Aluminum Bromide-Hydrocarbon Complexes

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There is considerable interest in developing a satisfactory mechanism for the Friedel-Crafts reaction. Such mechanisms as have been proposed are relatively vague as to the precise function of the catalyst and the catalyst complexes in the reaction mechanism. An understanding of these substances is essential before their role in the reaction can be understood. In order to gain insight into the exact nature and function of these catalysts and catalyst complexes, a study has been undertaken of a typical Friedel-Crafts catalyst, aluminum bromide, and its interaction with aromatic hydrocarbons in the presence and absence of hydrogen bromide.

There is ample evidence that aluminum bromide does react with benzene and other aromatics. Thus, Ulich (1) obtained a dipole moment of 4·9D for benzene solutions of aluminum bromide, and later Plotnikov (2) confirmed this, but found that for high concentrations, the dipole moment decreased to zero. This was attributed to dimerization of $AlBr_3$ at higher concentrations, and later workers (3, 6) have since shown that aluminum bromide is largely dimeric in hydrocarbon solutions.

Complexes have been isolated by a number of workers, notably Plotnikov (4), Eley (5) and Van Dyke (6), all of whom obtained the hydrocarbon: halide ratio of $1Ar{:}1AlBr_3$, the two former formulating the complex as $Ar{:}AlBr_3$ and the latter as $Ar_2{\cdot}Al_2Br_6$ to account for the dimeric nature of halide in such solutions.

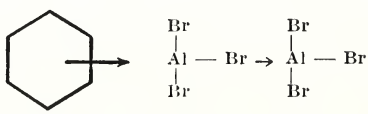
Vapor-pressure-composition studies have failed to confirm these earlier results, a complex of empirical formula $Ar{:}Al_2Br_6$ separating out at high concentrations (7). Molecular weight determinations using a vapor pressure lowering technique have shown that in solution at least two species occur, probably $Ar{:}AlBr_3$ and $Ar{:}Al_2Br_6$, in equilibria:

$$Ar + Al_2Br_6 \rightleftarrows Ar{\cdot}Al_2Br_6$$

$$Ar{\cdot}Al_2Br_6 + Ar \rightleftarrows 2Ar{\cdot}AlBr_3$$

Such equilibria would largely account for the change in dipole moment with concentration, removal of benzene decreasing the concentration of complex, with formation of dimeric Al_2Br_6 which would have no dipole moment.

The structure of the complex has not been confirmed, but it is believed to be a π bonded molecule, the π electrons of the benzene ring donating to a vacant orbital on the acceptor aluminum atom.



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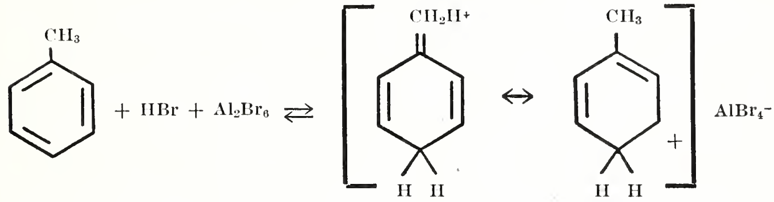
In the presence of hydrogen halide, aluminum halides form much different complexes with aromatic hydrocarbons. These are the highly colored (often red) oils which are usually observed during Friedel-Crafts reactions. They have attracted the attention of a large number of workers (8) and have been variously formulated as $AlBr_3 \cdot 3Ar$, $HBr \cdot Al_2Br_6 \cdot Ar$, $HBr \cdot Al_2Br_6 \cdot 2Ar$ and others involving various ratios of hydrogen bromide, aluminum bromide and aromatic. It has been shown that these complexes, which are ionic, may be formulated as $ArH^+AlX_4^-$ and $ArH^+Al_2X_7^-$.



3 equivalent forms.

Such complexes, in which the acceptor atoms (in this case a proton) is localized on a particular atom of the benzene ring, are described as σ complexes, in contrast to the previously described π complexes (9).

It is unlikely that π complexes participate to any extent in the Friedel-Crafts reaction, but σ complexes probably play a very important role. It has been proposed that the high solubility of aluminum halides in these Friedel-Crafts complexes is due to the formation of a series of higher complexes of this kind, with the general formula $[ArH]^+[rAlX_4]^-$. In other words, that aluminum halides dissolve in these liquid carbonium ion salts just as sulphur trioxide dissolves in sulphuric acid to form a series of higher acids.

H_2SO_4, $H_2S_2O_7$, $H_2S_3O_{10}$, $H_2S_4O_{13}$ etc.
$ArH^+AlX_4^-$, $ArH^+Al_2X_7^-$, $ArH^+Al_3X_{10}^-$, $ArH^+Al_4X_{13}$ etc.

It is suggested that these complexes play an important role in those Friedel-Crafts reactions involving carbonium ions by furnishing a highly polar medium in which ionic intermediates may form and react.

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