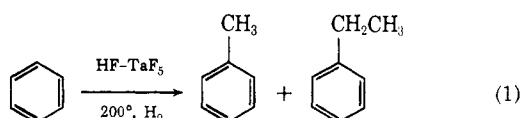# Communications to the Editor

Strong Acid Chemistry. I. Reactions of Aromatics in the Hydrogen Fluoride–Tantalum Pentafluoride (HF–TaF₅) Acid System

Sir:

We would like to report on an unexpected strong acid catalyzed direct conversion of benzene to toluene and ethylbenzene in the hydrogen fluoride–tantalum pentafluoride (HF–TaF₅) acid system.

Hydrocarbon chemistry or, more precisely, carbonium ion chemistry in acid systems which are composed of certain Lewis acids or Lewis acid–protonic acid mixtures has been extensively investigated in recent years.[1–3] The increase in the acidity of a solution on the addition of antimony pentafluoride to Brönsted acids such as fluorosulfonic acid[4] ($H_0 = -14.21$) or hydrofluoric acid ($H_0 = -11$) reflects an increase in concentration of the highly acidic $H_2SO_3F^+$ and H_2F^+ ions.[5–7] In this paper we report on the chemistry of hydrocarbons in the hydrogen fluoride–tantalum pentafluoride acid system. Both components of this polar liquid strong acid system are very thermally stable and not catalytically limited by irreversible reduction to inactive species under high hydrogen pressure above room temperature as are antimony pentafluoride containing systems.[8,9] This initial report will deal with the reactions of benzene and toluene. All reactions were carried out in a 1-l. Parr Model 4520 Hastelloy C stirred reactor or in a Parr Model 4712 Hastelloy C 45-ml screw cap reactor stirred with a magnetic stirring bar sealed in Teflon. Product identifications were confirmed by elemental analyses and infrared and nmr spectroscopy. Benzene reacts at 200° to form toluene and ethylbenzene (eq 1) as the

$$\text{C}_6\text{H}_6 \xrightarrow[\text{200°, H}_2]{\text{HF–TaF}_5} \text{C}_6\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \quad (1)$$

major products in 36 and 40% yields, respectively, based upon the benzene converted (~40%) in 16 hr in the presence of added hydrogen.

The reaction is accompanied by the formation of polyphenyls and more highly condensed aromatics which are formed *via* an oxidative cationic polymerization mechanism described previously by Kovacic and coworkers.[10]

(1) G. A. Olah, Ed., "Friedel–Crafts and Related Reactions," Vol. I–IV, Interscience, New York, N. Y., 1963–1965.

(2) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Vol. I–IV, Interscience, New York, N. Y., 1968–1973.

(3) G. A. Olah, *Chem. Eng. News*, **45** (12) 77 (1967).

(4) The 1:1 fluorosulfonic acid–antimony pentafluoride system has been dubbed "magic acid" ($H_0 > -17$).

(5) R. J. Gillespie, K. Ouchi, and G. P. Pez, *Inorg. Chem.*, **8**, 63 (1969).

(6) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *J. Amer. Chem. Soc.*, **93**, 5083 (1971); R. J. Gillespie and T. E. Peel, *ibid.*, **95**, 5173 (1973).

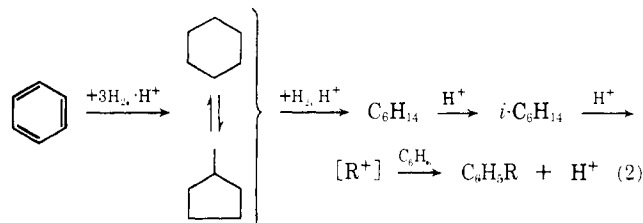(7) R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971).

(8) J. M. Oelderik, E. L. Mackor, J. C. Platteeuw, and A. van der Wiel, U. S. Patent 3,201,494, Aug 17, 1965, Col. 4, 1. 50–54.

(9) G. A. Olah, J. Shen, and R. Schlosberg, *J. Amer. Chem. Soc.*, **92**, 3831 (1970).

(10) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963); P. Kovacic and J. Oxiomek, *ibid.*, **29**, 100 (1964); P. Kovacic and F. W. Koch, *ibid.*, **28**, 1864 (1963); P. Kovacic and A. Kyriakas, *J. Amer. Chem. Soc.*, **85**, 454 (1963).

Analysis of early reaction products indicates that the initial products in the reaction of benzene includes biphenyl. The hydrogen required in the formation of toluene and ethylbenzene can be provided by these condensation reactions alone, but product yields are increased by 15–25% when the reaction is carried out in the presence of added hydrogen. In a solvent such as Freon 113 (1,1,2-trichlorotrifluoroethane), product yields are markedly suppressed indicating that the bimolecular initiation reaction of benzene to supply hydrogen and form biphenyl, etc., is required. The formation of small amounts of alkylbenzenes from benzene was observed in the presence of aluminum chloride as early as 1883 by Friedel and Crafts.[11] It has also been found with aluminum bromide,[12] aluminum chloride and hydrogen chloride,[13] nickel–silica–alumina,[14] and over a nickel on kieselguhr catalyst.[15] Ipatieff[16] pictured the reaction mechanistically as an ethylene alkylation of benzene, the ethylene being formed by cleavage of cyclohexane which was in turn formed by hydrogenation of benzene.

The cleavage of cyclohexane to three ethylene units as postulated by Ipatieff is a symmetry-allowed thermal cycloreversion process but is thermodynamically unfavorable by about 37 kcal/mol. A more likely source of the alkyl groups is through a hydrogenolysis to form hexanes followed by trapping of the reactive carbonium ion intermediates generated during the paraffin isomerization and cracking reactions at the high temperatures involved (eq 2). In other words, the migrating alkyl

$$\text{C}_6\text{H}_6 \xrightarrow{+3\text{H}_2, \cdot\text{H}^+} \left\{ \begin{array}{c} \text{cyclohexane} \\ \updownarrow \\ \text{methylcyclopentane} \end{array} \right\} \xrightarrow{+\text{H}_2, \text{H}^+} \text{C}_6\text{H}_{14} \xrightarrow{\text{H}^+} i\text{-C}_6\text{H}_{14} \xrightarrow{\text{H}^+} [\text{R}^+] \xrightarrow{\text{C}_6\text{H}_6} \text{C}_6\text{H}_5\text{R} + \text{H}^+ \quad (2)$$

carbonium ions from the cracking of hexyl cations and from dealkylation of larger alkylbenzenes are trapped by the excess aromatic solvent to form the observed major products and some other alkylaromatics. Similarly, in the case of toluene, in addition to normal disproportionation products, ethylbenzene (12%) and cumene (21%) are formed (eq 3). The formation of these compounds can be explained by a series of steps analogous to those proposed for benzene.

We have tried other Lewis acids in HF solution and only TaF₅ and NbF₅ were found to efficiently effect this conversion. The lack of any substantial reactivity of other metal fluorides (especially antimony, arsenic, and vanadium pentafluorides) is difficult to explain. The

(11) C. Friedel and J. M. Crafts, *Bull. Soc. Chim. Fr.*, **39**, 195 (1883); *ibid.*, **39**, 306 (1883).
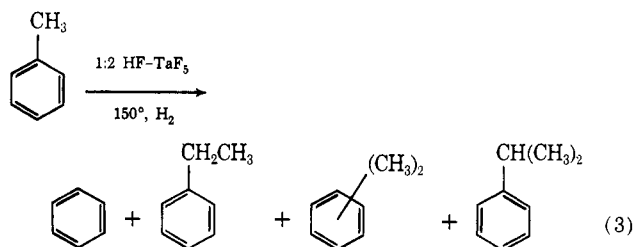
(12) E. Wetyporoch and H. Sagal, *Chem. Ber.*, **66**, 1306 (1933).

(13) V. N. Ipatieff and V. I. Komarewsky, *J. Amer. Chem. Soc.*, **56**, 1926 (1934).

(14) V. N. Ipatieff and G. S. Monroe, *J. Amer. Chem. Soc.*, **69**, 710 (1947).

(15) B. A. Kazanskii, M. Rozengart, and Z. F. Kuznetsova, *Dokl. Akad. Nauk SSSR*, **126**, 571 (1959).

(16) V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," Macmillan, New York, N. Y., 1936, pp 711–713.

$$\text{(3)}$$

answer probably lies in the nature of the Lewis acid-benzene complex. In the case of the very strongly acidic antimony pentafluoride, all of the fluoride is complexed with hydrogen fluoride. Upon addition of the aromatic in 10 molar excess a stable insoluble solid complex is precipitated.[17] In the more weakly acidic TaF_5 case, a soluble, relatively unstable complex is formed leaving some TaF_5 complexed with HF in solution. The formation of this polar liquid phase acid which is not subject to reduction by hydrogen provides a suitable reaction environment. Further work is in progress to unravel the scope of the possible new chemistry of hydrocarbons in the $HF-TaF_5$ acid system.

Acknowledgment. The authors gratefully acknowledge stimulating and helpful discussions with Dr. G. M. Kramer.

(17) G. A. Olah, P. Schilling, and I. M. Gross, *J. Amer. Chem. Soc.*, **96**, 876 (1974).

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Strong Acid Chemistry. II. Catalytic Hydrogenation of Aromatics in Hydrogen Fluoride–Tantalum Pentafluoride and Related Strong Acid Systems

Sir:

We wish to report what we believe to be the first example of catalytic hydrogenation of aromatics by a strong acid system which does not contain a noble metal or other conventional hydrogenation cocatalyst.

In order to verify that cycloalkanes could indeed be cleaved as postulated in the previous communication and the intermediate carbonium ions subsequently hydrogenated in $HF-TaF_5$, a series of reactions were carried out under milder conditions (50 vs. 200°) with cycloalkanes (10–20%) in Freon 113 or a paraffinic solvent, plus hydrogen. Under these conditions cyclohexane or methylcyclopentane (MCP) is selectively hydrogenated to saturated hexanes. Similarly, decalin is converted to a mixture of isobutane, cyclohexane, and methylcyclopentane, the cycloalkanes reacting further as described above.

In order to further pursue the extent of the hydrogenation ability of the system, a solution (257 ml) of benzene (5 mol %) in n-hexane was treated with hydrogen (175 psig at 25°, 0.42 mol) at 50° in a 10:1 $HF-TaF_5$ (2.0 mol/0.20 mol) system, in a 1-l. Hastelloy C Parr stirred reactor. The hydrogenation of benzene proceeded at a pseudo-first-order rate of 1.0×10^{-4} sec^{-1} ($t_{1/2} = 1.9$ hr). The benzene remains distributed almost entirely in the hydrocarbon layer, and therefore it is easy to simultaneously follow benzene disappear-

ance, cyclohexane formation, isomerization of cyclohexane to its equilibrium mixture with methylcyclopentane, and cleavage to the isohexane products. In a similar experiment in a continuous reactor $\sim$19 mol of benzene per mole of TaF_5 was passed over the catalyst with no significant change in activity. When the same reaction is carried out in n-pentane, the formation and equilibration of the saturated hexane isomers can also be observed.[1a] The rate and extent of benzene hydrogenation can of course be varied over a wide range by controlling the hydrogen partial pressure and ratio of catalyst to reactant.

One of the most significant aspects of our results is that we have shown that $HF-TaF_5$ and other suitable strong acid systems such as $HBr-AlBr_3$[1] and $HF-NbF_5$ can tolerate aromatics which were previously considered as catalyst poisons.[2,3] $HF-SbF_5$ can also efficiently effect this conversion until reduction to inactive SbF_3[2,4] or reaction of the aromatic with SbF_5 becomes significant.[5] Obviously, this concept is limited to acid systems which are not subject to reduction by hydrogen or which do not react with aromatics in incompatible side reactions such as sulfonation.

The ability of this system to operate as a hydrogenation catalyst can be associated with the formation of metastable acid–aromatic complexes and a stable and highly solvating polar liquid phase strong acid system, which are not subject to reduction. Hydrogen fluoride (bp 17.5°) is an ideal Brönsted acid cocatalyst because of its stability and the low temperatures and pressure required for maintaining a sufficient portion of the system in the liquid phase. Also, tantalum pentafluoride is itself a strongly acidic Lewis acid by virtue of the facts that it has five very electronegative fluorine atoms attached to a coordinatively unsaturated metal atom and is very resistant to reduction by hydrogen. The hydrogenation most probably proceeds in the acid layer via initial protonation of benzene[6] followed by hydride transfer from hydrogen directly, or more likely from one of the isoalkanes or MCP in solution, to form dihydrobenzene. Subsequent hydrogenation would energetically favor complete reaction of this species (eq 1).

$$\text{(1)}$$
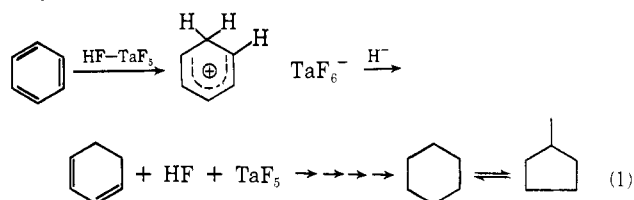
Work is now in progress to extend this discovery to more complex aromatic molecules.

(1) This experiment was carried out by (a) Dr. J. P. Wristers and (b) Dr. G. M. Kramer, of these laboratories.
(2) J. M. Oelderik, E. L. Mackor, J. C. Platteeuw, and A. van der Wiel, U. S. Patent 3,201,494, Aug 17, 1965, Col. 4, 1. 50–54.
(3) C. L. Thomas, "Catalytic Processes and Proven Catalysts," Academic Press, New York, N. Y., 1970, p 17.
(4) G. A. Olah, J. Shen, and R. Schlosberg, *J. Amer. Chem. Soc.*, **92**, 3831 (1970).
(5) G. A. Olah, P. Schilling, and I. M. Gross, *J. Amer. Chem. Soc.*, **96**, 876 (1974).
(6) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970).

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