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Mechanism of Olefin Disproportionation

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Disproportionation of olefins has been investigated under selective conditions. The primary products from the reaction of 1-pentene are ethylene and *n*-octenes, and 2-pentene yields 2-butene and *n*-hexenes. From the mixed olefins, 1-pentene and 2-pentene, propylene, *n*-heptenes, 1-butene, and *n*-hexenes are primary products. A mixture of 1-pentene and 1-hexene gives ethylene and *n*-nonenes as initial products. From these results and consideration of molecular orbital symmetry conservation, it is proposed that the reaction proceeds via adsorbed cyclobutane.

INTRODUCTION

A novel catalytic reaction of linear olefins, described as olefin disproportionation, has been reported by Banks and Bailey (*1*). In this reaction linear olefins are converted over supported molybdenum or related catalysts to homologs of lower and higher carbon number in approximately equimolar amounts. For propylene the products are almost exclusively ethylene and butenes; however, for higher homologs of carbon number *n* the product olefins are distributed nonselectively between C_2 and C_{2n-2}.

More recently, Bradshaw, Howman, and Turner have investigated the disproportionation* of 1-butene in detail (*2*). By choice of conditions or by sodium poisoning of the catalyst they obtained ethylene and 3-hexene as the major products. These results also indicated that propylene and 2-pentene, formed under nonselective conditions, arise from the reaction of 1-butene and 2-butene formed by double-bond isomerization. These workers suggest that the reaction pathway involves a four-center intermediate. Consistent with this view, ethylene reacts with internal olefins to yield two 1-olefins (*2*).

Discussion of olefin disproportionation should include the olefin metathesis reaction reported by previous investigators (*3, 4*). In the presence of tungsten hexachloride, ethanol, and ethylaluminum dichloride, 2-pentene yields 2-butene and 3-hexene exclusively. Deuterium tracer experiments showed that the reaction involves interchange of alkylidene groups, consistent with a four-center pathway, and this reaction is likely the same as olefin disproportionation.

Additional evidence for a four-center mechanism is provided in the work of Mol, Moulijn, and Boelhouwer (*5*). Examination of the disportionation products of 2-propylene-^{14}C showed that the butene formed was radioactive, in contrast with the ethylene which showed no radioactivity at all.

We wish to report the results of an investigation of the disproportionation and cross-disproportionation of higher-carbon-number olefins under selective conditions. These results provide further evidence of the four-center pathway. Consideration of these results and the role of transition metal oxides in the conservation of molecular orbital symmetry leads us to propose that the reaction proceeds via an adsorbed cyclobutane.

METHODS

Catalysts. The catalysts used in this investigation are commercial $CoO\text{-}MoO_3/Al_2O_3$ catalysts. Two catalysts of essen-

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* These authors have suggested the term dismutation for this reaction. See ref. (*2*).

tially equivalent performance were utilized: 3.5 wt % CoO, 12.5 wt % MoO_3 obtained from National Aluminate Corporation and an American Cyanamid catalyst containing 3.0 wt % CoO and 15.0 wt % MoO_3. These will be referred to subsequently as $CoO\text{-}MoO_3/Al_2O_3$.

Olefins. Olefins were obtained from Phillips Petroleum Company (pure grade, 99 mole % purity). After redistillation, the olefins were purged and stored under nitrogen.

Apparatus and procedures. The investigations were carried out in a bench-scale flow reactor equipped with conventional pressure-, temperature-, and flow-control devices. Most of the disproportionation reactions were at atmospheric pressure; for those runs at elevated pressure nitrogen (1 mole/mole of olefin) was metered in separately and used to provide better pressure control.

The catalysts (16–45 mesh) were dryed, *in situ*, in a stream of dry air for 5 hr at 538°C. After drying, the catalyst and system were purged with dry nitrogen at 538°C for 2 hr; purging was continued while the reactor was cooled to run temperature.

Following this catalyst activation, olefin was admitted to the system and material-balanced runs of 2 hr duration were made after a line-out time of 1 to 4 hr.

Liquid feed rates are expressed as grams per hour per gram of catalyst (weight hourly space velocity, WHSV). This and other experimental conditions are noted in the appropriate tables.

Analyses. The gaseous and liquid products were collected and analyzed separately. The noncondensable gases were analyzed by mass spectrometry techniques, and the liquid products were analyzed by gas-liquid chromatography.

Olefin isomers through the pentenes were identified individually in the chromatograms. Hexene isomers were identified; however, only partial resolution of the isomers was obtained and the results are reported by carbon number only. For the higher molecular weight olefins analysis was by carbon number only without identification of individual isomers. Heptene and higher olefins, however, were shown to be essentially all linear olefins (>99%) by hydrogenation of the olefins and identification (gas-liquid chromatography) of the resultant *n*-paraffins.

RESULTS

Conversion and selectivity. At high conversions over $Co\text{-}Mo/Al_2O_3$ catalysts a nonselective distribution of linear olefins between C_2 and C_8 is obtained from 1-pentene, as shown by the data of the first column of Table 1. The results show that octenes are the highest carbon number which can be considered a major disproportionation product. No significant amount of C_{10} olefins is formed and the results, consistent with the observations of Banks and Bailey (*1*), indicate that dimerization followed by cracking is not the mechanism of olefin disproportionation. Conversion of 1-pentene was reduced to 8.6% (3.3% 2-pentene in product) by decreasing both temperature and 1-pentene pressure, with the results shown in the second column of Table 1. Selectivity has shifted markedly and ethylene and *n*-octenes are clearly the primary products (63% selectivity) of 1-pentene disproportionation. It is important to note that 1-butene, a secondary product, is the only butene isomer obtained in significant concentration. Consistent with the results obtained with 1-butene (*2*) these data imply that a nonselective distribution at high conversion arises from secondary

TABLE 1

DISPROPORTIONATION OF 1-PENTENE

Temperature (°C):	77°	149°
WHSV (g^{-1}):	3.5	3.5
Pressure (atm):	31	1
Conversion (mole %):	59.5	8.6
	Product distribution (mole %)	
Ethylene	14.0	32.4
Propylene	19.4	5.2
1-Butene	14.6	11.6
cis- and *trans*-2-Butene	5.6	1.4
n-Hexenes	18.4	11.2
n-Heptenes	12.0	6.5
n-Octenes	13.3	31.0
n-Nonenes and higher	2.7	0.6

disproportionation reactions and disproportionation subsequent to olefin isomerization.

Disproportionation of pentene isomers. In addition to the reaction of 1-pentene the reaction of 2-pentene and the reaction of 1-pentene with 2-pentene (cross-disproportionation) have been investigated at low conversions, with the results shown in Table 2. The disproportionation of 2-pentene clearly leads to *cis*- and *trans*-2-butene and *n*-hexene (predominantly 3-hexene) as the major products. In sharp contrast to 1-pentene very little ethylene and octenes are formed.

TABLE 2

Disproportionation of Pentene Isomers[a]

Feed composition (mole %)			
1-Pentene:	100	—	50
cis- and *trans*-2-Pentene:	—	100	50
Conversion (mole %)	8.6	14.1	28.9
Double-bond isomerization (mole %)	3.3	1.5	—
Product distribution (mole %)			
Ethylene	32.4	0.5	4.3
Propylene	5.2	4.0	15.1
1-Butene	11.6	4.7	24.7
cis- and *trans*-2-Butene	1.4	43.6	7.0
n-Hexenes	11.2	44.0	28.4
n-Heptenes	6.5	3.4	13.6
n-Octenes	31.0	0.7	7.0
Nonenes and higher	0.6	0.1	0.0

[a] 149°C, atmospheric pressure, 3.5 WHSV.

The reaction products of the 1-pentene/2-pentene mixture are more complex. The products of 1-pentene alone (ethylene and *n*-octenes) and 2-pentene alone (2-butenes and *n*-hexenes) are found as expected. However, *n*-hexenes are formed in excess of 2-butenes, and the *n*-hexenes along with 1-butene must arise from the reaction of 1-pentene and 2-pentene. Propylene and *n*-heptenes are produced and also must be considered primary products of the 1-pentene/2-pentene reaction.

Reaction of 1-pentene and 1-hexene. The data of Table 3 illustrate further the products of reaction of two different olefins. For the 1-pentene/1-hexene reaction ethylene and a mixture of octenes, nonenes, and decenes are the major products. The distribution of these higher-molecular-weight olefins also is shown in Table 3. The octenes and decenes are the products of 1-pentene and 1-hexene disproportionation, respectively; however, the major product, nonenes, can be attributed to 1-pentene/1-hexene cross-disproportionation.

TABLE 3

The Reaction of 1-Pentene and 1-Hexene[a]

Feed composition (mole %)	
1-Pentene:	54.5
1-Hexene:	45.5
Conversion (mole %)	24.9
Product distribution (mole %)	
Ethylene	36.0
Propylene	9.9
1-Butene	11.9
cis- and *trans*-2-Butene	—
n-Heptenes	10.4
C_8–C_{10} *n*-olefins	31.2
Higher than decenes	0.6
Composition of C_8–C_{10} *n*-olefins (mole %)	
n-Octenes	36.9
n-Nonenes	44.5
n-Decenes	18.6

[a] 149°C, atmospheric pressure, 3.5 WHSV.

Discussion

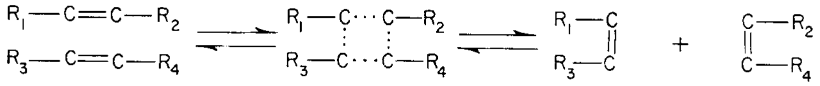
The results of disproportionation of the several olefins are summarized in Table 4.

TABLE 4

Primary Olefin Disproportionation Products

Reacting olefins	Product olefins
1-Pentene	Ethylene *n*-Octenes
2-Pentene	2-Butene *n*-Hexenes
1-Pentene/2-pentene	Propylene *n*-Heptenes 1-Butene *n*-Hexenes
1-Pentene/1-hexene	Ethylene *n*-Nonenes

These primary products are best accounted for by a four-center mechanism, illustrated below, as proposed by Bradshaw *et al.* (*2*).



An attractive pathway for this reaction is the concerted formation of a cyclobutane, the decomposition of which would lead to the expected products. Although the thermal electrocyclic formation of a cyclobutane from two olefins is forbidden by the molecular orbital symmetry postulate of Woodward and Hoffman (*6*), the recent theoretical consideration of transition metal catalysis by Mango and Schactschneider (7) makes a cyclobutane intermediate plausible. In the cyclobutanation process described by these authors metal orbitals combine with olefin orbitals of the required symmetry to give a ligand-bound olefin pair with molecular orbital symmetry SS, SA, AS, and AA orbitals (where A indicates antisymmetric and S, symmetric). According to these investigators, cyclobutane formation from the olefins results in a change of ligand–metal bonding in which electrons from the AS orbital move into the AS cyclobutane σ-bond and electrons from the SA bond move into the metal d_{zx} orbital (7). Thus the overall formation of an adsorbed cyclobutane is allowed, and the key role of the catalyst is conservation of molecular orbital symmetry.

From the experimental results and the above considerations, we conclude that the mechanism of olefin disproportionation consists of the reaction of two olefins with the transition metal oxide catalyst followed by a concerted cyclobutanation of the ligand-bound olefins and decomposition of the adsorbed cyclobutane to give product olefins with conservation of molecular orbital symmetry.

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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., Chen, H. Y., and Scott, K. W., *Tetrahedron Letters,* p. 3327 (1967).
4. Calderon, N., Chen, H. Y., and Scott, K. W., *Abstracts of Papers, 154th Meeting Am. Chem. Soc.,* Chicago, Illinois, 1967.
5. Mol, J. C., Moulijn, J. A., and Boelhouwer, C., *J. Catalysis* **11,** 87 (1968).
6. Hoffman, R., and Woodward, R. B., *J. Am. Chem. Soc.* **87,** 2046 (1965).
7. Mango, F. D., and Schachtschneider, J. H., *J. Am. Chem. Soc.* **89,** 2484 (1967).