COMMUNICATIONS TO THE EDITOR

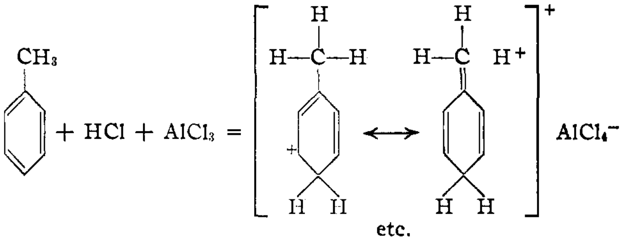
INTERACTION OF FRIEDEL-CRAFTS CATALYSTS WITH ALKYL HALIDES AND AROMATIC HYDROCARBONS

Sir:

The activity of Friedel–Crafts catalysts is usually attributed to the formation of strong complex acids, $HCl + AlCl_3 = HAlCl_4$, or to ionization of the alkyl halides, $RCl + AlCl_3 = R^+AlCl_4^-$. For several years we have been studying interaction of aluminum and gallium chlorides with hydrogen chloride, alkyl halides, and aromatic hydrocarbons in order to attain a better understanding of these catalysts. The paper by Van Dyke [This Journal, 72, 3619 (1950)] presents results with aluminum bromide that are in marked contrast to our own findings and prompts us to summarize our results and conclusions.

No reaction could be observed between hydrogen chloride and aluminum or gallium chloride under a variety of conditions (300 to −120°). Since no combination can be detected at −120°, it is improbable that appreciable concentrations of $HAlCl_4$ can exist at room temperature.

Aluminum chloride and toluene do not react at −80°. However, hydrogen chloride causes the aluminum chloride to dissolve, forming a brilliant green solution. One mole of hydrogen chloride is absorbed per mole of aluminum chloride in solution. Removal of the hydrogen chloride, precipitates aluminum chloride; the hydrocarbon is unchanged. The reaction is attributed to the formation of an ionized salt of toluene and $HAlCl_4$ (I) [Brown and Pearsall, Abstracts, A. C. S. Meeting, New York, 1947].



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Gallium chloride and hydrogen chloride react with toluene and mesitylene similarly. Therefore the free acids $HAlCl_4$ and $HGaCl_4$ do not exist independently, but form stable salts with weak organic bases, such as aromatic hydrocarbons and conjugated olefins. The oily complexes which invariably accompany the use of Friedel–Crafts catalysts must be organic salts of this kind. These complexes must be essential to the reaction in furnishing a polar medium in which the ionic intermediates can form and react.

Gallium chloride and alkyl halides (MeCl, MeBr, MeI, EtCl) form stable 1:1 addition compounds at −46 to −80°: $RX + GaCl_3 = RX{:}GaCl_3$. Thus, at −78.5° gallium chloride dissolves in excess methyl chloride to form a clear solution. As excess methyl chloride is removed, two pressure plateaus are observed: 26.0 mm. between 5.4:1 and 1:1 mole ratio $MeCl/GaCl_3$ and 3.2 mm. between 0.9:1 to 0.1:1. The first plateau corresponds to a saturated solution of addition compound in methyl chloride; the second to the dissociation of solid addition compound. Similar data were obtained for the other halides.

Molecular weight determinations support the existence of $MeCl{:}GaCl_3$ in solution. Vapor pressure at −78.5° of solution containing 0.447 mmole of gallium chloride in 3.067 mmole methyl chloride was 28.94 mm. (34.00 for pure solvent). Assuming free $GaCl_3$ in solution, mol. wt. 147; assuming 0.447 mmole solvent effectively removed to form $MeCl{:}GaCl_3$ in solution, mol. wt. 172. The latter is in good agreement with the actual molecular weight 176 for monomeric gallium trichloride.

Dissolved gallium chloride exchanges very slowly with methyl bromide at −80° (25% in 10 days). Evidently the addition compound involves a covalent carbon-halogen bond and ionization, $Me\text{–}Br{:}GaCl_3 = Me^+ [BrGaCl_3]^-$, must be a relatively slow process under these conditions, if it occurs at all.

Originally our observation of 1:1 compounds was in good agreement with the report by Van Dyke [Abstracts, A. C. S. Meeting, Atlantic City, 1949] that aluminum bromide forms similar addition compounds. However, in this recent paper in This Journal, he states that such compounds do not exist. He finds no compound $MeBr{:}AlBr_3$ at −56°. In view of our results, this observation is highly surprising and warrants reinvestigation.

We are continuing our studies in the field and hope to resolve the discrepancy.

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THE HÜTTIG MULTILAYER ADSORPTION ISOTHERM[1]

Sir:

Hüttig[2] has derived a new adsorption isotherm by a very fundamental modification of the well-known B.E.T. kinetic argument. Namely, he

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[1] The opinions expressed herein are those of the author and do not necessarily reflect the views of the Navy Department. Article not copyrighted.

[2] Hüttig, *Monatsh.*, 78, 177 (1948).