

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 TaF₅ case, a soluble, relatively unstable complex is formed leaving some TaF₅ 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-TaF₅ acid system.

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(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.

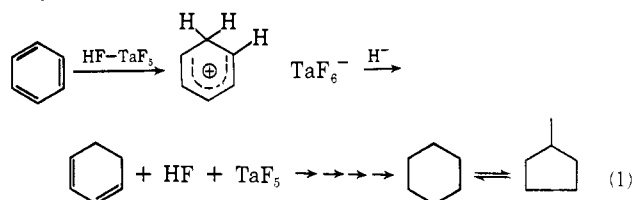
In order to verify that cycloalkanes could indeed be cleaved as postulated in the previous communication and the intermediate carbonium ions subsequently hydrogenated in HF-TaF₅, a series of reactions were carried out under milder conditions (50 vs. 200°) with cycloalkanes (10–20%) in Freon 113 or a 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-TaF₅ (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 ~19 mol of benzene per mole of TaF₅ 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-TaF₅ and other suitable strong acid systems such as HBr-AlBr₃¹ and HF-NbF₅ can tolerate aromatics which were previously considered as catalyst poisons.^{2,3} HF-SbF₅ can also efficiently effect this conversion until reduction to inactive SbF₃^{2,4} or reaction of the aromatic with SbF₅ 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 Brønsted 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 benzene⁶ 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).



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).

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