hydroxide was heated to 190° and 56 g. of distillate was collected. A foam-producing reaction set in near the end of the run. After treatment with 10 g. of sodium hydride (in oil) to remove the alcohol, the crude product was distilled. There was obtained 22 g. (35%) of butyl isopropenyl ether, b.p. 111–114°, $n^{25}\text{D}$ 1.4076.

Anal. Calcd. for $C_7H_{14}O$: C, 73.64; H, 12.36. Found: C, 73.19; H, 12.26.

To a stirred mixture of 12.6 g. (0.29 mole) of isocyanic acid, 25 ml. of benzene, and 0.05 g. of *p*-toluenesulfonic acid was added 22 g. (0.19 mole) of butyl isopropenyl ether over a period of 24 min. with a temperature rise to 44°. On distillation, there was obtained 22.2 g. (71%) of 1-butoxy-1-methylethyl isocyanate, b.p. 58° (18 mm.), $n^{25}\text{D}$ 1.4104.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.56; H, 9.60; N, 9.08.

The infrared spectrum showed absorption at 3.33 μ and 3.38 μ and 3.47 μ (saturated CH); 4.45 μ (NCO); 7.23 μ and 7.32 μ ($C(CH_3)_2$); and 8–10-μ region (C—O—C).

In an attempt to obtain the carbamate by reaction of this isocyanate with ethanol, a slow complex reaction occurred with the formation of ethyl carbamate and ethyl allophanate. The stoichiometry corresponded to about 2.3 moles of ethanol consumed per mole of isocyanate. Apparently, the initial reaction involved displacement of NCO with OC_2H_5 to give HNCO, which underwent further reaction with ethanol to form ethyl carbamate and ethyl allophanate.

On the Nature of the Catalytic Agent in Friedel–Crafts Isomerization

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Infrared spectra of solutions containing aluminum bromide, 1,2,4-trichlorobenzene, and small quantities of water suggest that Al_2Br_5OH is a possible catalytic species in the "homogeneous" isomerization of *n*-hexane in these systems.

The "homogeneous" isomerization of *n*-hexane was studied recently using 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene as solvents and aluminum bromide promoted with small amounts of water as the co-catalyst.[1] Water is known to be a good promoter of Friedel–Crafts catalysts, and several reasons have been advanced for this phenomenon.[2] Typical arguments are that water reacts with aluminum bromide: to form hydrogen bromide which adds to trace quantities of olefins to form alkyl bromides which serve as carbonium ion initiators, to form a protonic acid which converts trace olefins to carbonium ions, or to form a protonic acid which interacts directly with and causes the rearrangement of a paraffin without carbonium ion formation.

The object of the present study was to obtain a better understanding of this co-catalyst system by determining the infrared absorption of solutions of aluminum bromide, trichlorobenzene, and small amounts of water.

Results and Discussion

It was observed that, when a small quantity of water is gradually added to a solution of aluminum bromide in 1,2,4-trichlorobenzene, some of it reacts at the surface to form a precipitate, possibly a hydrated aluminum oxide or very basic aluminum bromide, while the major portion dissolves to form a "homogeneous" solution. The precipitate would account only for a small portion of the added water and it was not further characterized, but the clear solution was examined by infrared. It was found that an OH band in the 2.9-μ (3450-cm.$^{-1}$) region of the spectrum developed in intensity as the nominal water–aluminum bromide mole ratio increased from 0 to 0.5. Adding more water resulted in a *decrease* in the 2.9-μ band (Fig. 1). This behavior suggests that the species in solution possessing an OH group is altered or removed by further reaction with excess water.

Also, in the spectra of these solutions no bands were observed at $\sim$6.1 μ. A band in this spectral region is indicative of an H–O–H bending vibration, and its absence indicates that the added water did not simply form a hydrate with aluminum bromide, $Al_2Br_6{\cdot}xH_2O$. For example, typical hydrates such as $LiClO_4{\cdot}H_2O$ have a sharp band at 6.1 μ.[3] These spectra indicate that water reacts with aluminum bromide in 1,2,4-trichlorobenzene and forms a soluble complex containing a hydroxyl group.

While infrared absorption at 2.9 μ thus went through a maximum at a water–aluminum bromide mole ratio of 0.5, an exactly parallel behavior occurred in the 14.5–15-μ spectral region. Infrared bands in this region are due to the C–Cl vibrations of 1,2,4-trichlorobenzene.[4] This parallel behavior in the two spectral regions suggests that the soluble aluminum bromide complex interacts with trichlorobenzene to form a species which has infrared bands both at 14.5–15 and 2.9 μ. The interaction between 1,2,4-trichlorobenzene and the soluble aluminum bromide complex is weak, since the addition of excess water permitted the original spectrum of the solvent to be recovered (Fig. 2).

The result that water and aluminum bromide interact in 1,2,4-trichlorobenzene to form a species whose concentration is a maximum at a water–aluminum bromide mole ratio of 0.5 is supported by *n*-hexane isomerization rate measurements. In general, it was found previously that the *n*-hexane isomerization and cracking rates increased as the water–aluminum bromide mole ratio varied from 0 to 0.5,[1] but the solutions containing excess water, water–aluminum bromide >1, had no catalytic activity. Also, a slow evolution of hydrogen bromide from these solutions was detected during all of the *n*-hexane isomerization experiments. While hydrogen bromide may serve as a co-catalyst with aluminum bromide, hydrogen bromide adding to trace quantities of olefins to form alkyl bromides which serve as carbonium ion initiators, its contribution must be small since previous work[1] has shown that even in the presence

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[1] G. M. Kramer, R. M. Skomoroski, and J. A. Hinlicky, *J. Org. Chem.*, **28**, 1029 (1963).

[2] H. Pines, "Advances in Catalysis," Vol. I, Academic Press, New York, N. Y., 1948, p. 201.

[3] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

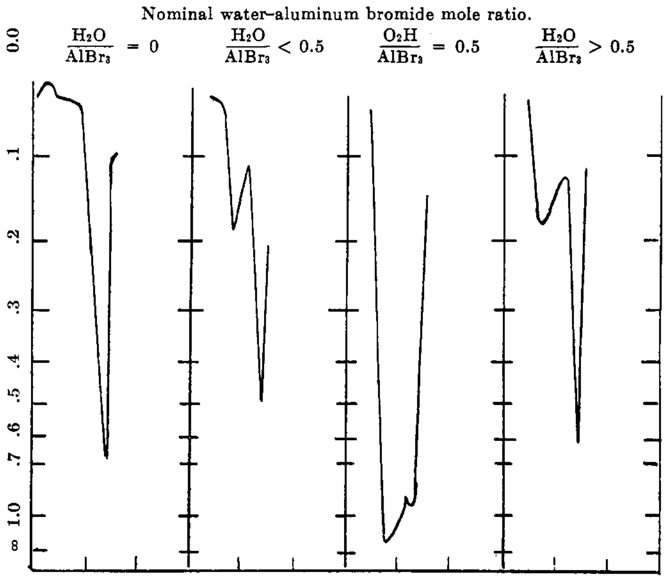
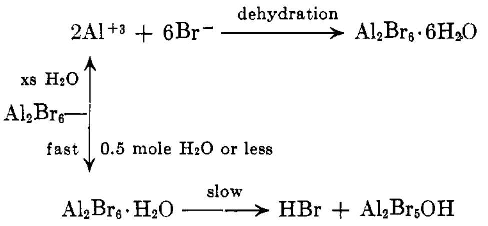


Fig. 1.—An OH band at 2.9 μ increases, and then decreases as the nominal water–aluminum bromide mole ratio passes through 0.5. Ordinate is wave length, μ; abcissa is absorbance.

of small amounts of added olefin much less activity is obtained.

These infrared studies of the water–aluminum bromide system and the isomerization rate measurements suggest that the active catalytic agent is a soluble aluminum bromide complex. It is postulated that its probable composition is Al_2Br_5OH or $AlBr_3{\cdot}AlOHBr_2$. The reactions which are thought to occur in the water–aluminum bromide system are shown.



$$2Al^{+3} + 6Br^- \xrightarrow{\text{dehydration}} Al_2Br_6\cdot 6H_2O$$

$$\text{xs } H_2O \uparrow \quad Al_2Br_6— \quad \text{fast} \downarrow \text{ 0.5 mole } H_2O \text{ or less}$$

$$Al_2Br_6\cdot H_2O \xrightarrow{\text{slow}} HBr + Al_2Br_5OH$$

Aluminum bromide ionizes readily in the presence of excess water and the hexahydrate can be recovered from solutions containing Al^{+3} and Br^- ions.[5] If a deficiency of water exists, acid–base interaction of aluminum bromide and water may occur to form $Al_2Br_6{\cdot}H_2O$. This complex of aluminum bromide loses hydrogen bromide slowly to form Al_2Br_5OH, which is responsible for the OH band that is observed in 1,2,4-trichlorobenzene.

It is interesting to speculate on the possible structure of the catalytic agent. A hydroxyl group might replace any of the six bromine atoms in Al_2Br_6. Thus, a possible structure is one in which an OH group replaces a Br atom forming a bridge between two aluminum atoms.

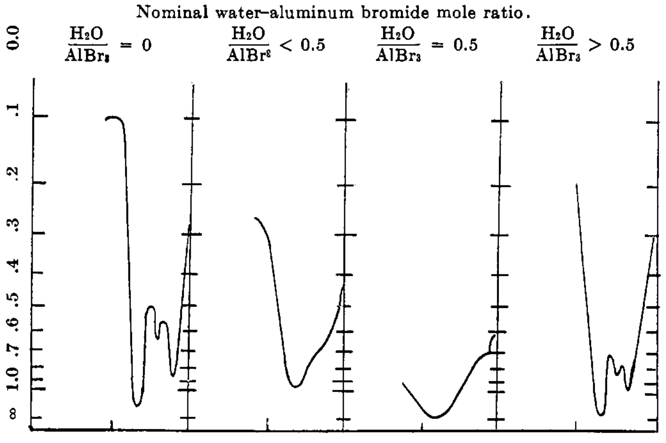
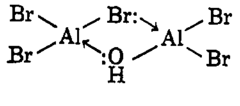


Fig. 2.—An interaction with C–Cl stretching vibration passes through a maximum at a nominal water–aluminum bromide mole ratio of 0.5. Ordinate is wave length, μ; abcissa is absorbance.



This complex may be more acidic than one in which a nonbridge bromine atom is replaced by OH, since the oxygen is held by two aluminum atoms more strongly here, and, therefore, it would be a more active isomerization catalyst. The isomerization catalyst could function as a strong protonic acid as mentioned previously.

Experimental

Aluminum bromide was prepared by doubly distilling commercially available material and using the heart cut of the second distillate.

1,2,4-trichlorobenzene, research grade, was obtained from the Matheson Coleman and Bell Co. Infrared analysis indicated that it contained about 5 wt. % of 1,2,3- and 1,3,5-trichlorobenzene.

Solutions were prepared by dissolving 0.05 mole of aluminum bromide in 25 cc. of 1,2,4-trichlorobenzene, and small amounts of water were added slowly to these solutions. The temperature of the solutions during preparation was kept approximately constant at 23 ± 3°. At a nominal water–aluminum bromide mole ratio of 0.5 the water concentration in solution was less than about 0.8 wt. %.

Infrared spectra were obtained using a Perkin-Elmer Infracord and a Perkin-Elmer Model 21 instrument. Sodium chloride cells, 0.104-mm. thickness, were used. All infrared spectra of the soluble aluminum bromide complex were obtained in the absence of *n*-hexane.

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