Ethyl ether	7	0.47	Ethylene	175	165
Ethyl ether	14	0.94	Propylene	100	130

forms viscous solutions at 50 to 55% aluminum chloride, but richer solutions are not viscous even at 0° C. The solutions of aluminum chloride in sulfur dioxide are increasingly viscous with concentration, the 80% solution having the consistency of tar. Molecular structures for complexes with some of these solvents and many others are proposed in citations summarized in reference (*18*, pages 48 to 55).

The high affinity of the solvents for the aluminum chloride is illustrated by the boiling point of the saturated solution in dimethyl ether, about 100° C., although the solvent boils at −23.7° C. Moreover, no ethyl ether could be found in products of isomerization of *n*-butane with an ether–aluminum chloride catalyst. However, the saturated solutions in acetone and ethyl acetate retain the characteristic odors of those solvents, indicating incomplete complex formation with the excess aluminum chloride.

It is not necessary to prepare the catalytic solutions in advance by dissolving the aluminum chloride in the solvent. This can be done by adding small portions with intermittent cooling, since the heat of solution is considerable. However, it is more convenient in the laboratory to add the calculated small amount of solvent to the hydrocarbon reagents, and then add aluminum chloride in solid form. With aliphatic hydrocarbon reagents the aluminum chloride extracts the oxygen-containing solvent and separates as a lower layer, requiring agitation for catalytic action. With aromatic hydrocarbon reagents, especially at elevated temperatures, and with ether (*6*) or nitroparaffins (*16*) as solvents, a homogeneous solution results, which is still catalytic. The homogeneous alkylation thus possible was considered advantageous in both investigations (*6, 16*) for some theoretical conclusions with regard to alkylation of aromatic hydrocarbons.

It has been suggested that these solutions with molar excess of aluminum chloride are really solutions of the latter in the complex as a solvent. This viewpoint may be helpful to some, but seems unnecessary since the properties of a homogeneous liquid mixture vary continuously with composition regardless of intermolecular complexes. In at least one solvent, ethyl acetate, there is no phase change in proceeding horizontally across the diagram at room temperature until the aluminum chloride curve is intersected on the right of the equimolar composition. The same is true of ethyl ether above 33° C., and of the other solvents at higher temperatures. It cannot be said accurately that solutions on the left half of Figure 1 (or analogous graphs with aliphatic solvents) are noncatalytic and those on the right half are catalytic. There is no sharp dividing line, although catalytic activity varies steeply with concentration, the most concentrated solutions being many thousands of times more active than dilute solutions. The equimolar complexes are intermediate in activity (*12*).

APPARATUS

The experiments were conducted in one of two Monel stirring autoclaves of 300-ml. and 1000-ml. capacity, respectively, each equipped with pressure gage, thermometer well, inlet and outlet valves, and a bath for heating with water and steam with manual control. The autoclave was precooled, charged, and closed in a cold room, at about −20° C. in the case of the butanes. The charge was in the order, solvent, paraffin hydrocarbon, solid aluminum chloride. In the alkylations (Table II) the olefins were charged from a lecture bottle to the indicated pressure intermittently until the pressure no longer decreased rapidly with time.

EXPERIMENTAL RESULTS

When the solvent was omitted in the alkylations, there was no alkylate because the induction period was more than 1 hour. The yield of alkylate from ethylene (nearly 90% on a 1 to 1 molar basis) was practically identical for the four solvents tried, indicating that the enhancing effect of the solvent is not specific but is largely a physical phenomenon. A more dilute solution, 66%, forming a milder catalyst, was used with propylene to avoid polymerization. This catalyst would have given a slow reaction with ethylene. Schmerling reported alkylation with propylene but not with ethylene, using his more dilute solutions in nitroparaffins (*16*).

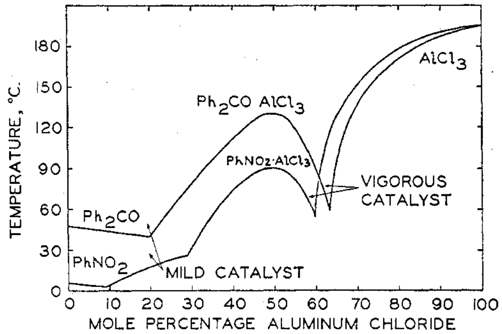

Figure 1. Freezing Point–Composition Diagram for Aluminum Chloride with Nitrobenzene and Benzophenone

Data from Menshutkin (*10*)

Schmerling claimed little or no isomerization of *n*-pentane at 100° C. or 125° C. using 50% solutions of aluminum chloride in nitropropane and nitromethane, respectively (*16*). That these negative results are due to a lack of molar excess of aluminum chloride is suggested by Tables III, IV, and V, which present the isomerization of *n*-pentane at lower temperatures. The extensive reaction at 70° C. and higher was largely the result of cracking to isobutane, an undesired side reaction. In order to diminish this reaction by use of lower temperature a nonaromatic solvent was required.

The effect of mole ratio is illustrated strikingly in Table IV. The second experiment with 0.63 mole of ether per mole of aluminum chloride caused extensive isomerization and some cracking in 102 minutes. By contrast, the third experiment with no ether, and the fourth with twice the amount of ether, or 1.26 moles, showed no reaction in nearly twice the time. The fifth, with an optimum mole ratio but too small a volume of catalyst for adequate contact, gave a moderate extent of reaction.

The first experiment in Table V with a mole ratio of only 0.32 mole of ethyl acetate to 1 of aluminum chloride (perhaps not all dissolved) showed excessive activity at 40° C. The other six experiments were made in the smaller autoclave with

Table III. Isomerization of *n*-Pentane

[103 g. (0.77 mole) aluminum chloride, 500 g. *n*-pentane]

Solvent	Amount, G.	Mole per Mole $AlCl_3$	Temp., ° C.	Time, Hr.	% Reacted
Nitrobenzene	63	0.66	70	1.8	80
Benzophenone	81	0.58	70	2.5	85
Same catalyst	..	0.58	99	3.0	81
Sulfur dioxide	23	0.47	40	3.2	60
Acetone	31.5	0.70	70	2.2	50
Isopropyl acetate	57	0.74	40	1.5	30
Isopropyl ether	57	0.74	40	1.5	40

Table IV. Isomerization of *n*-Pentane

(Aluminum chloride dissolved in ethyl ether, 500 g. *n*-pentane)

Aluminum Chloride, G.	Ether, G.	Moles per Mole $AlCl_3$	Temp., ° C.	Time, Hr.	% Reacted
103	36	0.63	70	2.1	80 (mostly isobutane)
103	36	0.63	40	1.7	80 (partly isobutane)
103	None	0	40	3.2	Negligible
103	72	1.26	40	2.8	Negligible
50	18	0.65	40	1.8	40

TABLE V. ISOMERIZATION OF *n*-PENTANE

(Aluminum chloride dissolved in ethyl acetate)

Aluminum Chloride, G.	Ethyl Acetate, G.	Moles per Mole $AlCl_3$	*n*-Pentane, G.	Temp., ° C.	Time, Hr.	% Reacted
103	22	0.32	300	40	2.2	94 (Mostly isobutane)
28	7	0.38	150	28	2.0	60
Same catalyst	..	0.38	150	28	2.0	20
Same catalyst	..	0.38	150	40	2.0	50
Same catalyst	..	0.38	150	40	1.5	40
Same catalyst	..	0.38	150	40	2.5	70
Same catalyst	..	0.38	150	50	2.0	60

the same catalyst, which was not quite as concentrated (0.38 mole of ethyl acetate). After each stage, the pentane product was decanted and replaced with fresh *n*-pentane for the next experiment. In successive runs the temperature was slightly raised to compensate for a slight loss in activity of the catalyst, which was believed to be due mainly to absorption of moisture from the atmosphere.

Comparable runs at different temperatures indicated a temperature coefficient of rate of isomerization corresponding to a doubling for a rise of 7° C. in temperature. On this basis, because a much more extensive isomerization of *n*-pentane was observed at 28° C. (Table V) than Schmerling found at 125° C. with his more dilute solution in nitromethane, it must be concluded that the present catalysts are many thousands of times more vigorous.

This investigation was not primarily concerned with preventing cracking. Small amounts of aromatic hydrocarbons or limited larger amounts of naphthenes or heterocyclics have been shown in other investigations (*9*, *11*, *13*) [see (*9*) for additional citations] to inhibit cracking, with only a moderate diminution in isomerization activity.

TABLE VI. ISOMERIZATION OF *n*-BUTANE

(Aluminum chloride dissolved in ethyl ether)

Aluminum Chloride, G.	Ethyl Ether, G.	Moles per Mole $AlCl_3$	*n*-Butane, G.	Temp., ° C.	Time, Hr.	% Isomerized
103	36	0.63	480	30	17	30
108	36	0.63	480	70	7	56
28	7	0.45	140	98	1.5	59
Same catalyst		0.45	140	98	2.0	63
40	None	0	180	100	4.9	15
40	16	0.72	180	100	5.5	47
40	22	0.99	180	100	4.4	46
40	28	1.26	180	100	4.0	10

TABLE VII. ISOMERIZATION OF *n*-BUTANE

(Aluminum chloride dissolved in sulfur dioxide)

Aluminum Chloride, G.	Sulfur Dioxide, G.	Moles per Mole $AlCl_3$	*n*-Butane, G.	Temp., ° C.	Time, Hr.	% Isomerized
28	7.5	0.56	90	95	3.5	61.5
28	None	0	120	95	3.0	25
28	15	1.12	120	95	3.0	2

Tables VI and VII present the isomerization of *n*-butane, a still more refractory reaction. This required a higher temperature for a reasonable reaction rate, although the first experiment of Table VI showed appreciable reaction at room temperature overnight. This is more extensive than any isomerization of *n*-butane reported (*2*) at comparable time and temperature, suggesting that a solvent is an even more active promoter than hydrogen chloride. The next three experiments produced isomerization practically to equilibrium, the last of these being a repeat run with fresh butane without removal of catalyst. This time there was no apparent loss in activity of the catalyst, perhaps because it was blanketed with butane vapor during the replacement of reagent. The last four runs of Table VI show the effect of varying the mole ratio of ether with 0, 0.72, 0.99, and 1.26 moles to 1 mole of aluminum chloride. The first and last of these gave only a slight reaction. Similar results were obtained with sulfur dioxide as a solvent as illustrated in Table VII. A mole ratio of 0.56 gave equilibrium isomerization; but with twice as much sulfur dioxide, the reaction is negligible. A slight reaction results from aluminum chloride without solvent under nearly the same conditions.

ANALYSIS OF PRODUCTS

As the isomerization of butane gave practically no by-products, the butane mixture was analyzed by its critical solution temperature with pure *o*-nitrotoluene, as described previously (*3*). Critical solution temperatures are 12.5° C. with *n*-butane and 32.8° C. with isobutane. The analysis is so convenient that small samples were withdrawn and analyzed occasionally, giving a measure of the progress of the reaction.

The pentane isomerizate was analyzed by fractional distillation, a method which was only approximate with respect to isopentane. In those experiments in which cracking was slight the pentane mixture was analyzed by critical solution temperature with nitrobenzene, 24° C. with *n*-pentane, 32° C. with isopentane (*3*). This method was used also as a control test in the later investigation (*11*), but final results were based on Podbielniak analyses.

The alkylates of Table II consisted largely of hexanes from ethylene and of heptanes from propylene, with appreciable amounts of isopentane in both cases. The principal isomers formed were 2-methylpentane and 2,3-dimethylbutane, and 2,3- and 2,4-dimethylpentanes, respectively, as in most aliphatic alkylations (*1*). These data were ascertained by fractional distillation and physical properties.

LITERATURE CITED

(1) Caesar, P. D., and Francis, A. W., IND. ENG. CHEM., **33**, 1426 (1941).
(2) Egloff, G., Hulla, G., and Komarewsky, V. I., "Isomerization of Pure Hydrocarbons," pp. 28–30, 218–28, New York, Reinhold Publishing Corp., 1942.
(3) Francis, A. W., U. S. Patent 2,303,265 (1942); IND. ENG. CHEM., ANAL. ED., **15**, 447 (1943).
(4) Francis, A. W., U. S. Patent 2,368,653 (1945).
(5) Francis, A. W., and James, W. H., *Ibid.*, 2,389,250 (1945).
(6) Francis, A. W., and Reid, E. E., *Ibid.*, 2,397,542 (1946); IND. ENG. CHEM., **38**, 1194 (1946).
(7) Groggins, R. H., "Unit Processes in Organic Syntheses," 3rd ed., pp. 723, 769, New York, McGraw-Hill Book Co., 1947.
(8) Matsumara, K., *J. Am. Chem. Soc.*, **52**, 4433 (1930).
(9) Mavity, J. M., Pines, H., Wackher, R. C., and Brooks, J. A., IND. ENG. CHEM., **40**, 2374 (1948).
(10) Menshutkin, B., *J. Russ. Phys. Chem. Soc.*, **42**, 58, 1298, 1310 (1910); through Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," 3rd ed., Vol. I, pp. 86–8, New York, D. Van Nostrand Co., 1940.
(11) Myers, C. G., Hansford, R. C., and Sachanen, A. N., U. S. Patent 2,424,953 (1947).
(12) Olivier, S. C. J., *Rec. trav. chim.*, **45**, 817 (1926).
(13) Perry, S. F., *Trans. Am. Inst. Chem. Engrs.*, **42**, 639 (1946).
(14) Reid, E. E., and co-workers, *J. Am. Chem. Soc.*, **44**, 206 (1922); **49**, 3142 (1927); *J. Org. Chem.*, **9**, 13 (1944).
(15) Ross, J., Brandt, R. L., and Percy, J. H., U. S. Patent 2,245,721 (1940).
(16) Schmerling, L., IND. ENG. CHEM., **40**, 2072 (1948).
(17) Schmerling, L., *J. Am. Chem. Soc.*, **68**, 275 (1946).
(18) Thomas, C. A., "Anhydrous Aluminum Chloride in Organic Chemistry," pp. 48–55, 461, 873–4, New York, Reinhold Publishing Corp., 1941.
(19) Tilicheev, M. D., and Kuruindin, K. S., *Neftyanoe Khoz.*, **19**, 586 (1930); *Chem. Zentr.*, **1931**, **I**, 2560.

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