Olefin Dismutation: Reactions of Olefins on Cobalt Oxide–Molybdenum Oxide–Alumina

C. P. C. BRADSHAW, E. J. HOWMAN, AND L. TURNER

From the Chemicals Division, British Petroleum Research Centre, Chertsey Road,

Sunbury-on-Thames, Middlesex, England

A study of the conversion of n-butenes into olefins of lower and higher carbon number ("dismutation") on catalysts containing cobalt, molybdenum, and aluminum oxides has shown that the product spectrum is markedly affected by double-bond isomerization which accompanies the dismutation, and that the reaction may be made highly selective for the production of either ethylene plus hexene-3, or propylene plus n-pentenes, by suitable choice of the reaction conditions or by poisoning the catalyst with controlled amounts of sodium ion.[*] The reaction has been shown to be reversible,[†] e.g., ethylene and butene-2 react to give propylene with a selectivity of over 90%. The cleavage of internal olefins by ethylene to give 1-olefins of lower carbon number is a useful general reaction ("ethenolysis").

The results of this study of the dismutation of various olefins suggest that the reaction must proceed via a "quasi-cyclobutane" intermediate.

One of the most interesting reactions to be discovered recently is the so-called "dismutation"[‡] of olefins, revealed in publications from the laboratories of the Phillips Petroleum Company (*1, 2, 3*). In the presence of molybdenum or tungsten oxides (optionally containing cobalt oxide) on alumina (*1, 2, 3*), or of the corresponding hexacarbonyls on alumina (*2, 3*), an acyclic olefin is converted at 90° to 260°C into a series of lower and higher homologues, e.g.,

$$C_4H_8 \rightarrow C_2H_4 + C_3H_6 + C_5H_{10} + C_6H_{12}$$

The dismutation of propylene has been studied in some detail (*3*) and higher olefins have been shown to dismutate (*1, 2*), but no systematic study has yet been published of the latter. An examination of the reactions of n-butenes has now thrown much

light on the reaction, and is reported here. It has been shown that double-bond isomerization of the feed, which could not be studied in the case of propylene, has a marked effect on the course of the reaction, and that its selectivity can be controlled by controlling the isomerization of both feed and products. Under these conditions dismutation can give easily purified olefins with a very high selectivity.

The results obtained in the dismutation of n-butenes have enabled tentative ideas to be formulated about the course of the reaction. Bailey and Banks (*3*) obtained amounts of ethylene and butene-2 from propylene corresponding to the thermodynamic equilibrium, which implies that the reaction is reversible. This has now been confirmed, and a useful new reaction, "ethenolysis," for the conversion of internal to 1-olefins has been discovered.

EXPERIMENTAL

1. Materials. A commercial cobalt-molybdenum-alumina (30–60 BSS) referred to

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[*] British Patent applied for, 42700/64.

[†] British Patent applied for, 47053/64.

[‡] Phillips workers use the terms "dismutation" and "disproportionation" for this reaction. The former is preferred here because it is less ambiguous.

throughout as $CoO \cdot MoO_3 \cdot Al_2O_3$, from P. Spence and Co., was used in all experiments. It contained CoO 3.8 wt % and MoO_3 13.8 wt %.

Butenes-1 and -2 (99% cis) were Phillips Pure Grade materials and were dried over silica gel and 3A molecular sieve before use. Ethylene was scrubbed with aqueous silver nitrate to remove acetylene, and dried as above.

4-Methylpentene-2 (4MP2) was a fractionally distilled cut of hexene isomers containing 4MP2, 96.6%; 4MP1, 2.2%; 2MP1, 0.2%; 2MP2, 0.1%; hexene-1, 0.2%; and 2-methylpentane, 0.6%.

2. Dismutation procedure. The catalyst (1 to 10 ml according to the GHSV of feed) was packed between plugs of quartz wool in a horizontal silica tube 40 × 1.6 cm in a tube furnace, and was activated at 550 — 580°C for 1 hr in a stream of dry air, and for 1.5 hr in dry nitrogen. It was cooled to the reaction temperature in dry nitrogen, and dry butene was then admitted via a three-way tap such that the reactor was never opened to the atmosphere. A liquid product was collected by passing the effluent through a trap at 0°C, and uncondensed gas was collected over a 30 wt % solution of aqueous potassium carbonate. The liquid product was quickly weighed in the tightly stoppered receiver, cooled to about −5°C, sampled with a well-cooled hypodermic syringe, and analyzed by gas-liquid chromatography (GLC) on a 2 m × 6 mm column of 20% squalene on Embacel at 120°C, with helium as carrier gas and a katharometer detector.

The volume of gaseous product was recorded and it was analyzed by GLC on an 8 m × 6 mm column of 20% "dimethylsulpholane" on Embacel at 20°C, with a katharometer detector.

3. Ethenolysis procedure. (a) cis-Butene-2 and ethylene were dried in separate trains as above, mixed, and passed over the catalyst as described in the previous paragraph. (b) Dry ethylene was bubbled through the 4-methylpentane-2 at 45°C via a glass sinter. The mixture was then dismutated as above.

4. Preparation of sodium-poisoned $CoO \cdot MoO_3 \cdot Al_2O_3$. Distilled water (120 ml) was added to the $CoO \cdot MoO_3 \cdot Al_2O_3$ (12 ml), and 120 ml of aqueous sodium bicarbonate was added with stirring over 2 hr. The strength of the added bicarbonate solution was such as to give a final solution of 0.01, 0.03, 0.06, 0.10, 0.20 or 0.30 N, according to the degree of poisoning required. After a total of 14 hr stirring the catalyst was filtered, slurried once with 240 ml of distilled water for 15 min, filtered, and dried at 110°C.

RESULTS

The effect of temperature on the dismutation of butene-1 at a constant gas hourly

TABLE 1

EFFECT OF TEMPERATURE ON PRODUCTS OF BUTENE-1 DISMUTATION[a]

Temperature (°C):	122°	140°	160°	180°	200°	222°	245°
% Dismutation	18.3	23.1	31.9	41.4	35.2	34.4	23.4
% Butene-2 in product butenes	16.5	23.7	52.3	71.7	77.9	81.9	81.9
Products other than C_4H_8 (mole %)							
C_2H_4	25.2	21.9	15.0	8.9	6.0	4.3	4.1
C_3H_6	25.2	29.7	37.2	46.1	48.6	49.1	48.3
C_5H_{10}	27.0	28.9	31.4	32.8	35.5	36.5	38.3
C_6H_{12}	20.3	17.7	12.5	9.2	7.4	7.0	6.4
C_7H_{14}	1.4	1.2	1.8	1.9	1.5	1.5	1.3
C_8H_{16}	0.8	0.6	1.4	0.9	0.9	1.2	1.5
C_9H_{18}	0.1	tr	0.7	0.2	0.1	0.4	0.1
Selectivity to $C_3 + C_5$	52.2	58.6	68.6	78.9	84.1	85.6	86.6
Selectivity to $C_2 + C_6$	45.5	39.5	27.5	18.1	13.4	11.3	10.5

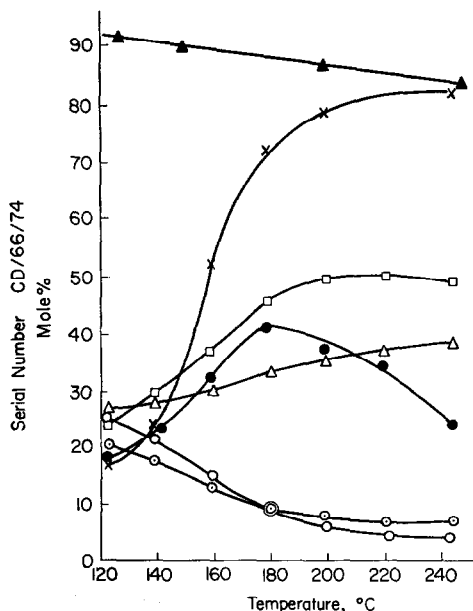[a] Catalyst, $CoO \cdot MoO_3 \cdot Al_2O_3$; GHSV, 2000. Samples collected over first 30 min.

FIG. 1. Dismutation of butene-1: effect of temperature. Catalyst: $CoO \cdot MoO_3 \cdot Al_2O_3$; GHSV = 2000. ×, Butene-2 in product butenes; □, C_3H_6; △, C_5H_{10}; ●, dismutation; ○, C_2H_4; ⊙, C_6H_{12}; ▲, butene-2 in n-butenes at equilibrium.

space velocity (GHSV) of 2000 was studied over the range 122° to 245°C. The product was collected for 30 min and analyzed for the C_2 to C_9 olefins, giving the results shown in Table 1. In addition, the gaseous products were sampled after 5, 10, and 30

min of operation, and were analyzed. At any one temperature below 160°C these analyses were similar, but at temperatures above 160°C there was a significant fall in the concentrations of ethylene and propylene with time. In Fig. 1 are shown (i) the percentage dismutation, (ii) the percentage of butene-2 in the recovered n-butenes, and (iii) the yields of C_2, C_3, C_5, and C_6 olefins based on n-butenes converted, as a function of the temperature.

The effect of space velocity on the composition of the products from the dismutation of butene-1 at 160°C is shown in Table 2 for GHSV's of 500 to 10 000. In Fig. 2 the composition of the products is plotted as a function of GHSV. A similar experiment was carried out with butene-2 at 157°C and GHSV's of 500 to 5000, with the results shown in Table 3.

When it became obvious that the selectivity in dismutation was varying with the extent of isomerization of butene-1 to butene-2, attempts were made to poison the $CoO \cdot MoO_3 \cdot Al_2O_3$ by treatment with sodium ions, and so to study the products of

TABLE 2
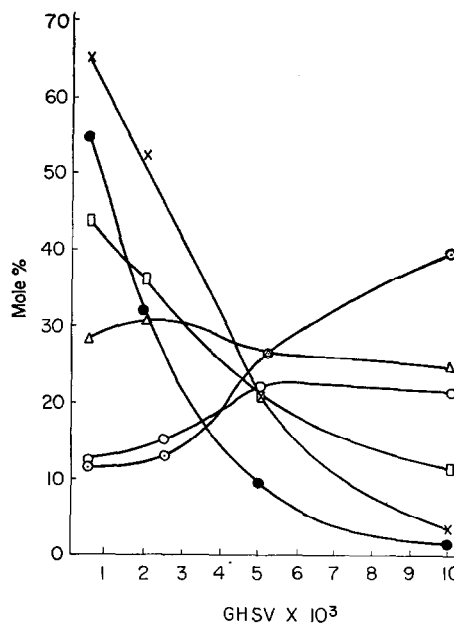#### EFFECT OF SPACE VELOCITY ON PRODUCTS OF BUTENE-1 DISMUTATION[a]

GHSV:	500	2000	5000	10,000
% Dismutation	54.5	31.9	9.0	1.7
% Butene-2 in product butenes	64.9	52.3	21.3	8.0
Products other than C_4H_8 (mole %)				
C_2H_4	12.3	15.0	22.4	21
C_3H_6	43.6	36.8	21.4	11
C_5H_{10}	28.2	31.5	26.2	25
C_6H_{12}	11.9	12.7	26.6	40
C_7H_{14}	3.0	1.8	1.0	1
C_8H_{16}	1.0	1.4	2.8	2
C_9H_{18}	tr	0.8	tr	tr
Selectivity to $C_2 + C_6$	24.2	27.7	49.0	61

[a] Catalyst, $CoO \cdot MoO_3 \cdot Al_2O_3$; Temp., 160°C. Samples collected over first 30 min.

FIG. 2. Dismutation of butene-1: effect of space velocity. Catalyst, $CoO \cdot MoO_3 \cdot Al_2O_3$; temperature, 160°C. ×, Butene-2 in product butenes; ⊙, C_6H_{12}; △, C_5H_{10}; ○, C_2H_4; □, C_3H_6; ●, dismutation.

TABLE 3

Effect of Space Velocity on Products
of Butene-2 Dismutation[a]

GHSV:	500	2000	5000
% Dismutation	30.0	14.6	3.2
% Butene-1 in product butenes	3.3	3.1	5.2
Products other than C_4H_8 (mole %)			
C_2H_4	1.4	0.4	0.5
C_3H_6	48.4	45.9	41.0
C_5H_{10}	37.7	43.3	33.2
C_6H_{12}	8.1	4.4	3.6
C_7H_{24}	2.2	1.7	1.3
C_8H_{16}	1.7	4.1	20.1
C_9H_{18}	0.5	0.3	0.2
Selectivity to $C_3 + C_5$	86.1	89.2	74.2

[a] Catalyst, $CoO \cdot MoO_3 \cdot Al_2O_3$; Temp., 157°C. Samples collected over first 30 min.

dismutation at various levels of isomerization. A series of progressively more poisoned catalysts was made, and tested for butene-1 dismutation at 180°C and a GHSV of 2000. For the present argument it proved sufficient to take the normality of the sodium bicarbonate solution used in poisoning as a measure of the extent of poisoning. The percentage dismutation, the percentage of butene-2 in total n-butenes, and the per-
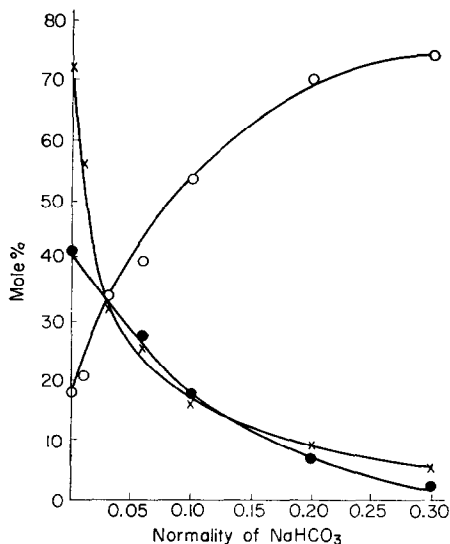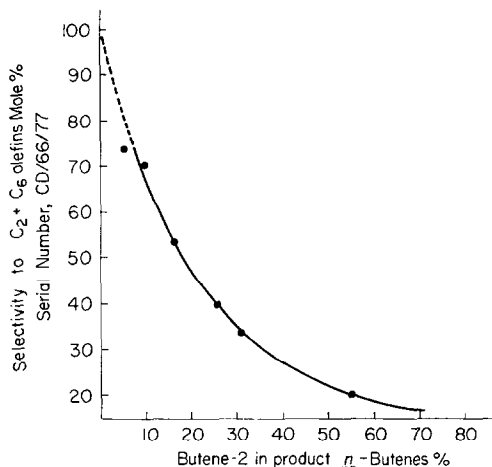

FIG. 4. Butene-1 dismutation at 180°C, GHSV = 2000. Variation of selectivity with butene isomerization.

centage selectivity to $C_2 + C_6$ olefins, are plotted against this normality in Fig. 3. The variation of the selectivity to $C_2 + C_6$ olefins with the amount of butene-2 in the total n-butenes left is shown in Fig. 4.

The reverse dismutation was studied by passing a mixture of ethylene and cis-butene-2 over $CoO \cdot MoO_3 \cdot Al_2O_3$ at 180°C and a GHSV of 1800. In Table 4 are shown the product composition and, for comparison, the composition of the product which would have been obtained had each olefin dismutated separately. The reaction gave mainly propylene.

FIG. 3. Butene-1 dismutation on Na^+-poisoned $CoO \cdot MoO_3 \cdot Al_2O_3$; temperature, 180°C; GHSV = 2000. ×, Butene-2 in n-butenes; ○, selectivity to $C_2 + C_6$; ●, dismutation.

TABLE 4

Ethenolysis of Butene-2[a]

	Feed (mole %)	Products (mole %)	Products if individual olefins had dismutated separately (mole %)
C_2H_4	66.7	54.3	65.9
C_3H_6	—	24.6	6.7
$2 - C_4H_8$	33.3	19.9	22.7
C_5H_{10}	—	1.2	4.1
C_6H_{12}	—	0	0.6
Conversion of butene		13.4 mole	
Theoretical propylene		26.8 mole	
Selectivity (molar) to propylene		92% based on butene converted	

[a] Catalyst, $CoO \cdot MoO_3 \cdot Al_2O_3$; Temp., 180°C; Total GHSV, 1800. Sampled after 10 min.

TABLE 5
Ethenolysis of 4-Methylpentene-2[a]

	C_2H_4	C_3H_6	C_4H_8	3MB1	2MB2	2MB1	$n\text{-}C_4H_{10}$	4MP2	C_6H_{12}[b]	>C_6
Feed (mole %)	70	—	—	—	—	—	—	29	1	—
Products (mole %)	57.3	11.4	4.2	9.3	1.7	0.3	0.7	10.8	2.9	1.4

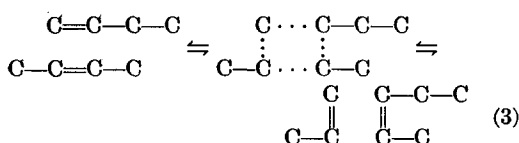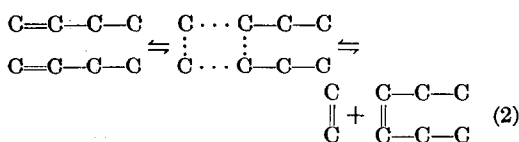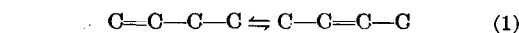[a] Catalyst, CoO·MoO₃·Al₂O₃; Temp, 160°C; Total GHSV, 1430. Samples collected over first 30 min.

[b] Other than 4MP2.

4-Methylpentene-2 and ethylene reacted at 160°C to give mainly 3-methylbutene-1 and propylene (Table 5).
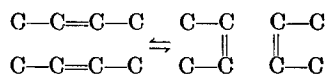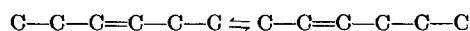
DISCUSSION

Dismutation of n-Butenes

Patents to the Phillips Petroleum Company (1, 2) show that on a CoO·MoO₃·Al₂O₃ catalyst the n-butenes dismutate to olefins ranging from C₂ to C₈, with ethylene, propylene, pentenes, and hexenes as the main products. This lack of selectivity lessens the utility of the reaction. It has now been found that by suitable choice of the temperature and GHSV, or by careful poisoning of the catalyst, the selectivity to certain pairs of olefins can be raised to high values. To aid the interpretation of our results and to clarify the discussion it is convenient to deal first with ideas about the course of the reaction. All the results which have been obtained so far support the theory that dismutation occurs via a "quasi-cyclobutane" intermediate formed by the correct alignment of the carbon atoms at the double bonds of two reacting olefins. Applied to the n-butenes, with allowance for the isomerization of butene-1 to butene-2, the reaction of butene-1 is pictured as follows:
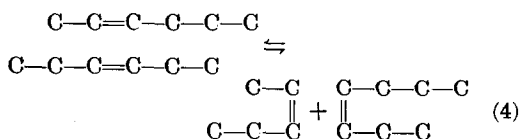
$$C=C-C-C \rightleftharpoons C-C=C-C \qquad (1)$$

$$\begin{matrix} C=C-C-C \\ C=C-C-C \end{matrix} \rightleftharpoons \begin{matrix} C\cdots C-C-C \\ C\cdots C-C-C \end{matrix} \rightleftharpoons$$

$$\begin{matrix} C \\ \| \\ C \end{matrix} + \begin{matrix} C-C-C \\ \| \\ C-C-C \end{matrix} \qquad (2)$$

$$\begin{matrix} C=C-C-C \\ C-C=C-C \end{matrix} \rightleftharpoons \begin{matrix} C\cdots C-C-C \\ C-C\cdots C-C \end{matrix} \rightleftharpoons$$

$$\begin{matrix} C \\ \| \\ C-C \end{matrix} \begin{matrix} C-C-C \\ \| \\ C-C \end{matrix} \qquad (3)$$

The reaction of two molecules of butene-2 would not produce new olefins

$$\begin{matrix} C-C=C-C \\ C-C=C-C \end{matrix} \rightleftharpoons \begin{matrix} C-C \\ \| \\ C-C \end{matrix} \begin{matrix} C-C \\ \| \\ C-C \end{matrix}$$
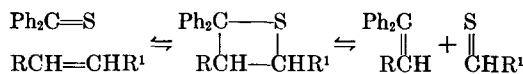
Isomerization of, for example, the C₅ and C₆ products, followed by secondary dismutations would account for the formation of olefins with 7, 8 . . . etc., carbon atoms, e.g.,

$$C-C-C=C-C-C \rightleftharpoons C-C=C-C-C-C$$

followed by

$$\begin{matrix} C-C=C-C-C-C \\ C-C-C=C-C-C \end{matrix} \rightleftharpoons$$

$$\begin{matrix} C-C \\ \| \\ C-C-C \end{matrix} + \begin{matrix} C-C-C-C \\ \| \\ C-C-C \end{matrix} \qquad (4)$$

Evidence for the above scheme will be brought out during the discussion of results which follows. A formally similar scheme was recently proposed by Kaiser and Wulfers (4) for the reaction of olefins with thiobenzophenone.

$$\begin{matrix} Ph_2C=S \\ RCH=CHR^1 \end{matrix} \rightleftharpoons \begin{matrix} Ph_2C-S \\ | \quad | \\ RCH-CHR^1 \end{matrix} \rightleftharpoons \begin{matrix} Ph_2C \\ \| \\ RCH \end{matrix} + \begin{matrix} S \\ \| \\ CHR^1 \end{matrix}$$

The extent of dismutation of butene-1 varied with temperature as shown in Table 1 and Fig. 1, rising to a maximum at about 180°C (GHSV 2000) in the vapor-phase reaction at atmospheric pressure. Bailey and Banks (3) found this maximum to be at 163°C in the reaction under pressure with a weight hourly space velocity between 3 and 4. The amount of butene-2 found in the product butenes rose steadily with temperature until at 220°C it very closely approached the equilibrium value. The amount of butene-2 found in the product must not be taken as a direct measure of the extent

of isomerization because some of the olefin is consumed in reaction (3) above.

The variation of the distribution of C_2 to C_6 olefins with temperature, also shown in Fig. 1, is very significant. At the lowest temperature (122°C), when the rate of formation of butene-2 must be at its lowest, the C_2, C_3, C_5, and C_6 olefins are formed in nearly equimolar amounts. The ratio of butene-1 to butene-2 in the products at this temperature is 5 to 1. As the temperature of the reaction increases, so the olefins other than butenes split into two pairs—the selectivity to $C_3 + C_5$ rises, and that to $C_2 + C_6$ falls. This is evidence that they are formed in two separate reactions i.e., (2) and (3) above. Furthermore, the selectivity to $C_3 + C_5$ olefins rises as the amount of butene-2 in the products rises, which supports the suggestion that they derive from a butene-2/butene-1 reaction, and the selectivity to $C_2 + C_6$ olefins falls as more butene-1 is isomerized to butene-2, which is consonant with the theory that the C_2/C_6 olefins come from a butene-1/butene-1 reaction. No attempt has been made to determine the activation energies, or rates, of any of the reactions, because there are at least three taking place, and these are so interdependent that any such calculation would have little value. However, it is clear from the results of the run at 122°C (Table 1), for example, that the butene-1–butene-2 reaction, is faster than the butene-1–butene-1 reaction, because the ratio, butene-1/butene-2 in the product is about 5 whereas the ratio, yield of $C_2 + C_6$/yield of $C_3 + C_5$ is approximately 1.

The existence of a maximum, at about 180°C, in the extent of dismutation is due to the increasingly rapid rate of catalyst decay as the temperature is raised. This was proved by analyzing the gaseous product after 5, 10, and 30 min of operation, at 180°C, when a significant fall in the concentrations of propylene and ethylene was apparent with time. In the experiments recorded in Fig. 1 and Table 1, products were sampled over the first 30 min of a run, fresh catalyst being used for each temperature. At below 160°C the rate of decay was found, by similar analyses, to be less signifi-

cant over 30 min. The decrease in conversion above 180°C is not the result of unfavorable changes in the thermodynamics of the system, since, as the figures in Table 6 show, the equilibrium conversion varies little in the temperature range 100–245°C. As can be seen in Fig. 1, at above 200°C the rate of isomerization of butene-1 to

TABLE 6
BUTENE-1 DISMUTATION: THERMODYNAMIC
EQUILIBRIUM CONVERSIONS

Temperature (°C)	Equilibrium Conversions[a] (mole %)
122°	66.5
140°	67.6
160°	66.8
180°	62.5
200°	60.0
222°	57.6
245°	57.6

[a] Calculated on the assumptions that (1) the amount of butene-1 in n-butenes found in the product at a particular temperature is the same in the thermodynamic equilibrium mixture of products; (2) only three reactions are taking place:

$$2\,C_4-1 \rightarrow C_2 + C_6 - 3$$
$$C_4-1 \rightarrow C_4-2$$
$$C_4-1 + C_4-2 \rightarrow C_3 + C_5 - 2.$$
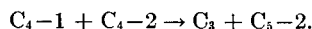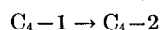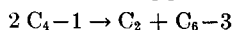
butene-2 is so fast relative to dismutation that the unconverted butenes have nearly the equilibrium composition, i.e., the effective feed to dismutation is of constant composition. Thus the fall in the extent of dismutation at above 200°C cannot be attributed to an unfavorable change in butene-1 to butene-2 ratio.

The results of a brief study of the effect of space velocity on the dismutation of butene-1 at 160°C, shown in Table 2 and Fig. 2, are in line with the above interpretation. At low space velocities the extent of isomerization of butene-1 to -2 is maximal, and the selectivity to $C_3 + C_5$ olefins should be high. As the space velocity is increased less butene-2 will be formed and the selectivity to $C_2 + C_6$ olefins (from butene-1) should rise. This trend is certainly apparent in the results, but is somewhat blurred by the analytical inaccuracies which occur when the extent of dismutation

is very low, e.g., 9.0 and 1.7% at GHSV's of 5000 and 10 000, respectively. Because of these inaccuracies, and the multiplicity of reactions occurring, it was felt that attempts to determine the order of individual reactions were not warranted.

A similar study of the effect of space velocity on the dismutation of butene-2 at 157°C gave the results collected in Table 3. At 157°C the maximum amount of butene-1 which can be present is the equilibrium amount, i.e., 10% of total n-butenes. Hence the main dismutation reaction to be expected is that between butenes-1 and -2 giving $C_3 + C_5$ olefins, and in fact the selectivity to these products was high over the range of GHSV's studied.

In all the above work it would be expected, ideally, that equimolar amounts of C_2 and C_6, and of C_3 and C_5 olefins would be formed. Reference to Tables 1–3 shows that this is rarely the case, a fact which must be attributed to further reactions of the primary products, for example as in Eq. (4).
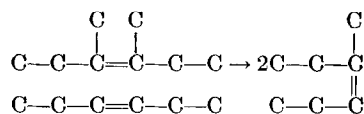
The above studies established that by varying the temperature and space velocity butene-1 could be made to yield mainly ethylene and hexenes or propylene and pentenes, and butene-2 could be converted mainly to propylene plus pentenes. If the course of the dismutation is correctly represented by reactions (1) to (3) above, then preventing the isomerization of butene-1 to butene-2 should eliminate reaction (3) and lead to very high selectivities to ethylene and hexene-3 from reaction (2). This proved to be so. The results of dismutating butene-1 on a series of $CoO \cdot MoO_3 \cdot Al_2O_3$ catalysts which had been poisoned with solutions of sodium bicarbonate of increasing strength are shown in Fig. 3. The extent of dismutation and the amount of butene-2 in the product butenes fell in a parallel manner, with increasing strength of the bicarbonate solution, at the same time as the selectivity to $C_2 + C_6$ olefins rose. When, as in Fig. 4, the selectivity to $C_2 + C_6$ olefins is plotted against the amount of butene-2 in the product butenes, the curve can be reasonably extrapolated to a 100% selectivity at zero butene-2 production. This

is good evidence that butene-1 if uncontaminated by butene-2 would dismutate exclusively to ethylene and hexene. The highest selectivity was obtained in a separate run on the catalyst treated with 0.2 N sodium bicarbonate; butene-1 at 140°C and a GHSV of 2000 gave a 90.7% molar selectivity to ethylene plus hexene at a 10.5% conversion. It would be predicted from reaction (2) that the C_6 product should be hexene-3; in fact this latter run gave a C_6 product which contained >99% of hexene-3 (cis plus trans).

More evidence about the course of the reaction (we are deliberately avoiding the term "mechanism of reaction" which implies a deeper knowledge of the reaction than we in fact possess) was obtained by consideration of the structure of the C_5–C_8 products of butene-1 dismutation, analyzed after combining the appropriate fractions from several runs at 140–160°C, GHSV 2000:

	C_5	C_6	C_7	C_8
% linear	100	99.6	88.2	14
% branched	0	0.4	11.8	86

If the C_5 and C_6 olefins are formed in reactions (2) and (3) they would be 100% linear—the "quasi-cyclobutane" theory of dismutation requires that no increase in branching can occur. The production of linear C_7 and C_8 olefins can be accounted for by secondary reactions such as (4) above. The branched C_7 olefins could arise from branched C_8 olefins, for example as follows:

$$\begin{array}{c} \text{C} \quad \text{C} \qquad\qquad\qquad \text{C} \\ | \quad\ | \qquad\qquad\qquad\quad | \\ \text{C--C--C=C--C--C} \rightarrow 2\text{C--C--C} \\ \\ \text{C--C--C=C--C--C} \qquad \text{C--C--C} \end{array}$$

and it therefore remains to explain why such a high percentage of the C_8 olefins are branched. If dismutation were wholly explained by reactions (1) to (4) then one would expect to obtain a regular falling off in the yields of C_6, C_7, C_8 . . . olefins. However, reference to Table 2 shows that in the dismutation of butene-1 at the higher space velocities there is a peak at C_8, while Table

3 shows that in the butene-2 reaction at high space velocities and low conversions C_8 olefins can account for as much as 20% of the products. This suggests that the catalyst contains enough acid sites to promote a small amount of cationic polymerization of the butenes to C_8 dimers which, because the mechanism is cationic, would be heavily branched.

Reverse Dismutation and Ethenolysis

In the Phillips' work to date only single olefins have been dismutated. If dismutation follows the course suggested in reactions (2) and (3) then the reaction must be reversible—this is borne out by the fact that Banks and Bailey (3) obtained from propylene the *equilibrium* mixture of C_2, C_3 and C_4 olefins. At first sight the reaction of two olefins A and B would not seem very useful because a mixture of products from three simultaneous reactions (A–A, B–B, and A–B) would be obtained. This is illustrated in the reactions of butenes-1 and -2 above. However, ethylene is known to be virtually inert towards dismutation catalysts (3), so that if A is ethylene only reactions A–B and B–B will occur. The reaction B–B should be suppressed by the presence of an excess of ethylene, so that under these conditions a clean "ethenolysis" should occur. No net change will occur when B is a 1-olefin
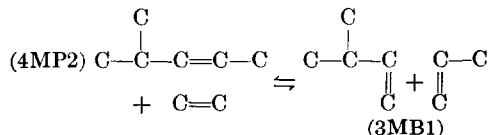
$$R^1R^2C{=}CH_2 \atop +{} \atop CH_2{=}CH_2 \quad \rightleftharpoons \quad {R^1R^2C \atop \|\atop CH_2} + {CH_2 \atop \|\atop CH_2}$$
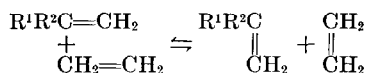
but internal olefins will be split to 1-olefins by ethylene (hence the term "ethenolysis")

$$R^1R^2C{=}CR^3R^4 \atop CH_2{=}CH_2 \quad \rightleftharpoons \quad {R^1R^2C \atop \|\atop CH_2} + {CR^3R^4 \atop \|\atop CH_2}$$
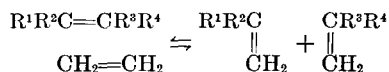
The above reasoning proved to be correct. When an excess of ethylene plus butene-2 was passed over the $CoO\cdot MoO_3\cdot Al_2O_3$ catalyst a 40% conversion of the butene occurred to give propylene with a selectivity of 92% molar. The only by-product was n-pentene, from the butene-2/butene-1 reaction. The disappearance of ethylene and the low yield of pentenes (Table 4) proved that the products were not formed by the dismutation of butene-2 (or derived butene-1) only. Further, the predicted olefins, viz., 3-methylbutene-1 (3MB1) and propylene, were formed by the ethenolysis of 4-methylpentene-2 (4MP2)

$$(4MP2)\ \underset{+\ C{=}C}{C{-}\overset{\overset{C}{|}}{C}{-}C{=}C{-}C} \quad \rightleftharpoons \quad \underset{\underset{C}{\|}}{C{-}\overset{\overset{C}{|}}{C}{-}C} + \underset{\underset{C}{\|}}{C{-}C}$$
$$\text{(3MB1)}$$

At a 62.5% conversion of 4MP2 the molar selectivity to 3MB1 and propylene was 66%. The results in Table 5 show that double-bond isomerization of both feed and products had taken place. Of the isomers of 4MP2, the 1-olefins 2MP1 and 4MP1 would be unaffected by ethenolysis (see above), and 2MP2 would yield isobutene and butene-1 thus accounting for the butenes reported in Table 5. Because some of the 3MB1 had isomerized to 2MB1 and 2MB2, and some n-pentene was also formed, the 3MB1 constituted only 77.5% of the C_5 fraction.

Ethenolysis is thus a novel reaction, of great potential, for splitting internal olefins into two molecules of 1-olefin.

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