chromia-alumina catalyst (Table 1). Equilibrium distributions of the 1-phenylbutene isomers may be determined from these data. Thermodynamic data to calculate these distributions are unavailable at the present time. Experimental distributions of four of the different isomers are shown in Table 3. 1-Phenyl-3-butene, the fifth possible isomer, was not identified. It was probably present only in a very small amount. The difference between the olefin distribution of Experiment No. 2, at a liquid hourly space velocity (LHSV) of 36.6, and Experiment No. 3, at an LHSV or 8, suggests that the initial dehydrogenation rate to 1-phenyl-2-butenes is faster than that to the 1-phenyl-1-butenes. Equilibrium between the olefin isomers is probably reached in Experiments 3, 4, and 5. Similar isomer distributions were observed over platinum-on-silica gel catalyst (*1*).

The cis/trans ratio of the 1-phenyl-1-butenes is substantially lower than the cis/trans ratio calculated from thermodynamic data (*5*) for the 1-phenyl-1-propenes (0.15 versus 0.65 at 371°C, Table 2). The difference may have steric reasons. There should be considerably more steric interference between the ethyl and phenyl groups of *cis*-1-phenyl-1-butene than between the methyl and phenyl groups of *cis*-1-phenyl-1-propene. There would be no such interference in the corresponding trans olefins.

Equilibrium distributions of the four 1-phenylbutene isomers between 371° and 482°C temperatures are shown in Fig. 1. Variation of the observed 1-phenylbutene isomer distribution with temperature follows the general pattern of olefin isomer distributions; that is, at higher temperatures the concentrations of the individual isomers converge.

REFERENCES

1. CSICSERY, S. M., *J. Catalysis* **9**, 336 (1967) (this issue).

2. PINES, H., AND CHEN, C. T., *J. Am. Chem. Soc.* **82**, 3562 (1960).

3. PINES, H., AND GOETSCHEL, C. T., *J. Catalysis* **6**, 371 (1966).

4. CSICSERY, S. M., AND PINES, H., *J. Catalysis* **1**, 329 (1962).

5. ROSSINI, F. D., *et al.* "Selected Values of Properties of Hydrocarbons and Related Compounds." API Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, (1959).

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Received July 31, 1967; revised September 25, 1967

The Selective Hydrogenation of Unsaturated Hydrocarbons over Various Electron Donor–Acceptor Complexes*

It was previously demonstrated (*1*) that the H_2–D_2 exchange reaction proceeds reversibly at room temperature over the electron donor–acceptor (EDA) complexes of sodium (or magnesium) with various aromatic compounds such as polycondensed aromatic hydrocarbons, their nitro-, and cyano-substituted derivatives, and quinones, while it does not take place over each of such electron acceptor compounds or donor metals alone even at higher temperatures. It was also found that the activity of the EDA complexes for the H_2–D_2 exchange reaction was strongly dependent not only upon the electron affinity of acceptor molecules, but also upon the ionization potential of the donor molecules employed (*2*). The H_2–D_2 exchange reaction proceeded negligibly over the EDA complexes of too strong or too weak acceptors

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with sodium or magnesium even at higher temperatures. The EDA complexes "active" for the H_2–D_2 exchange reaction exhibited a considerable amount of hydrogen adsorption at room temperature.

In this communication we should like to report that a highly selective hydrogenation of olefins and acetylenic compounds was observed over the EDA complexes of sodium, and that the selectivity was attributed to the controlled poisoning of the catalyst surface by the chemisorption of hydrogen and unsaturated compounds.

A closed circulating or static system was employed to study the hydrogenation of olefins and acetylenic compounds. Various EDA complexes were prepared on the wall of glass reactors by successive evaporation of the components, sodium and each of the acceptor molecules in a vacuum, as described previously (*1*, *2*). The reaction products were analyzed by gas chromatography using an activated alumina column.

When a mixture of ethylene and hydrogen gas (1:1 mixture of 25 cm Hg total pressure) was admitted to the EDA complexes of sodium (~0.01 mole) with phthalonitrile, anthracene, *p*-quinone, tetrachlorophthalonitrile, anthraquinone, tetracyanobenzene, *p*-chloranil, pyrene, and violanthrene B (~0.001 mole) at temperatures between 50° and 120°C, small amounts of ethane (the yield was estimated to be about 10%) were formed in 40 hr only over the EDA complexes of such acceptors as tetracyanobenzene, tetrachlorophthalonitrile, anthraquinone, perylene, and violanthrene B. Propylene (10 cm Hg) was also hydrogenated at 100°C over these EDA complexes active for the ethylene hydrogenation, and the yield of propane in 40 hr was in the same order of magnitude as that of the ethylene hydrogenation over each of these EDA complexes. It is interesting that the rate of the ethylene or propylene hydrogenation was dependent upon the relative partial pressures of ethylene or propylene to hydrogen. When the ratio was varied from 1 to 5, the hydrogenation rate increased considerably over the EDA complexes of violanthrene B, Fe-phthalocyanine, or tetrachlorophthalonitrile with sodium.

When the mixture of H_2–D_2 and ethylene (or propylene) was admitted to these EDA complexes, the H_2–D_2 exchange reaction was retarded by increasing the relative content of ethylene (or propylene), which suggests that ethylene (or propylene) and hydrogen adsorb competitively over the EDA complexes. The hydrogenation of olefins, accordingly, seems to proceed more easily when hydrogen and olefins are adsorbed to comparable amounts on the catalyst surface.

Acetylene, a stronger acceptor gas, was not hydrogenated over these EDA complexes, probably because its chemisorption is too strong to allow hydrogen adsorption. The H_2–D_2 exchange reaction proceeded negligibly even at higher temperatures over the active EDA complexes when a small amount of acetylene was mixed in the hydrogen. However, when weaker acceptor gases such as methylacetylene, butadiene, and dimethylacetylene (10 cm Hg) were added to the H_2–D_2 mixture, the H_2–D_2 exchange reaction proceeded over the EDA complexes at 100°C, and hydrogenation took place to propylene, a mixture of 2- and 1-butenes, and *cis*-2-butene, respectively. It was also found that the H_2–D_2 exchange reaction was only partially retarded by these olefins or methyl- and dimethylacetylenes. The extent of the retardation by these gases is to be correlated with their affinity with the complex surface. It is, consequently, understandable that methylacetylene was hydrogenated only to propylene and not to propane, as far as methylacetylene was present in the ambient gas.

A similar selective hydrogenation was observed in the case of butadiene and dimethylacetylene over these EDA complexes, where only butenes were formed in the first stage and then butane was produced.

When an artificial graphite was employed as an electron acceptor to form a complex with sodium or potassium, the hydrogenation of ethylene, propylene, methylacetylene, 1-butene, and butadiene proceeded with a considerable rate at 25°C over the complexes under similar reaction conditions as employed in the other systems. From methylacetylene, propylene and propane were produced quantitatively, step by step with a complete selectivity. Butadiene was hydrogenated first to a mixture of *cis*-2- and *trans*-2-butenes rapidly and then to butane at 25°C over the complexes of graphite with sodium or potassium. When a mixture of dimethylacetylene and D_2 was introduced into the graphite–Na complex system pretreated by D_2 at 80°C, *cis*-2-butene-d_2 was only obtained at 25°C in 40 hr.

REFERENCES

1. ICHIKAWA, M., SOMA, M., ONISHI, T., ANI TAMARU, K., *J. Phys. Chem.* **70,** 2069, 302((1966); *J. Catalysis* **6,** 366 (1966).

2. ICHIKAWA, M., SOMA, M., ONISHI, T., ANI TAMARU, K., *Trans. Faraday Soc.* **63,** 997 1215 (1967); *Bull. Chem. Soc. Japan* **40,** 1015 1294 (1967); *Trans. Faraday Soc.,* in press.

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Received September 5, 1967