

kinetic equation for the last 5 hr when both water concentration and temperature, contrary to what happens in the first steps of the process, assume nearly constant values.

TABLE 1  
WATER CONTENT IN REFLUX STREAM

Time (hr)	Distill. speed (mole/hr)	
	0.81 (% H <sub>2</sub> O)	1.77 (% H <sub>2</sub> O)
0.25	25.2	20
2	18.7	17.5
4	5.3	17.4
7	2.8	11.8

The higher distillation speed gives the higher water concentration in the reaction mixture. This effect results from the higher dissolved water content in the reflux stream (in Table 1 the % weight H<sub>2</sub>O content in samples taken from the reflux at increasing times are shown to depend on the speed of distillation, for wet resin-catalyzed runs). To the higher water concentration and the lower temperature corresponds a lower process rate.

#### DISCUSSION

Our experimental results are in agreement with Eq. (1), which involves deactivation of the catalyst by water. However,

we should point out that the decrease of the process rate with increasing water concentration must be attributed, in part, to the decrease of the reaction temperature.

The failure of the bimolecular equation to hold over the first steps of reaction, reported by Levesque and Craig (1), may be interpreted on the basis of the variations of the water concentration and of the temperature in the reaction mixture.

The speed of distillation has a marked effect on the process rate, in that it controls the water contents and reaction temperature.

#### REFERENCES

1. LEVESQUE, C. L., AND CRAIG, A. M., *Ind. Eng. Chem.* **40**, 96 (1948).
2. BOCHNER, M. B., GERBER, S. M., VIETH, R. W., AND RODGER, A. J., *I. E. C. Fundamentals* **4**, 314 (1965).

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## The Mechanism of Olefin Disproportionation

Since the initial discovery of olefin disproportionation by Banks and Bailey (1), Bradshaw, Howman, and Turner have published on the mechanism of the reaction (2). The latter authors suggested that the reaction intermediate was a "quasi-cyclobutane." Calderon and workers have recently published on a homogeneous catalyst based upon a tungsten complex. They too proposed a four-center intermediate (3). However, Mol, Moulijn, and Boelhouwer have offered an alternate explanation and have postulated a  $\pi$ -bonded cyclo-

butadiene formed by the transfer of four hydrogen atoms from two olefin molecules to the catalyst surface.

An examination of the structures and distribution of products from a highly selective catalyst (a potassium hydroxide-treated molybdena-alumina catalyst) has given further support for the "quasi-cyclobutane" intermediate. This support is provided by the following experimental observations: 1-octene was converted to ethylene and 7-tetradecene (Table 1); 2-octene was converted to 2-butene and

TABLE 1  
DISTRIBUTION OF PRODUCTS FROM THE  
OLEFIN MUTUAL CLEAVAGE REACTION

Product (mole %)	Starting material		
	1-Octene	2-Octene	3-Heptene
C <sub>2</sub> H <sub>4</sub>	— <sup>a</sup>	None	None
C <sub>3</sub> H <sub>6</sub>	—	0.9	Trace
C <sub>4</sub> H <sub>8</sub>	—	47.6 <sup>c</sup>	1.2
C <sub>6</sub> H <sub>10</sub>	—	1.1	2.5
C <sub>6</sub> H <sub>12</sub>	—	0.1	45.6 <sup>e</sup>
C <sub>7</sub> H <sub>14</sub>	—	0.4	—
C <sub>8</sub> H <sub>16</sub>	—	—	45.6 <sup>f</sup>
C <sub>9</sub> H <sub>18</sub>	5.5	1.0	3.2
C <sub>10</sub> H <sub>20</sub>	0.6	0.4	1.9
C <sub>11</sub> H <sub>22</sub>	1.2	2.8	Trace
C <sub>12</sub> H <sub>24</sub>	0.9	44.3 <sup>d</sup>	—
C <sub>13</sub> H <sub>26</sub>	10.9	1.4	—
C <sub>14</sub> H <sub>28</sub>	80.9 <sup>b</sup>	Trace	—
C <sub>16</sub> H <sub>30</sub>	Trace	—	—

<sup>a</sup> No quantitative determination of the ethylene was made. Only traces of propylene and butenes were found in the ethylene off-gas.

<sup>b</sup> *trans*-7-Tetradecene (91%) and *cis*-7-tetradecene (9%).

<sup>c</sup> *trans*-2-Butene (62%) and *cis*-2-butene (38%).

<sup>d</sup> *trans*-6-Dodecene (71%) and *cis*-6-dodecene (29%).

<sup>e</sup> *trans*-3-Hexene (76%) and *cis*-3-hexene (24%).

<sup>f</sup> *trans*-4-Octene (78%) and *cis*-4-octene (22%).

6-dodecene (Table 1); 3-heptene was converted to 3-hexene and 4-octene (Table 1); 2-octene was cleaved by ethylene to yield 1-heptene (Table 2); and 2,3-dimethylbutene-2 was cleaved by ethylene to yield isobutene as the sole product (Table 3).

All of the above reactions are consistent with the original cyclobutane proposal. However, in the ethylene cleavage of 2,3-dimethylbutene-2, the mechanism suggested by Mol and workers would require the migration of two methyl groups and two hydrogen atoms to the catalyst as well as their return to the same carbon atom on which they were originally located. Thus, the inability to even detect methylbutenes, propylene, and *n*-butenes in the product makes the possibility of a cyclobutadiene intermediate remote.

#### EXPERIMENTAL

The gas chromatographic analyses were carried out with either a 10-ft (1/4-inch id) column packed with 20% D.C.-200

TABLE 2  
THE CLEAVAGE OF 2-OCTENE WITH ETHYLENE

Temperature: 125°C Pressure: 800 psig Mole ratio of C <sub>2</sub> H <sub>4</sub> /C <sub>8</sub> H <sub>16</sub> : 6.5 Conversion of octene: 29%	
Products (mole %)	
C <sub>3</sub> H <sub>6</sub>	1.7 <sup>a</sup>
C <sub>4</sub> H <sub>8</sub>	10.1 <sup>b</sup>
C <sub>5</sub> H <sub>10</sub>	2.8
C <sub>6</sub> H <sub>12</sub>	Trace
C <sub>7</sub> H <sub>14</sub>	81.8 <sup>c</sup>
C <sub>8</sub> H <sub>16</sub>	—
C <sub>9</sub> H <sub>18</sub>	0.4
C <sub>10</sub> H <sub>20</sub>	Trace
C <sub>11</sub> H <sub>22</sub>	0.2
C <sub>12</sub> H <sub>24</sub>	3.0

<sup>a</sup> Most of the propylene escaped from the system in the large excess of ethylene.

<sup>b</sup> The butene most likely arose from the reaction of propylene with itself.

<sup>c</sup> The heptene was 98.4% 1-heptene.

silicone oil on Chromasorb P, a 25-ft column (1/4-inch id) packed with 17% *tris*-(cyanoethoxy)propane on Chromasorb P, or a 150-ft squalane capillary column. The olefins were Phillips Pure Grade olefins and were carefully dried and stored under a nitrogen atmosphere. All boiling points and melting points are uncorrected. The infrared analyses were performed on a Perkin-Elmer Model 21 spectrograph. All temperatures are in Centigrade degrees.

The catalyst was a molybdena-alumina composition which was treated with

TABLE 3  
THE ETHYLENE CLEAVAGE OF  
2,3-DIMETHYLBUTENE-2

Atmospheric pressure Temperature: 165°C Ratio of C <sub>2</sub> H <sub>4</sub> /C <sub>6</sub> H <sub>12</sub> : 9:1 2,3-Dimethylbutene-2: 99 mole %	
Products <sup>a</sup> (mole %)	
Propylene	<sup>b</sup>
Isobutene	10.8
2,3-Dimethylbutene-2	72.3
2,3-Dimethylbutene-1	16.8
2-Methy-2-butene	<sup>c</sup>

<sup>a</sup> Ethylene was omitted from the table. The effluent was 87.7 mole % ethylene.

<sup>b</sup> No propylene was detected in the effluent.

<sup>c</sup> No methylpentenes (or *n*-pentenes) were detected.

aqueous potassium hydroxide. The aqueous solution was decanted and the catalyst was activated by heating in a furnace at 500° for 5 hr and then transferred to a bottle (hot) and stored under nitrogen while it cooled. It remained under a nitrogen atmosphere until it was used. All catalyst transfers and manipulations were carried out under a nitrogen blanket.

**1-Octene.** Pure 1-octene (99 mole %) was refluxed in a glass column containing 40 g of activated, base-treated catalyst under a nitrogen atmosphere. The ethylene produced in the reaction was allowed to escape from the system. When the pot temperature reached 178°, the reaction was stopped. The analysis of the pot material (with the octene being omitted) is shown in Table 1. The product contained 17.6% octenes, of which 94.9% was 1-octene and 5.1% was 2-octenes. The product was fractionally distilled to obtain a tetradecene fraction (b.p. 96–97°/3.5 mm,  $n_D^{20}$  1.4374) which contained 0.7% tridecene as the sole observable impurity. Infrared analysis indicated 91% trans olefin content.

**Ozonolysis of 7-tetradecene.** A solution of the above 7-tetradecene (7.7 g) in 50 ml of *n*-heptane was chilled to –78° and ozone from a Welsbach T-23 Ozonizer (2.2 liter/min oxygen flow, 80 V, 8 psig) was passed through it at 0.3 liter/min. The ozonide slowly crystallized from solution and after 2 hr the reactor was plugged. The mixture was warmed to 0° (it was homogeneous at this temperature) and transferred to a bottle containing triphenylphosphine (13 g). The bottle was sealed and heated at 100° for 2 hr according to the procedure of Lorenz and Parks (5). Analysis of the supernatant solution (after cooling to 25°) on a 10-ft DC-200 silicone oil column showed *n*-heptane (85.8%), *n*-heptaldehyde (5.7%), and tetradecene (8.6%). There were several minor components, including tridecene and a small amount (~0.03%) of a material with the same retention time as that of *n*-octanal. No *n*-hexanal was detected. The 2,4-dinitrophenylhydrazone of the ozonolysis product melted at 107–107.5°. The

corresponding derivative of *n*-heptanal melted at 107.5–108°. A mixed melting point showed no depression. A mixed melting point with the *n*-hexanal derivative was 94–98°.

**2-Octene.** This reaction was carried out in a manner similar to that used for 1-octene. The 2-octene (217.6 g, 32% *trans*) was refluxed through 31 g of the catalyst. The material not condensed by the water condenser was caught in a cold trap at –78°. After 2 hr and 40 min the pot temperature had risen from 125° to 170°. A total of 36 g of volatiles was trapped. Analysis of this product by gas chromatography indicated ethylene (trace), propylene (1.3%), butenes (96.1%; 62% *trans*-2-butene and 38% *cis*-2-butene), and pentenes (2.6%). The pot material (166.5 g) contained butenes (1.53%), pentenes (0.12%), hexenes (0.04%), heptenes (0.30%), octenes (28.1%; 45% *trans*-2-octene, 55% *cis*-2-octene), nonene (1.47%), decane (0.50%), undecene (3.63%), dodecene (62.2%), tridecene (2.14%), and tetradecene (trace). The combined analysis is shown in Table 1. The pot material was fractionated at 22 mm, leaving a pot residue of 2 g. The main fraction (88.9 g,  $n_D^{20}$  1.4324, b.p. 101°) was 99.8% dodecene and 0.2% undecene. Infrared analysis indicated 71% trans olefin content.

**Ozonolysis of 6-dodecene.** A solution of the dodecene (7.7 g) (prepared from 2-octene in the above experiment) in *n*-heptane (80 ml) was ozonized at 0° until ozone was detected in the effluent from the reactor. The sample was transferred to a bottle containing triphenylphosphine (14 g) and treated similarly to the tetradecene product. The chromatogram showed *n*-heptane (92.3%), *n*-hexanal (7.58%), unknown A (0.03%), unknown B (0.01%), and dodecene (0.05%). The products were 98.8% *n*-hexanal, 0.6% dodecene, and 0.6% unknowns. The *n*-hexanal was identified by the identity of its gas chromatographic retention time with that of authentic *n*-hexanal and by the identity of its 2,4-dinitrophenylhydrazone (m.p. 108–108.5°) with that of *n*-hexanal. The mixed melting point showed no depression.

**3-Heptene.** A sample of 3-heptene (164 g) was refluxed through a catalyst bed containing 29 g of the activated, base-treated catalyst. A 14-inch column filled with Stainless Steel packing was placed on top of the catalyst column so that the hexene product could be removed by fractionation as it formed. After 2 hr and 50 min the pot temperature was 115° and a total of 54.2 g of distillate had been obtained. The pot material weighed 91.8 g and 6.2 g of liquid was caught in a cold trap at -78°. These samples were analyzed on a 10-ft DC-200 silicon oil column. The pot material analyzed as butenes (0.15%), pentenes (0.07%), hexenes (1.87%), heptene (28.2%; 76% *trans*-3-heptene and 24% *cis*-3-heptene), 4-octene (61.8%), nonene (4.58%), decene (3.35%), and undecene (trace). The distillate showed butenes (0.83%), pentenes (3.69%), hexene (75.9%; 76% *trans*-3-hexene and 24% *cis*-3-hexene), heptene (19.6%), and octenes (trace). The combined analysis is shown in Table 1.

**The cleavage of 2-octene with ethylene.** The reaction of ethylene and 2-octene was carried out in an apparatus similar to that described by Banks and Bailey (1) with the exception that the ethylene was passed through a flow meter and the products were condensed in a cold trap at -78°. The ethylene and most of the propylene were allowed to escape from the system. The analysis of the trap material is given in Table 2. The identity of 1-heptene was established by its gas chromatographic retention time and infrared spectrum.

**The cleavage of 2,3-dimethylbutene-2 with ethylene.** This reaction was affected

by passing the gaseous reactants (in a ratio of 9 moles of ethylene to 1 mole of 2,3-dimethylbutene) over the base-treated molybdena-alumina catalyst (17.4 g) for 85 min at 165°. A total of 50 ml of 2,3-dimethylbutene-2 was used. The reactor effluent was sampled at 5-min intervals throughout the reaction. Gas chromatographic analyses of these samples gave a constant composition. A typical analysis, omitting the ethylene which was 87.7 mole % of the effluent, is shown in Table 3. The reactor effluent was also condensed in a cold trap at -78° and the uncondensable ethylene was allowed to escape. Analysis of the condensate by gas chromatography on a 10-ft silicone oil column showed essentially the same ratio of 2,3-dimethylbutenes and isobutylene as was found in the total reactor effluent. There was no indication that either propylene or isoamylene was present as a reaction product.

#### REFERENCES

1. BANKS, R. L., AND BAILEY, G. C., *Ind. Eng. Chem., Prod. Res. Develop.* **3**, 170 (1964).
2. BRADSHAW, C. P. C., HOWMAN, E. J., AND TURNER, L., *J. Catalysis* **7**, 269 (1967).
3. CALDERON, N., OFSTEAD, E. A., WORD, J. P., JUDY, A., AND SCOTT, K. W., *J. Am. Chem. Soc.* **90**, 4133 (1968).
4. MOL, J. C., MOULIJN, J. A., AND BOELHOUWER, C., *J. Catalysis* **11**, 87 (1968).
5. LORENZ, O., AND PARKS, C., *J. Org. Chem.* **30**, 1976 (1965).

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