The methyl and ethyl carbonium ions are apparently rapidly removed by normal butane by reactions analogous to reaction (4) to form methane and ethane, respectively. Presumably n-$C_4H_9^+$ does not isomerize directly to iso-$C_4H_9^+$ but goes instead by way of a combination of reactions (6) and (7), in agreement with a suggestion recently made by Greensfelder and Samaniego (*5*). Removal of propylene will tend to block the reaction (7) and hence the isomerization of the n-butane.

The decomposition of isobutane apparently also is influenced by removing the olefins. The formation of surface methyl carbonium ions is effected presumably by shifting reaction (7) from right to left in the above scheme.

Further details of interpretation will be reserved for the more complete paper now being prepared covering our kinetic studies on the cracking of propane, isobutane, normal butane, and also normal hexane. The relation of the present observations to the kinetics of the decomposition of these hydrocarbons without removal of olefins will also be discussed in the fuller report of the work.

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REFERENCES

1. FRANKLIN, F. L., AND NICHOLSON, D. E., *J. Phys. Chem.* **60**, 59–62 (1956).

2. KALLO, D., AND SCHAY, G., *Acta. Chim. Hung.* **39**, 183–212 (1963).

3. YOUNG, R. E., PRATT, M. K., AND BIALE, J. B., *Anal. Chem.* **24**, 551–555 (1952).

4. COULSON, D. M., *Anal. Chem.* **31**, 906–910 (1959).

5. GREENSFELDER, B. S., AND SAMANIEGO, J. A., "Isomerization," *Scuola Azione* (Part I, No. 15), 61–104; (Part II, No. 16), 3–27; (Part III, No. 17), 3–37 (1960–1961).

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Proton Acids as Electron Acceptors on Aluminosilicates

Perylene and other polynuclear aromatics are converted to cation radicals upon adsorption on silica-alumina, zeolites, and certain other acid catalysts. Several investigators have attributed this fact to the presence of strong Lewis acid centers on these catalysts (*1–4*).

Aalbersberg *et al.* (*5*) have reported that molecular oxygen, in the presence of strong Bronsted acids, converts these aromatics to cation radicals. Radical-ion formation was found to strongly depend on the acid strength of the medium. The results were interpreted on the basis that oxygen was the electron acceptor. Stringent removal of oxygen, such as by hydrogen treatment at elevated temperatures, markedly reduces or eliminates the formation of cation radicals by silica-alumina (*3, 6–8*). Accordingly, it has been suggested that the electron acceptor on silica-alumina is adsorbed oxygen rather than Lewis sites (*6, 8*).

Hirschler and Hudson (*8*) found that the H_R acid strength of solid acids influenced the extent of perylene radical-ion formation in a manner similar to that observed by Aalbersberg (*5*) for liquid Bronsted acids, and showed that for both solid and liquid acids the ability to generate radical ions substantially ceased below an H_R acid strength corresponding to about 57–60% H_2SO_4. It was therefore proposed that on silica-alumina, adsorbed oxygen accepted an electron from perylene under the catalytic influence of Bronsted acids.

We would now like to suggest an alternative explanation for the conversion of aromatics to cation radicals on solid acid catalysts and solutions of strong Bronsted acids, namely that the electron removed from the aromatic is trapped by acid protons, with the oxygen serving as a catalyst rather than as an electron acceptor. This suggestion stems from recent work by Aly *et al.* (*9*), which showed that ferrocene transfers an electron to proton acids, molecular oxygen serving as a catalyst for the reaction. The rate of this reaction is proportional to the first power of the concentrations of oxygen, acid, and ferrocene. For four different proton acids, the velocity constant k was related to the proton transfer constants K by a Bronsted equation. This was taken to indicate that partial proton transfer occurs in a bridged activated complex, and that this is easier if the acid is relatively strong.

The hypothesis that electrons are trapped by acid protons provides a better explanation of the role of acid strength on radical-ion formation on silica-alumina (*8*) than the assumption that oxygen is the electron acceptor. An aromatic proton complex is considered an unlikely intermediate in the transfer of an electron to oxygen because it should lose an electron much less readily than the neutral hydrocarbon.

The belief of Aalbersberg *et al.* (*5*) that oxygen was a reactant was supported by their finding that

$$\frac{[\mathrm{Ar}^{\underset{\cdot}{+}}]}{[\mathrm{Ar}]\,[\mathrm{O_2}]} = \text{constant} \qquad (1)$$

which they defined as the equilibrium constant. However, the constancy of this expression is consistent with the view that oxygen is only a catalyst if one assumes a reversible equilibrium where the rate of radical-ion formation is proportional to the concentrations of oxygen, acid, and aromatic hydrocarbons (as found for ferrocene) and the rate of decomposition of the complex is proportional to the concentration of complex. Then, if k_f and k_b are the velocity constants for the forward and back reactions,

$$K = \frac{k_\mathrm{f}}{k_\mathrm{b}} = \frac{[\mathrm{Ar}^{\underset{\cdot}{+}}\mathrm{BH}^{-}]}{[\mathrm{Ar}]\,[\mathrm{O_2}]\,[\mathrm{BH}]} \qquad (2)$$

which reduces to (1) at a constant acid concentration as in the experiments of Aalbersberg.

It also follows from (2) that if the reaction is a reversible equilibrium, and if oxygen is reversibly adsorbed on a catalyst surface, that pumping off the oxygen will reduce the radical-ion concentration just as if oxygen were a true reactant rather than a catalyst for electron transfer to proton acids.

The results of Aly *et al.* (*9*) thus provide some additional support for the existence of Bronsted acids on silica-alumina and zeolite catalysts, and for the view (*8*) that these Bronsted sites, rather than Lewis sites, are responsible for the chemisorption of perylene. Also, since perylene chemisorption was found to be related to H_R acid strength, it is an indication that triphenylcarbinol and other H_R indicators are converted to their carbonium ions by Bronsted sites rather than by Lewis sites as proposed by Hall and co-workers (*10, 11*).

REFERENCES

1. BROUWER, D. M., *Chem. and Ind.*, p. 177 (1961); *J. Catalysis* **1**, 372 (1962).

2. ROONEY, J. J., AND PINK, R. C., *Proc. Chem. Soc.*, p. 70 (1961); *Trans. Faraday Soc.* **58**, 1632 (1962).

3. HALL, W. K., *J. Catalysis* **1**, 53 (1962).

4. FLOCKHART, B. D., AND PINK, R. C., *J. Catalysis* **4**, 90 (1965).

5. AALBERSBERG, I. J., HOIJTINK, G. J., MACKOR, E. L., AND WEIJLAND, W. P., *J. Chem. Soc.*, p. 3055 (1959).

6. FOGO, J. K., *J. Phys. Chem.* **65**, 1919 (1961).

7. IMAI, H., ONO, Y., AND KEII, T., *J. Phys. Chem.* **69**, 1082 (1965).

8. HIRSCHLER, A. E., AND HUDSON, J. O., *J. Catalysis* **3**, 239 (1964).

9. ALY, M., BRAMLEY, R., UPADHYAY, J., WASSERMANN, A., AND WOOLLIAMS, P., *Chem. Commun.*, p. 404 (1965).

10. LEFTIN, H. P., AND HALL, W. K., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960,* **1**, p. 1353, 1307 (Editions Technip, Paris, 1961).

11. PORTER, R. P., AND HALL, W. K., Paper presented at American Chemical Society meeting, Atlantic City, N. J., September, 1965.

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