COMMUNICATIONS TO THE EDITOR

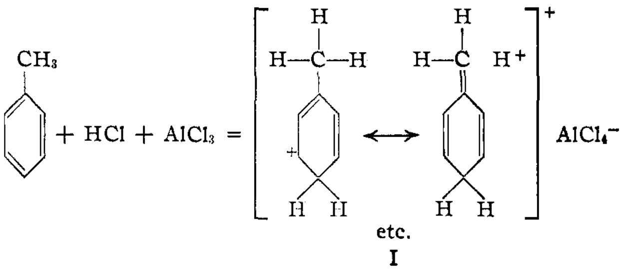
INTERACTION OF FRIEDEL-CRAFTS CATALYSTS WITH ALKYL HALIDES AND AROMATIC HYDROCARBONS

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).

assumes that, for example, the rate at which the number of molecules in the second layer increases is proportional to the number of "uncovered" first layer molecules (in agreement with B.E.T.) and the rate at which this number decreases is proportional to the *total* number of molecules in the second layer (in disagreement with the B.E.T. theory which uses instead the number of *uncovered* second layer molecules). These two rates are equated at equilibrium. Otherwise the two theories have identical assumptions. Ross[3] and Fergusson and Barrer[4] have examined and extended the Hüttig theory in some detail.

The Hüttig equation may be useful as an empirical equation but in the writer's opinion the derivations[2,4] on which the equation is based are fallacious[5]:

(1) The Hüttig kinetic derivation violates the principle of microscopic reversibility because the equilibrium condition (for example, for the second layer) is obtained by equating the rates of two molecular processes which are *not* the reverse of each other.[6]

(2) In the statistical derivation of Fergusson and Barrer different layers are treated as different "phases" in equilibrium. The equilibrium condition is taken as $\mu_1 = \mu_2 = \mu_3 = \ldots$, where the μ_i are chemical potentials. However, it is easy to show by the standard method of minimizing the total free energy of the combined "phases" that this is *not* the correct equilibrium condition here, since the free energy of the i-th layer ("phase") depends not only on the number of molecules in the i-th layer but *also* on the number of molecules in the $(i - 1)$-th layer.[4] That the Hüttig free energy is not the correct minimum (B.E.T.) free energy is the essential reason why, for the same value of the B.E.T. constant c, the Hüttig isotherm is always below the B.E.T. isotherm and hence accounts for the accidental better agreement of the Hüttig isotherm with experiment for $p/p_0 < 0.8$ (*i. e.*, for *other* reasons, the B.E.T. model has too low a free energy).

Actually, those assumptions which the B.E.T. and Hüttig theories have in common are sufficient to lead uniquely to the B.E.T. equation, as is clear from a statistical argument[7] which makes no assumption about kinetic mechanism.

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(3) Ross, *J. Phys. and Colloid Chem.*, **53**, 383 (1949).

(4) Fergusson and Barrer, *Trans. Faraday Soc.*, **46**, 400 (1950).

(5) However, in fairness to Fergusson and Barrer it should be emphasized that they intentionally set out to find the statistical treatment which would lead to Hüttig's kinetic result. To accomplish this the assumption $\mu_1 = \mu_2 = \mu_3 = \ldots$ in (2), below, had to be used. The fact that this assumption does not lead to the minimum free energy for the system of adsorbed molecules is of course just a reflection of the violation of the principle of microscopic reversibility already present in the original kinetic derivation (see (1) below).

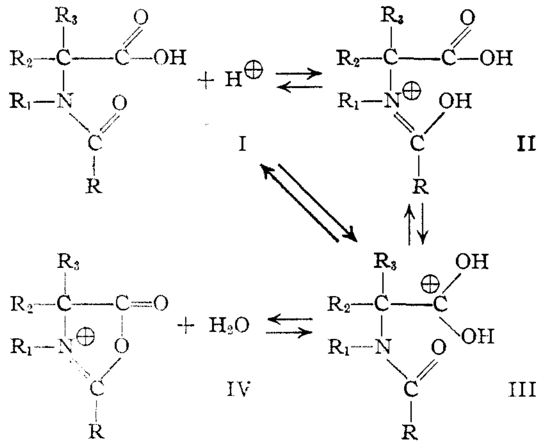
(6) Tolman, "Principles of Statistical Mechanics," Oxford Univ. Press, New York, N. Y., 1938, p. 163.

(7) Hill, *J. Chem. Physics*, **14**, 263 (1946); see also THIS JOURNAL, **68**, 535 (1946).

THE ACID CATALYZED CYCLIZATION OF α-ACYLAMINO ACIDS

Sir:

In the course of an investigation of the ionization of certain polyfunctional compounds in absolute sulfuric acid solutions the following van't Hoff "i" factors[1-3] were observed: glycine, 2.2; acetylglycine, 2.5; benzoylglycine, 3.6; and benzoylsarcosine, 3.8. These data suggested that in sulfuric acid solutions α-acylamino acids are cyclized, at least in part, to the corresponding oxazolonium ions via the following reaction mechanism:



The above conclusion was confirmed when it was found that an intense red-violet color, characteristic of basic solutions of azlactones derived from the *p*-nitrobenzoylamino acids,[4,5] was formed when a sulfuric acid solution of *p*-nitrobenzoylalanine was quickly poured into an excess of cold aqueous potassium hydroxide, and when a sulfuric acid solution of α-acetamidocinnamic acid, which had been allowed to stand overnight at room temperature, was poured into cold water to give 2-methyl-4-benzal-5-oxazolone, m. p. 150–152°,[6] either alone or when mixed with an authentic sample.

The influence of the R, R_1, R_2 and R_3 groups in determining the "i" factor can only be evaluated by consideration of their respective influences in the several equilibrium reactions noted above. The limited cyclization of acetylglycine in sulfuric acid solutions is in accord with the reported ease of hydrolysis of 2-methyl-5-oxazolones,[7] the equilibrium in this case favoring the noncyclic structures II and III. In contrast the "i" values indicate that the cyclization of benzoyl-

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(1) L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **55**, 1900 (1935).

(2) H. P. Treffers and L. P. Hammett, *ibid.*, **59**, 1708 (1937).

(3) M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

(4) E. Waser and E. Brauchli, *Helv. Chim. Acta*, **7**, 757 (1924).

(5) P. Karrer and R. Keller, *ibid.*, **26**, 50 (1943).

(6) M. Bergmann and F. Stern, *Ann.*, **448**, 20 (1926).

(7) H. E. Carter, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 198.