JOURNAL OF CATALYSIS 9, 416–420 (1968)

NOTES

The Reactions of *n*-Butylbenzene over Nonacidic Chromia-Alumina

Equilibrium Distribution of the 1-Phenylbutene Isomers

Earlier we discussed the reactions of *n*-butylbenzene over platinum-containing catalysts (*1*). Here we report our *n*-butylbenzene results over nonacidic chromia-alumina. This catalyst was similar to the one used by Pines and Chen (*2*). Experimental and analytical procedures were the same as described before (*1*).

n-Butylbenzene is isomerized over nonacidic chromia-alumina to *sec*-butylbenzene (Table 1). (Practically no isobutylbenzene is formed.) The reaction proceeds by a radical mechanism involving phenyl or vinyl migration (*3*). Cyclization is limited, producing mostly methylindan. At 482°C, cyclization to a five-membered ring is favored over cyclization to a six-membered ring by a factor of more than 5.

Ethylbenzene (or styrene) and ethylene (or ethane) are the predominant products of hydrogenolysis. Hydrogenolysis probabilities of the different bonds of *n*-butylbenzene over nonacidic chromia-alumina are shown in Table 2.

Hydrogenolysis between secondary–secondary carbon atoms is 4 to 12 times higher

TABLE 1
REACTIONS OF *n*-BUTYLBENZENE OVER CHROMIA-ALUMINA CATALYSTS

	Experiment No.				
	1	2	3	4	5
H_2: *n*-butylbenzene mole ratio:	3.05	3.0	3.44	3.05	3.05
Reaction temperature (°C):	316	371	371	427	482
LHSV:	9	36.6	8	9	9
Residence time (sec):	0.33	0.10	0.31	0.27	0.25
Feed partial pressure (atm):	0.246	0.36	0.225	0.246	0.246
Liquid sample collected (min):	40–80	10–21	40–80	40–80	40–80
Products (moles per 100 moles of feed)					
Ethane, ethylene	—	—	—	0.05	0.17
Propane, propylene	—	—	—	—	0.16
1-Phenylbutenes	0.009	0.165	0.203	2.602	11.204
1-Methylindan	—	0.0016	0.0036	0.042	0.231
Methylindenes	—	—	—	0.0061	0.065
Naphthalene	—	—	—	—	0.057
sec-Butylbenzene	0.0041	0.0017	0.0040	0.039	0.157
Isobutylbenzene	—	—	—	0.0015	0.0044
1-Methyl-2-isopropylbenzene	—	—	—	—	0.037
1-Methyl-2-*n*-propylbenzene	—	—	—	0.0023	0.024
Benzene	0.0002	0.0004	0.0007	0.015	0.052
Toluene	0.0007	0.0009	0.0007	0.017	0.168
Ethylbenzene	0.001	0.001	0.001	0.055	0.240
n-Propylbenzene	—	—	—	0.0042	0.0093
Other	—	—	0.004	0.010	0.175
Total *n*-butylbenzene converted, mole %	0.015	0.171	0.214	2.798	12.42

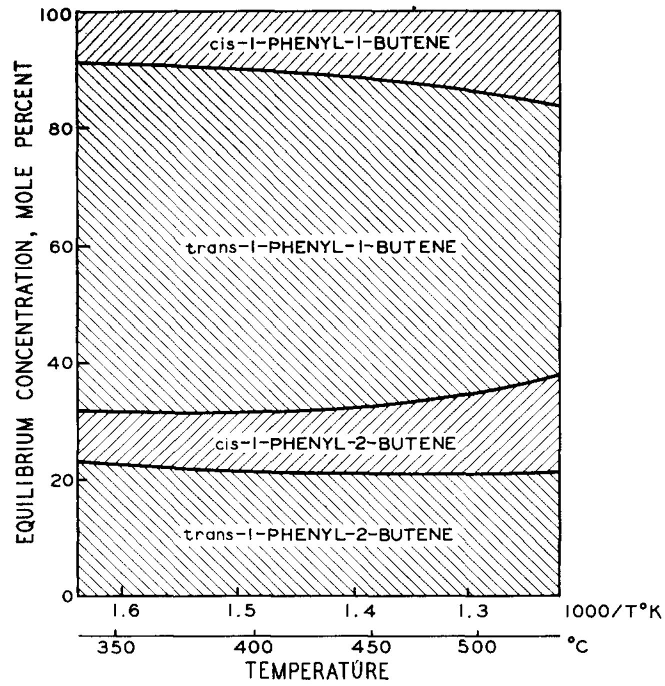

FIG. 1. Equilibrium distribution of the 1-phenylbutene isomers.

TABLE 2

PROBABILITIES OF C–C BOND HYDROGENOLYSIS

Bond broken:	Phenyl–α	α–β	β–γ	γ–δ
Percent of total hydrogenolysis at 427°C	16	19	60	5
Percent of total hydrogenolysis at 482°C	11	36	51	2

than breakage of the primary–secondary bond. A similar relationship was found by Csicsery and Pines (*4*) for the hydrogenolysis of C_5–C_8 paraffins. The reaction probably involves free radical intermediates.

Dehydrogenation to 1-phenylbutenes is the predominant (more than 90% of the total conversion) reaction over nonacidic

TABLE 3

DISTRIBUTION OF THE 1-PHENYLBUTENE ISOMERS IN THE DEHYDROGENATION OF *n*-BUTYLBENZENE OVER NONACIDIC CHROMIA-ALUMINA CATALYSTS

	Experiment No.				
	1	2	3	4	5
Temperature (°C):	316	371	371	427	482
LHSV:	9	36.6	8	9	9
Total conversion to 1-phenylbutenes (mole %):	0.009	0.165	0.203	2.605	11.204
Isomer Distribution (% of 1-Phenylbutenes)					
cis-1-Phenyl-1-butene	—	7	9	10	12.5
trans-1-Phenyl-1-butene	—	44	59.5	58	53.6
cis-1-Phenyl-2-butene	—	16	9.5	11	12.6
trans-1-Phenyl-2-butene	—	33	22	21	21.3
cis/trans Ratios					
1-Phenyl-1-butenes	—	0.16	0.15	0.17	0.23
1-Phenyl-2-butenes	0.47	0.48	0.42	0.55	0.59
1-Phenyl-1-propenes (calculated equilibrium ratio[a])	0.62	0.65	0.65	0.68	0.71

[a] Calculated from data published in ref. (*5*).

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).

SIGMUND M. CSICSERY

Chevron Research Company
Richmond, California

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

---

* Reactivity of Electron Donor–Acceptor Complexes. Part XII.