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Dehydrocyclodimerization

IV. The Reactions of Butenes

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Results with light paraffins suggest that olefins may be the key intermediates in dehydrocyclodimerization. Here we attempt to clarify the role of olefins by reacting butene at dehydrocyclodimerization conditions. At very short contact times over Pt–alumina, C_5–C_8 olefins and naphthenes represent a large fraction of the reaction product suggesting these compounds as intermediates in butene aromatization. C_5–C_8 olefins and naphthenes and some aromatics are also formed over acidic catalysts not containing any dehydrogenation component. These results strongly indicate that dehydrocyclodimerization proceeds by first converting the light paraffins to olefins then dimerizing these olefins and finally aromatizing the dimers. The mechanism is more fully explained in Paper V of this series.

Results of the previous parts of this series (1, 2) suggest olefins as key intermediates in dehydrocyclodimerization. In order to clarify the role of olefins, we reacted butene over various catalyst systems. The results were particularly useful in understanding the function of the acid component of dehydrocyclodimerization catalysts and in explaining the reaction mechanism.

Experimental Methods

Reaction conditions, catalysts, and analytical procedure are described in Part I of this series (*1*). Our feed was *trans*-2-butene (Matheson, C. P.), 99.84% pure by gas chromatographic analysis. It contained 0.13% *cis*-2-butene, 0.01% 1-butene, 0.01% *n*-butane, and 0.01% propylene.

Results and Discussion

Olefins over Pt–Alumina

Because *trans*-2-butene at our reaction conditions is completely converted to an equilibrium mixture of the butene isomers, similar reaction product distributions are expected from any C_4 olefin. Main reaction products at 560°C as a function of space velocity are shown in Fig. 1. More detailed reaction product distributions are two space velocities are shown in Table 1. Conversion to aromatics is about one and one-half times as high as that of butane under the same conditions. At 560°C and at residence times of 0.57 and 5.7 sec, 7 and 27% of the butene is converted to aromatics, respectively. The butenes/butadiene ratio is nearly constant (about 25:1) through the space velocity range investigated. This shows that the butene $\rightleftarrows$ butadiene equilibrium is established very fast. Olefin hydrogenation is slow; both iso- and *n*-butanes are produced. Butenes crack less and coke more than butanes.

Table 2 shows that the amount of C_5–C_8 olefins and naphthenes is significant at very short contact time. Figure 2 shows the variation of the C_6–C_8 product distribution with space velocity. The product contains more aromatics and less naphthenes at longer residence times. These concentration variations suggest that the aromatization of butenes proceeds through C_6–C_8 olefins and naphthenes.

TABLE 1

DEHYDROCYCLODIMERIZATION OF *n*-BUTENE OVER 0.8% PLATINUM ON ALUMINA CATALYST AT 560°C

Liquid hourly space velocity:	8.8	0.88	
Reaction effluent sampling time (min):	10	10	75
Product composition (wt %)			
n-Butane	1.60	5.95	5.03
Isobutane	0.80	3.34	3.27
Butenes	78.00	8.30	37.62
Butadiene	3.33	0.38	1.12
Pentenes, pentadienes	0.97	0.26	2.38
C_6–C_8 olefins, diolefins, and naphthenes	1.02		
Benzene	0.46	3.76	1.25
Toluene	1.03	7.08	3.50
Ethylbenzene, *m*- and *p*-xylenes	3.52	8.96	6.70
o-Xylene	1.17	2.88	2.16
C_9 aromatics	0.46	1.75	1.31
C_{10} aromatics	0.11	0.18	0.14
Naphthalene	0.08	0.67	0.50
$C_{11}+$ aromatics	0.33	1.87	1.40
Methane	1.03	16.22	6.20
Ethane, ethylene	1.65	11.52	4.33
Propane	0.16	6.78	1.16
Propylene	1.80	4.10	4.77
Hydrogen	0.60		1.26
Coke	1.88	16.00	15.90
Total	100.00	100.00	100.00
Total aromatics (wt %)	7.16	27.15	16.96
Ultimate yield (wt %)	58	38	38

Olefins over Acid Catalysts

As shown above, Pt–alumina catalyzes the dimerization of butenes. Our earlier correlations between catalyst acidity and the rate of dehydrocyclodimerization suggest that this dimerization is acid catalyzed. To verify this, we reacted *trans*-2-butene over various acid catalysts which do not contain any dehydrogenation component.

The extent of possible thermal reactions of *trans*-2-butene was checked in a reactor filled with inactive α-alumina (Alundum). At 560°C, isomerization to 1-butene and *cis*-2-butene is the only significant thermal reaction. The other products are *n*-butane (0.03%), butadiene (0.1%), and C_1–C_3 hydrocarbons (0.8%).

Over silica–alumina and alumina double-bond isomerization to an equilibrium mixture of all three *n*-butene isomers is complete above 370°C. Up to 13% of butenes is converted to aromatics over these acid catalysts. However, Table 3 shows that more C_5–C_8 olefins and naphthenes and much less bi- and polycyclic aromatics are formed over alumina and silica–alumina than over catalysts containing a dehydrogenation component. This shows the importance of the dehydrogenation component in converting the C_6–C_8 aliphatic and naphthenic intermediates to aromatics.

Figure 3 and Table 4 show that over silica–alumina the aromatization of the dimers increase with increasing temperature. C_9–C_{10} aromatics are mostly tri- and

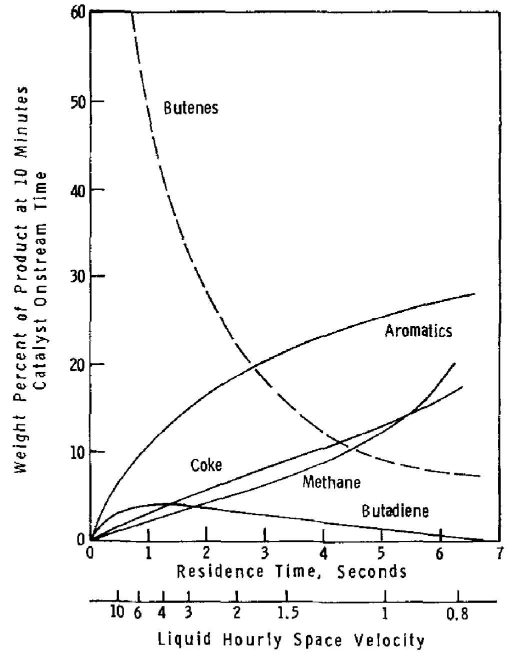

FIG. 1. Effect of space velocity on product composition in the dehydrocyclodimerization of n-butenes over 0.8% platinum on alumina catalyst at 560°C and 1 atm pressure.

TABLE 2

DISTRIBUTION OF C_6–C_8 HYDROCARBONS FORMED FROM *trans*-2-BUTENE OVER 0.8% PLATINUM ON ALUMINA AT 560°C 1 ATM PRESSURE WITH AN LHSV OF 8.8 (MOLE %)

	C_6	C_7	C_8
Aliphatic olefins and diolefins	2		1.8
Alkylcyclopentenes and dienes			
Monoalkyl	3.7	0.2	
Dialkyl		0.3	1.0
Trialkyl			1.4
Alkylcyclohexenes			
Unsubstituted	0.5		
Monoalkyl		0.6	0.2
Dimethyl			0.9
Alkylcyclohexadienes			
Unsubstituted	0.2		
Monoalkyl		0.3	0.5
Dialkyl			0.2
Aromatics			
Unsubstituted	4.0		
Monoalkyl		8.0	2.9
Dialkyl			29.0

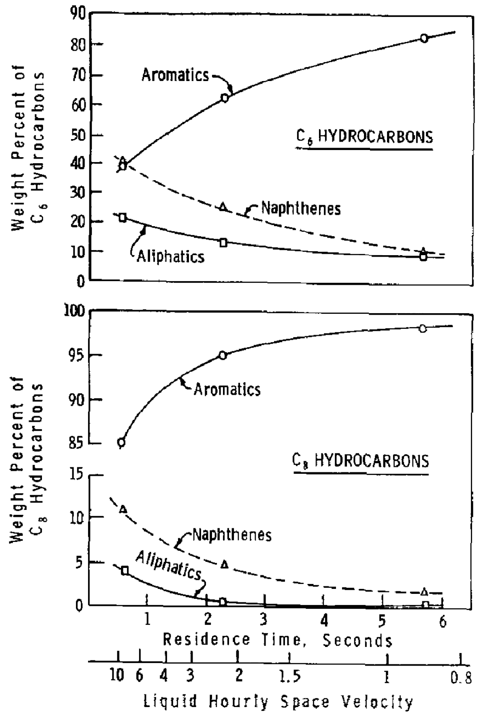

FIG. 2. Effect of space velocity on the distribution of C_6 and C_8 hydrocarbons in the dehydrocyclodimerization of butenes at 560°C over 0.8% platinum on alumina.

tetramethylbenzenes. Temperature affects the distribution of the various aromatic species. Relative amounts of benzene and toluene increase at the expense of the C_9 and C_{10} aromatics with increasing temperature, probably as a result of dealkylation (Fig. 4). Some of the C_{10} and higher aromatics may be formed from butene trimer intermediates. (Xylene disproportionation is a likely alternative.) Trimerization is less favored at higher temperatures; thus, the concentration of C_9–C_{10} aromatics is expected to decrease with increasing temperature.

Both skeletal isomerization to isobutylene and hydroisomerization (*3*) to isobutane were observed over silica–alumina. Skeletal isomerization, as shown in Fig. 5, approaches equilibrium above 480°C. However, one can determine from Fig. 5 that the isobutane/n-butenes ratio is higher than the equilibrium ratio of either the paraffins or the olefins. This is evidence

TABLE 3

Aromatization of *trans*-2-Butene at 560°C

Catalyst:	Pt (0.8%) alumina	Silica–alumina	Eta-alumina	Alumina from K-aluminate
Potassium conc (wt %):	0	0	0	3.78
LHSV:	8.8	2.2	2.2	2.2
Product composition (wt %)				
C_1–C_3	4.7	23.3	10.3	3.2
Butenes	78.0	39.9	56.5	83.3
n-Butane	1.6	4.1	1.9	0.5
Isobutane	0.8	8.7	1.4	—
Butadiene	3.3	0.1	0.6	2.7
C_5–C_8 aliphatics	1.0	9.8	3.1	2.5
Aromatics	7.2	9.3	13.0	3.8
Composition of the C_6–C_{11} fraction (wt %) (from liquid product analyses)				
C_6 olefins, dienes, naphthenes	8.2	14.6	8.3	10.9
C_7 olefins, dienes, naphthenes	2.2	2.9	3.2	9.3
Vinylcyclohexene	0.6		0.4	2.2
Other C_8 olefins, dienes, naphthenes	9.3	4.7	4.9	16.7
Benzene	5.0	1.7	6.1	9.5
Toluene	11.8	9.8	16.8	15.6
Ethylbenzene	5.0	1.4	4.9	8.4
o-Xylene	12.3	7.2	8.0	9.1
m-Xylene	27.5	21.5	20.6	6.0
p-Xylene	9.2		7.2	7.6
Styrene	1.0		0.8	1.3
Trimethylbenzenes	2.1	16.5	6.8	2.5
Other C_9 aromatics	1.6	4.5	4.8	0.9
Tetramethylbenzenes	0.4	3.3	1.2	
Other C_{10} alkylbenzenes	0.4	2.9	2.0	
Methylindans, indenes	0.9		1.5	
Naphthalene	2.5	0.6	1.2	
Methylnaphthalenes		1.8	1.3	
Higher aromatics		6.6		

that hydroisomerization does occur. As the temperature increases, hydroisomerization selectivity (i.e., the isobutane/*n*-butane ratio) decreases. Simple hydrogenation (*n*-butenes → *n*-butane) is much slower than hydroisomerization, as seen by the isobutane/*n*-butane ratio in Fig. 5.

Coking and cracking increase with increasing temperature. At 370°C the product contains 8.1 wt % propane and propylene, 9.3 wt % C_5, and only 0.15 wt % methane. This stoichiometry suggests that most C_3 and C_5 are formed via C_8 intermediates:

$$2\,C_4H_8 \rightarrow C_8H_{16} \rightarrow C_5H_{10} + C_3H_6.$$

Direct, one-step cracking of butenes:

$$C_4 \rightarrow CH_4 + C_3 \quad \text{or:} \quad C_4 \rightarrow 2\,C_2,$$

is insignificant at 370°C. One-step cracking of butene becomes important only above 500°C.

Over acidic eta-alumina, relatively more benzene and toluene and less C_9–C_{11} aromatics are formed than over silica–alumina (Table 3). Hydroisomerization is not observed.

We may conclude here that, in the absence of a dehydrogenation component, acid catalysis plays a predominant (but

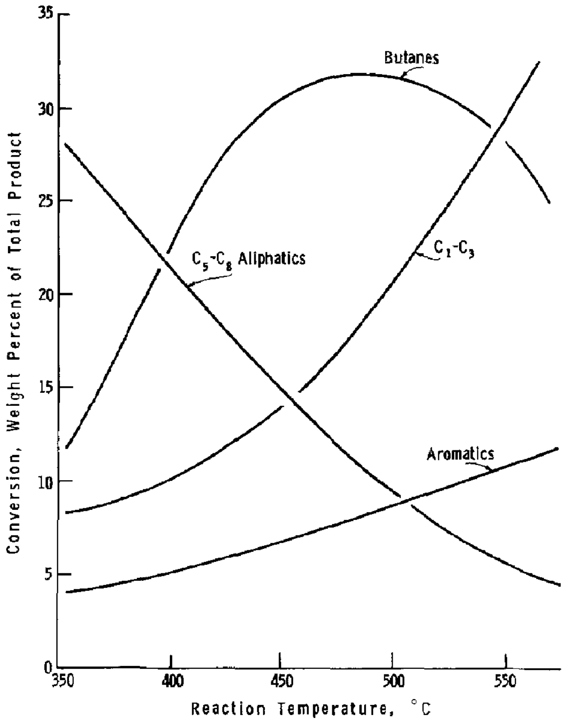

FIG. 3. Reaction of *trans*-2-butene over silica–alumina; effects of temperature on product distribution.

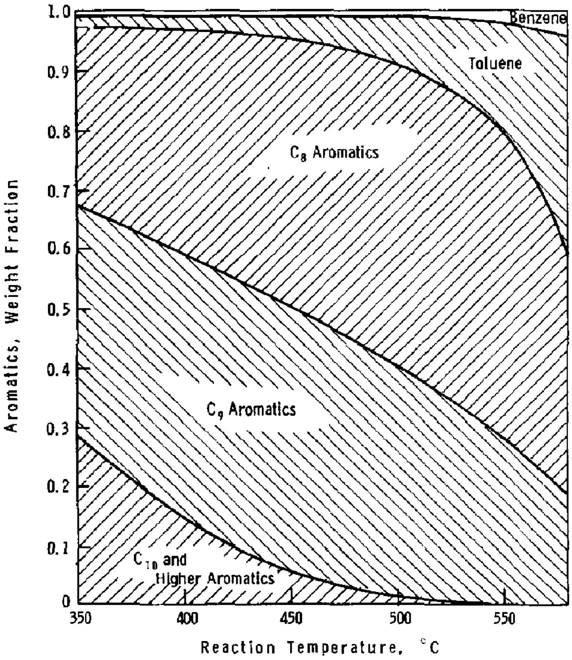

FIG. 4. Effects of temperature on the distribution of aromatics in the reaction product of *trans*-2-butene over silica–alumina.

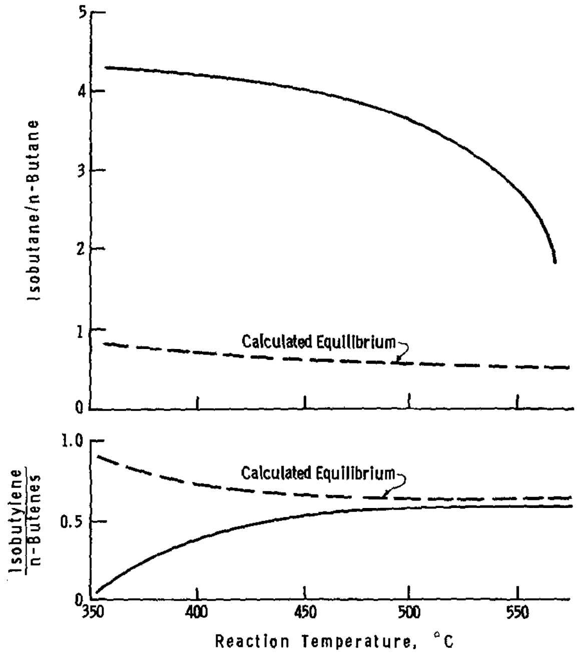

FIG. 5. Hydroisomerization of *trans*-2-butene over silica-alumina.

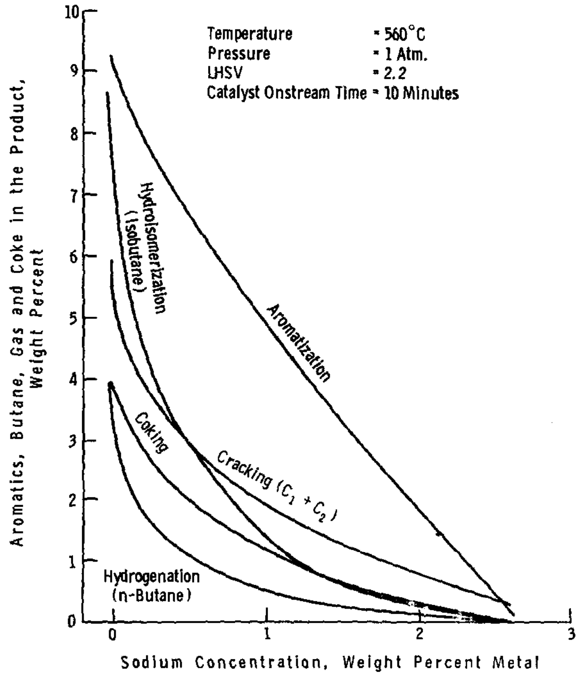

FIG. 6. Effect of sodium on the activity of silica-alumina in the reactions of *trans*-2-butene.

TABLE 4

Reactions of *trans*-2-Butene over Silica–Alumina at Atmospheric Pressure with a LHSV of 1.1 (reaction effluent samples taken at 10-min catalyst onstream times)

Temp (°C):	370	480	560
Product composition (wt %)			
Butenes	43.0	22.0	15.4
n-Butane	2.8	6.6	7.8
Isobutane	12.0	25.2	18.2
C_5 aliphatics	9.3	7.2	3.9
C_6–C_8 aliphatics	16.4	3.8	1.2
C_6–C_{10} aromatics	4.1	7.8	11.2
Methane	0.15	1.9	4.8
Ethane, ethylene	0.3	2.4	6.3
Propane	0.5	4.6	7.2
Propylene	7.6	9.0	13.7
Coke	3.8	9.5	10.3

TABLE 5

Hydrogen Transfer in the Reaction of Butenes over Alumina and Silica–Alumina Catalysts at 560°C

Catalyst	Butane/ butenes	Isobutylene/ *n*-butenes
Silica–alumina	0.8	0.65
Silica–alumina with 0.43% Na	0.08	0.35
Eta-alumina	0.06	0.47
Alumina with 3.8% potassium	0.006	0.04
Silica–alumina with 2.6% Na	0.001	0.02
Alundum (α-alumina)	0.0006	0

not exclusive) role in butene dimerization, aromatization of the dimers, disproportionation of polyalkylbenzenes, hydrogenation of the olefins, cracking, and coking. Skeletal isomerization is almost exclusively acid catalyzed. These were proved by reacting *trans*-2-butene over silica–alumina containing various amounts of alkali metals. Sodium was introduced by impregnation with Na_2CO_3. Aromatization, hydrogenation, cracking, coking, olefin skeletal isomerization, and hydroisomerization decrease with increasing sodium concentration (Fig. 6). Hydrogenation and skeletal isomeriza-

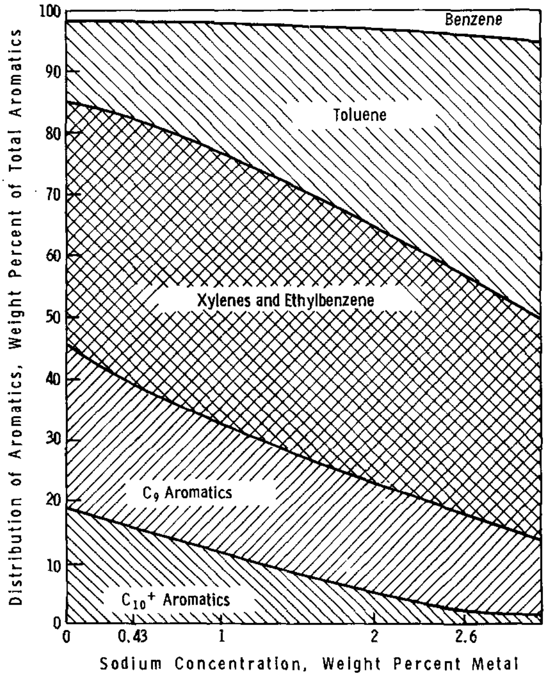

Fig. 7. Effect of sodium in silica–alumina on the distribution of aromatic species formed from *trans*-2-butene at 560°C.

tion are most affected. Additional evidence is shown in Table 5, which correlates acidity, hydrogenation, and skeletal isomerization. Hydrogenation activities of silica-alumina, acidic aluminas, potassium-containing alumina, and Alundum catalysts are in the ratios of 1000:100:10:1.

Butene dimerization is less affected by the neutralization of acid sites than dimer aromatization. Relatively more C_5–C_8 naphthenes and aliphatics and less aromatics are formed over the alkali-containing catalysts than over pure silica–alumina or alumina. The C_8 aromatic fraction using alkali–containing catalysts contains more ethylbenzene (up to 40%) and less *m*-xylene than required by equilibrium because *m*-xylene cannot be obtained from two *n*-butane molecules without skeletal isomerization. Dealkylation of the aromatics increases; transalkylation decreases with increasing sodium concentration (Fig. 7).

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