

**234.** *Some Reactions of cycloPropane and a Comparison with the Lower Olefins. Part III.\* The Friedel-Crafts Reaction.*

By C. F. H. TIPPER and D. A. WALKER.

The kinetics of the reaction of *cyclopropane* and of propene with benzene in the presence of aluminium chloride in homogeneous solution have been investigated at *ca.* 25°. Some comparative results were obtained with toluene and chlorobenzene. Traces of water and/or hydrogen chloride were necessary as co-catalysts. With *cyclopropane* the initial rate depended only on the catalyst concentration at "high" gas pressures and concentrations of aromatic compound, while at "low" concentrations the rate also varied with the pressure of gas and the nature and concentration of the aromatic compound. With propene the rate actually fell as the benzene concentration was increased above a certain value.

The nature of the effective catalyst and the mechanism of the reaction are discussed and a scheme is put forward to explain the kinetic results. It is suggested that several complexes involving the various reagents were present in the solution.

OLEFINS readily combine with many aromatic compounds in the presence of Friedel-Crafts catalysts, and Schmerling<sup>1</sup> showed that, when *cyclopropane* was passed into a solution of aluminium chloride and benzene in nitromethane at room temperature, *n*-propylbenzene was formed quantitatively. With propene the product was *isopropylbenzene*. The kinetics of these reactions have been investigated and the results are now presented.

#### EXPERIMENTAL

The rate of uptake of *cyclopropane* or propene was followed by means of the conventional constant-pressure apparatus used previously. It was found that the rate did not increase as the speed of shaking of the reaction flask was increased, provided this was above 250 times per minute. The standard shaking speed was thus fixed at about 400 times per minute. The flask was cleaned before an experiment by washing it with alcohol, drying it thoroughly and flaming it.

\* Part II, *J.*, 1955, 2045.

<sup>1</sup> Schmerling, *Ind. Eng. Chem.*, 1948, 40, 2072.

*cyclo*Propane and propene from cylinders were purified as described,<sup>3</sup> and dried [ $\text{Mg}(\text{ClO}_4)_2$ ]. Ethylene from a cylinder was passed through 82.5% sulphuric acid and a trap at  $-78^\circ$ , and dried. Chlorobenzene, and "AnalaR" benzene, nitrobenzene, and diethyl ether were dried thoroughly, and fractionally distilled in a stream of dry nitrogen. The toluene was shaken several times with concentrated sulphuric acid, washed, and distilled from sodium. The nitromethane was purified as recommended by Thompson, Coleman, and Helm.<sup>3</sup>

Hydrogen chloride was passed through concentrated sulphuric acid and then over heated aluminium turnings ("specially pure," 99.9%). The aluminium chloride formed was condensed in a receiver with a side tube. After a suitable amount had been collected, dry nitrogen was passed for several hours to remove excess of hydrogen chloride. The receiver was then cooled in ice and the purified nitromethane or nitrobenzene run in with nitrogen still passing. The solution was colourless but slowly deteriorated, becoming brown, and thus a fresh solution was prepared every few days. Any appreciable quantity of hydrogen chloride or water gave a yellow tint or a white cloudiness respectively, and such samples were discarded. The reactants were protected from atmospheric moisture during storage, measurement of the appropriate volumes, and transfer to the reaction flask. If required, water was added to the reaction mixture from a microburette, and hydrogen chloride by shaking a bulk sample of the aluminium chloride solution with the dried gas.

Two very dry solutions of aluminium chloride and benzene in nitromethane were prepared in a vacuum system by a method similar to that used by Fairbrother, Scott, and Prophet.<sup>4</sup> The solutions were stored in an atmosphere of dry carbon dioxide in sealed tubes until required.

## RESULTS

The following systems were studied: I, aluminium chloride–nitromethane–benzene–*cyclo*propane (with and without added water and hydrogen chloride); II, aluminium chloride–nitromethane–benzene–propene; III, aluminium chloride–nitrobenzene–benzene–*cyclo*propane; IV, aluminium chloride–nitromethane–diethyl ether–benzene–*cyclo*propane; V, aluminium chloride–nitromethane–toluene–*cyclo*propane; and VI, aluminium chloride–nitromethane–chlorobenzene–*cyclo*propane. The solubilities of *cyclo*propane in nitromethane, benzene, and 0.1M-aluminium chloride in nitromethane are roughly 0.16, 0.46, and 0.24 mole/l. respectively at  $25^\circ$  and atmospheric pressure. The solubility of propene is also greater in benzene than in nitromethane.

Removal of traces of water and hydrogen chloride in the vacuum apparatus gave solutions which did not react at an appreciable rate with *cyclo*propane. With reactants prepared in the normal manner, however, reaction took place with systems I to VI. After a very rapid absorption, due to physical solution of the gas, the rate of uptake ("initial rate") remained constant for some time and then decreased gradually. Rates were reproducible to within 5–10% and were almost certainly equal to the rates of reaction. The effect of conditions on the initial rate was studied.

The initial rate of reaction with propene was several times greater than with *cyclo*propane under the same conditions (systems II and I), but ethylene was absorbed only very slowly. Addition of roughly 0.1 mole/l. of hydrogen chloride to system I increased the initial rate by about 1.5–2.5 times, depending on the benzene concentration. Fig. 1 shows the effect of adding water to the same system. Very small amounts increased the initial rate to 10 times the value with reactants purified in the normal manner, but further additions reduced the rate again although not to zero, and precipitation occurred. The results are consistent with the fact that there was no reaction with completely dry reagents.

The initial rate increased rapidly with increasing aluminium chloride concentration (Fig. 2). The plots are slightly curved but the order with respect to catalyst concentration is approximately unity for both *cyclo*propane and propene. Variation of the gas pressure had little effect on the initial rate, whether the solvent was nitromethane or nitrobenzene and the aromatic reactant benzene or toluene (Fig. 3). In the presence of hydrogen chloride however, the rate with system I decreased somewhat with increasing *cyclo*propane pressure (650–900 mm.). The results

<sup>3</sup> Lawrence and Tipper, *J.*, 1955, 713.

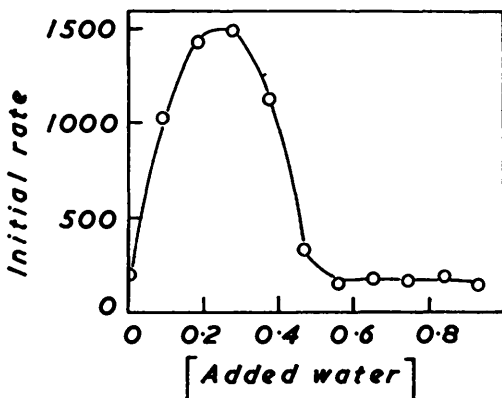
<sup>3</sup> Thompson, Coleman, and Helm, *J. Amer. Chem. Soc.*, 1954, **76**, 3445.

<sup>4</sup> Fairbrother, Scott, and Prophet, *J.*, 1956, 1164.

are rather scattered due to the difficulty of measuring the high rates accurately. The plots must pass through the origin, and therefore at low pressures the rate must depend on the con-

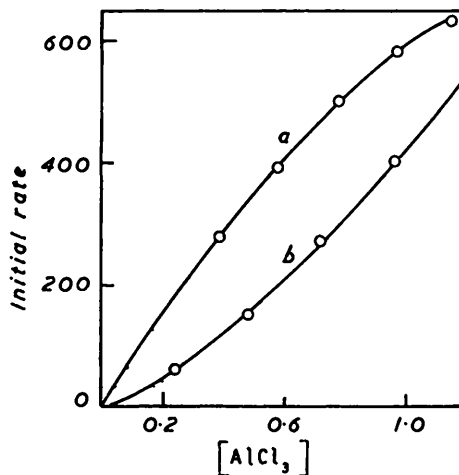
In all Figures, concentrations are in moles/l.

FIG. 1. Effect of added water on the initial rate (ml. at N.T.P./l./min.) of uptake of cyclopropane (pressure 760 mm.) at 24.7° c. Solvent, nitromethane;  $[AlCl_3]$ , 0.32;  $[C_3H_6]$ , 1.82.



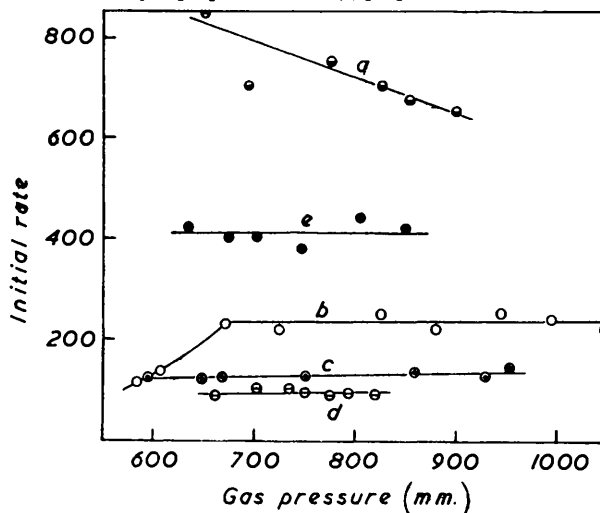
At concentrations greater than that of the experimental point corresponding to the highest rate there was precipitation.

FIG. 2. Effect of concentration of aluminium chloride on the initial rate of uptake of gas (pressure, 760 mm.) at 24.1° c. Solvent, nitromethane.



(a) cycloPropane:  $[C_3H_6]$ , 4.35.  
(b) Propene:  $[C_3H_6]$ , 5.45.

FIG. 3. Effect of pressure on the initial rate of uptake of gas at 24.7° c. Gas; curves (a)—(d), cyclopropane; curve (e) propene.

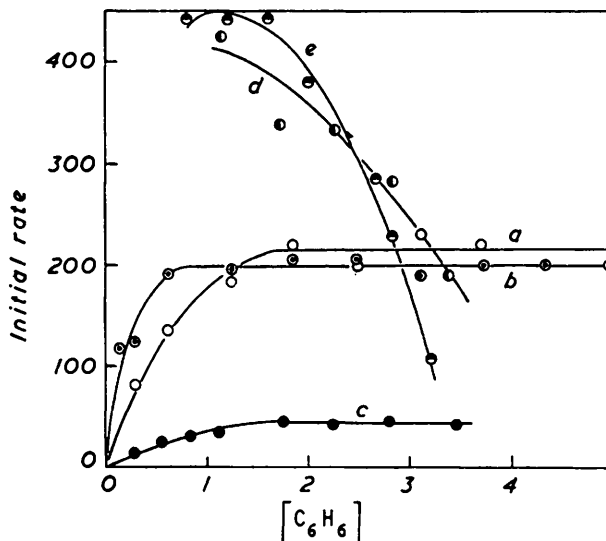


(a) Solvent, nitromethane; HCl (0.1 mole/l.) added;  $[C_3H_6]$ , 2.73;  $[AlCl_3]$ , 0.48.  
(b) Solvent, nitromethane;  $[C_3H_6]$ , 2.48;  $[AlCl_3]$ , not determined.  
(c) Solvent, nitromethane;  $[C_3H_6Me]$ , 1.60;  $[AlCl_3]$ , 0.088.  
(d) Solvent, nitrobenzene;  $[C_3H_6]$ , 2.73;  $[AlCl_3]$ , 0.187.  
(e) Solvent, nitromethane;  $[C_3H_6]$ , 4.35;  $[AlCl_3]$ , 0.17.

centration of cyclopropane or propene in the solution. There is some experimental evidence of this (Fig. 3, curve b; see also Fig. 5).

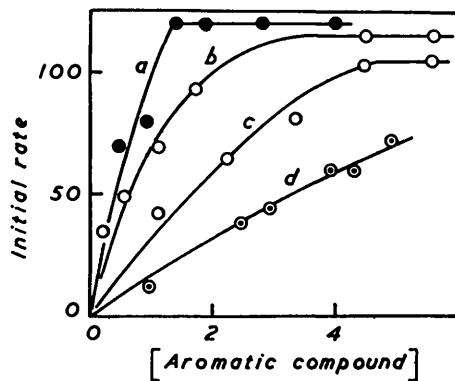
With system I and constant concentrations of aluminium chloride and cyclopropane the initial rate increased at first with increasing benzene concentration, and then became constant

FIG. 4. *Effect of benzene concentration on the initial rate of uptake of gas (pressure 760 mm) at 24.7° c. Gas: curves (a)—(d), cyclopropane; (e) propene.*



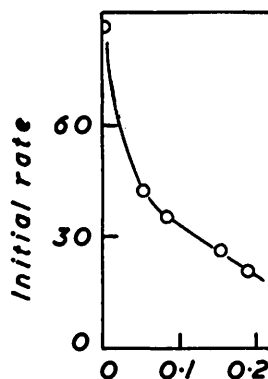
- (a) Solvent, nitromethane; [AlCl<sub>3</sub>], not determined.
- (b) Solvent, nitromethane; water (0.06 mole/l.) added; [AlCl<sub>3</sub>], 0.074.
- (c) Solvent, nitrobenzene; [AlCl<sub>3</sub>], 0.292.
- (d) Solvent, nitromethane; HCl (0.1 mole/l.) added; [AlCl<sub>3</sub>], 0.48; ordinate and abscissa × 2.
- (e) Solvent, nitromethane; [AlCl<sub>3</sub>], 0.12; ordinate and abscissa × 2.

FIG. 5. *Effect of concentration of benzene, toluene, and chlorobenzene on the initial rate of uptake of cyclopropane at 24.7° c. Solvent, nitromethane.*



- (a) Toluene; [AlCl<sub>3</sub>], 0.067; gas pressure, 760 mm.
- (b) Benzene; [AlCl<sub>3</sub>], 0.067; gas pressure, 885 mm.
- (c) as (b); gas pressure, 613 mm.
- (d) Chlorobenzene, [AlCl<sub>3</sub>], 0.130; gas pressure, 760 mm.

FIG. 6. *Effect of replacement of nitromethane by diethyl ether on the initial rate of uptake of cyclopropane (pressure, 760 mm.) at 24.1° c. [AlCl<sub>3</sub>], 0.057 [C<sub>3</sub>H<sub>6</sub>], 0.91.*



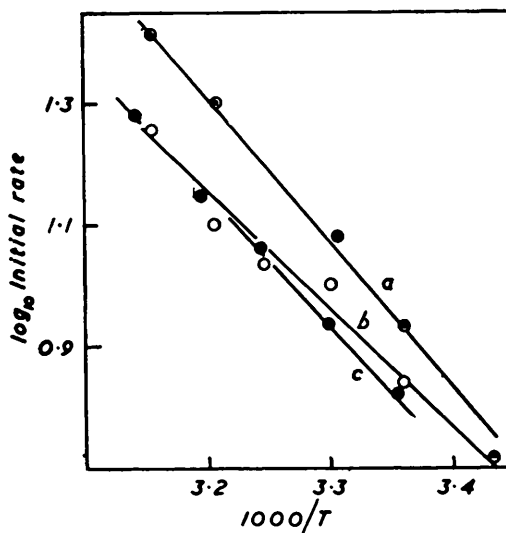
*Moles ether/Mole nitromethane*

(Fig. 4, curve *a*). With a very small addition of water the rate became independent of benzene concentration at a much lower value of this concentration (curve *b*). Replacement of the nitromethane by nitrobenzene reduced the rates considerably, but the form of the dependence on benzene concentration was the same (curve *c*). With addition of hydrogen chloride or with propene however, the initial rate fell rapidly as the benzene concentration was increased above a relatively small value (curves *d* and *e*). With added hydrogen chloride about 60% of the fall in rate is accounted for by the increase in *cyclopropane* concentration with increase in benzene concentration.

Fig. 5 shows the effect on the initial rate of uptake of *cyclopropane* of the concentrations of benzene, toluene, and chlorobenzene, the same catalyst solution being used with the first two

FIG. 7. Effect of temperature on the initial rate of uptake of *cyclopropane* (pressure, 760 mm.).

- (a) Solvent, nitromethane;  $[\text{AlCl}_3]$ , 0.061;  
 $[\text{C}_6\text{H}_5\text{Me}]$ , 4.0.  
 (b) Solvent, nitromethane;  $[\text{AlCl}_3]$ , 0.061;  
 $[\text{C}_6\text{H}_6]$ , 5.5.  
 (c) Solvent, nitrobenzene;  $[\text{AlCl}_3]$ , 0.098;  
 $[\text{C}_6\text{H}_6]$ , 4.05.



compounds. As the concentration of benzene or toluene was increased the rate increased to a constant value which was nearly the same for the two substances. However, the actual concentration at which the rate became independent of the amount of aromatic increased in the order: toluene, benzene ("high" *cyclopropane* pressure), benzene ("low" *cyclopropane* pressure). With chlorobenzene, the rate continued to increase with increasing concentration within the range used.

Replacement of increasing amounts of nitromethane by ether led to a rapid decrease in the initial reaction rate (system IV) (Fig. 6).

The effect of temperature on the initial rate of *cyclopropane* uptake was investigated with systems I, III, and V, under conditions where the rate was independent of benzene or toluene concentration (Fig. 7). The overall activation energies are 8.9, 10.2, and 10.9 kcal./mole with I, III, and V, respectively.

#### DISCUSSION

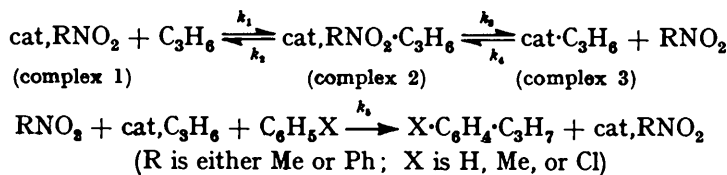
The fact that a co-catalyst was required for the addition of *cyclopropane* to benzene agrees with observations of other workers on many types of Friedel-Crafts reaction.<sup>5</sup> Traces of water and hydrogen chloride were undoubtedly present in the reactants purified in the normal manner. However, consideration of the effective catalyst will be deferred until after a scheme has been proposed to explain the observed kinetics. In this scheme the active form of the aluminium chloride will be denoted as "cat."

The theory of Friedel-Crafts reactions has been discussed recently by Nelson and Brown.<sup>6</sup> It is generally considered that in an alkylation the alkylating agent first combines with the catalyst and then the complex reacts with the aromatic compound. In this

<sup>5</sup> Brooks, Boord, Kurtz, and Schmerling (Editors), "The Chemistry of Petroleum Hydrocarbons," Reinhold Publishing Corporation, 1955, Vol. 3, pp. 185, 511.

<sup>6</sup> Nelson and Brown, ref. 5, p. 510.

work the higher solubility of *cyclopropane* in a solution of aluminium chloride in nitromethane than in the solvent alone suggests the existence of a catalyst- $C_3H_6$  complex. Also Schmerling<sup>1</sup> has obtained a solid 1 : 1 complex of aluminium chloride and nitromethane. Several complexes have to be postulated in the reaction scheme given below, and these have been chosen with these considerations in mind.



It is assumed that all the catalyst was in the form of complexes 1, 2, and 3, and that the presence of a solvent molecule was necessary in reaction 5 to combine with the catalyst released.

$$\text{Rate of uptake} = -d[C_3H_6]/dt = k_1[1][C_3H_6] - k_2[2]$$

It being assumed that in a very short time stationary concentrations of complexes 2 and 3 were attained, then

$$\begin{array}{l} k_1[1][C_3H_6] + k_4[3][RNO_2] = k_2[2] + k_3[2] \\ \text{and } k_3[2] = k_4[3][RNO_2] + k_5[3][RNO_2][C_6H_5X] \\ \therefore -d[C_3H_6]/dt = k_5[3][RNO_2][C_6H_5X] \\ \text{Also } [1] + [2] + [3] = [\text{cat}] \end{array}$$

Thus solving for the stationary concentration of complex 3 gives

$$[3] = k_1k_3[\text{cat}][C_3H_6]/\{k_1x + k_5x[C_6H_5X] + k_1k_3[C_3H_6] - k_3k_4\}$$

where  $x = k_1[C_3H_6] + k_2 + k_3$

$$\therefore -d[C_3H_6]/dt = k_1k_3k_5[\text{cat}][C_3H_6][C_6H_5X]/\{k_3k_4 + (k_1k_4 + k_3k_5)[C_3H_6] + k_5(k_2 + k_3)[C_6H_5X] + k_1k_5[C_3H_6][C_6H_5X]\} \quad (a)$$

This theoretical relation agrees with the experimental dependence of the rate on aluminium chloride concentration, on the assumption that this was proportional to the actual catalyst concentration during the appropriate sets of experiments.

At high concentrations of both *cyclopropane* and the aromatic compound the expression reduces to

$$-d[C_3H_6]/dt = k_3[\text{cat}] \quad (b)$$

the rate being independent of the concentration of both organic reagents, and actually independent of the aromatic compound itself with the same solvent and catalyst solution. This was found experimentally with benzene and toluene. Probably with chlorobenzene the rate would have become independent of the concentration if it had been possible to make this large enough. Equation (a) implies a dependence of the rate on the concentration at low concentrations of aromatic compound, as found.

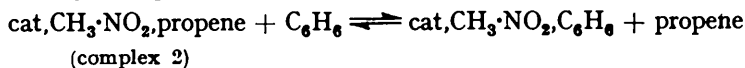
The lower rates obtained with nitrobenzene, compared to those with nitromethane as solvent, suggest that  $k_3$  was smaller with the former and thus that complex 2 was more stable with nitrobenzene than with nitromethane. According to equation (b), the variation of the initial rates of uptake with temperature should give the activation energies for the decomposition of complex 2 to complex 3, since the concentrations of aromatic substance and *cyclopropane* were "high." It might be expected therefore that the activation energy for the reaction of *cyclopropane* and benzene in nitromethane solution would be less than in nitrobenzene solution, as found experimentally. However, the activation energy for the reaction with toluene was somewhat greater than with benzene, instead of being approximately the same. This was probably due to the appreciably different environment of complex 2, since a considerable fraction of the solution consisted of molecules of

benzene or toluene ( $N_{O,H,x} \sim 0.3$ ). The marked effect of small amounts of ether on the rate can have been due only in part to a reduction in the dielectric constant of the solvent, and it is probable that the aluminium chloride and ether tended to form an inactive complex, possibly  $AlCl_3 \cdot Et_2O$ .<sup>7</sup>

Equation (a) agrees with the experimental findings that the rate became dependent on the gas pressure at "low" pressures, and that the higher the pressure of *cyclopropane* the lower the benzene concentration at which the rate became independent of the concentration.

It can be seen from Fig. 5 that  $k_5$  increased in the order  $C_6H_5Cl < C_6H_6 < C_6H_5 \cdot CH_3$ . This implies that complex 3 was an electrophilic reagent, and suggests a carbonium-ion mechanism for reaction 5, in agreement with other work.<sup>8</sup>

With propene the decrease in rate with increasing benzene concentration at the higher concentrations may be explained by postulating that the equilibrium



occurred in addition to the other reactions. With system 1 in the presence of added hydrogen chloride the small retarding effect of *cyclopropane* at "high" pressures must presumably have been due to formation of an inactive *cyclopropane*-catalyst complex.

The scheme suggested is of course not the only one which will explain the kinetic results, but it does appear to be the simplest which does not contradict the other evidence concerning the mechanism of Friedel-Crafts reactions. Brown *et al.*<sup>9</sup> have investigated the alkylation of benzene and toluene by alkyl bromides in the presence of aluminium bromide. In particular they found that *isopropylation* was too fast to measure even in 1 : 2 : 4-trichlorobenzene. Their reaction scheme is very similar to that suggested here. The differences between the rates and kinetics with the two systems is probably at least partly due to the highly polar nature of nitromethane and nitrobenzene, which caused complex 2 to be relatively stable.

The nature of the actual catalyst in a Friedel-Crafts alkylation is by no means clear. Many workers have considered that in the presence of hydrogen chloride (which could be produced by the hydrolysis of some aluminium chloride; cf. Bercaw and Garrett<sup>10</sup>),  $HAICl_4$  is formed and combines with the olefin, giving  $C_nH_{2n+1}^+AlCl_4^-$ . This would be complex 3 in our scheme. Recent work<sup>11</sup> has shown that the  $AlCl_4^-$  ion can only be formed from aluminium chloride and hydrogen chloride if there is a proton acceptor present, and results by Fairbrother and Frith,<sup>12</sup> who studied the effect of water on aluminium bromide, have cast doubt on the possibility of rapid hydrolysis of aluminium chloride by traces of water. They present strong evidence for the complex  $AlBr_3 \cdot H_2O$ , and it is noteworthy that in this work the maximum in the curve of rate against concentration of added water corresponds to approximately one mole of water per mole of aluminium chloride (the curve being extrapolated to zero rate). The reduction in the rate with larger additions of water was probably due to precipitation of some or all of the aluminium. This precipitate presumably could catalyse the reaction to some extent since the rate did not fall to zero. However, the effect of added hydrogen chloride can hardly be attributed completely to traces of water which escaped the drying process so that it seems likely that the active catalyst was in effect the proton, the negative ion being  $AlCl_4^-$  and  $AlCl_3 \cdot OH^-$ . Addition of relatively small amounts of water or hydrogen chloride increased the number of protons made available, though the former was the much more effective co-catalyst. It is useless

<sup>7</sup> Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," Reinhold Publishing Corporation, 1941.

<sup>8</sup> Nelson and Brown, ref. 5, p. 159.

<sup>9</sup> Brown and Jungk, *J. Amer. Chem. Soc.*, 1956, **78**, 2182; Jungk, Smoot, and Brown, *ibid.*, p. 2185.

<sup>10</sup> Bercaw and Garrett, *J. Amer. Chem. Soc.*, 1956, **78**, 1841.

<sup>11</sup> Brown and Pearsall, *J. Amer. Chem. Soc.*, 1951, **73**, 4681.

<sup>12</sup> Fairbrother and Frith, *J.*, 1953, 2975.

to speculate on the structures of complexes 1 and 2 but it is probable that the *cyclopropane* ring or the double bond were broken as *n*- or *iso*-C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions, respectively, were formed.

One of us (D. A. W.) thanks the University of Liverpool for a postgraduate scholarship.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,  
UNIVERSITY OF LIVERPOOL.

[Received, September 20th, 1956.]

---