REACTIONS OF BUTENES AND METHYL BUTENES ON A ZINC OXIDE CATALYST[1]

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ABSTRACT

Reactions of butene-1, isobutene, 3-methyl butene-1, and 2-methyl butene-2 on ZnO catalysts have been investigated at 615°. The formation of the observed products is discussed in terms of a sequence of surface processes incorporating dissociation of the bonds in β position to the double bond, with formation of chemisorbed allyl and substituted allyl radicals.

INTRODUCTION

A study of dehydrogenation of butene-1 on semiconducting oxide catalysts between 500 and 650° has been conducted recently in this laboratory (1). The activity and selectivity to butadiene formation of "valency-controlled" ZnO and NiO catalysts were discussed in terms of their electrical properties. Thus, after it was doped with lithia, zinc oxide became inactive, while the catalysts with small additions of gallia, although showing the same activity as pure zinc oxide, were distinctly more selective. An explanation was suggested by assuming an important role in these reactions of "excess" electrons in the *n*-type semiconductors.

The present work has been carried out in an attempt to obtain further information on the mechanism of dehydrogenation on zinc oxide catalysts from a comparative study of the reactions of several structurally related olefins. Zinc oxide containing 1 atom % Ga^{+++} in the lattice was used because of its somewhat greater selectivity (1). The reactions were carried out at 615°.

EXPERIMENTAL

The apparatus used is illustrated in Fig. 1. It consisted of a reactor, circulating pump, boiler, and storage lines. The reactor consisted of a silica tube connected to the rest of the apparatus by pyrex–silica graded seals. The catalyst pellets were placed in a silica spoon as shown. Two leads through tungsten–glass seals were provided for conductivity measurements. Larger flat pellets containing Pt-foil leads were used for conductivity determinations by means of an a-c. bridge. In most of the work small cylindrical pellets of the catalyst ($\frac{1}{8}$ in. × $\frac{1}{8}$ in. × $\frac{1}{8}$ in.) were used. A 14/30 standard joint facilitated catalyst removal and changing. The temperature of the furnace round the reactor was controlled by a chromel–alumel thermocouple placed in a well in the silica tube.

The olefins were introduced to the evacuated 2-liter flask, then mixed with nitrogen to give a total pressure of about 760 mm Hg. The ratio of the olefin to nitrogen was about 1:12 in all experiments. Nitrogen was also let into the reactor system, so that with the water in the boiler boiling vigorously, the total pressure in the reactor section was also about 760 mm. The stopcocks isolating the 2-liter volume from the reaction system could then be opened, and the gases circulated continuously using a reciprocating plunger pump as described by Watson (2). The pumping rate and the volume of the reaction system were such that the gas phase was circulated once in just over 2 minutes. Average run duration was about 30 to 40 minutes, with occasional runs up to 90 minutes. During a run samples of the gas phase were withdrawn at intervals into 50-ml receiving bulbs, and the condensable content frozen out with liquid nitrogen. The permanent

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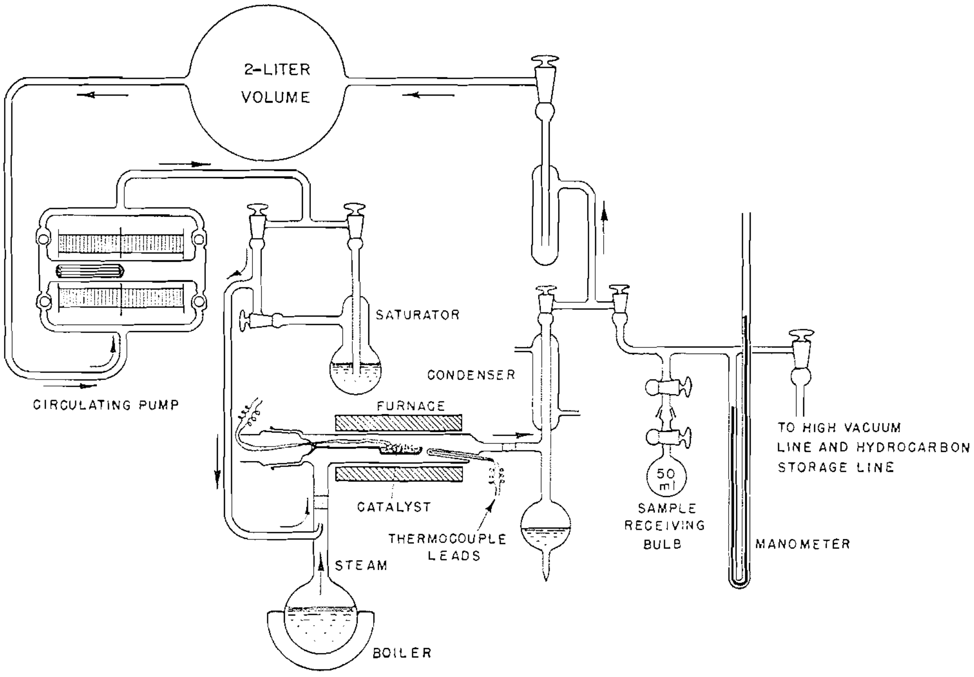


FIG. 1. Diagram of the apparatus.

gases were then pumped away, and the residual samples analyzed by means of a mass spectrometer. Analyses for H_2 and CH_4 in the large excess of non-condensable gas were as a rule not made. To distinguish between certain isomers in the products, gas chromatographic analysis was sometimes used.

Research grade olefins were employed.

RESULTS

Reactions of the following olefins were investigated: butene-1, isobutene, 3-methyl butene-1, and 2-methyl butene-2.

Butene-1

Butene-1 undergoes extensive dehydrogenation, the main products being C_4H_6, C_3H_6, and C_2H_4 in the approximate ratio 2:2:1. The production of butadiene is favored by the presence of moisture, which suppresses side reactions rather than aiding dehydrogenation directly. The results are summarized in Table I. The average dehydrogenation selectivity is about 40% for about 40% decomposition of butene-1.

Isobutene

Isobutene undergoes practically no decomposition and no butadiene is formed. This indicates that no isomerization of the carbon skeleton of the molecule occurs.

3-Methyl Butene-1

3-Methyl butene-1 is very reactive, the main products being C_4H_8 and C_4H_6 in the presence of moisture, that is, the loss of a methyl group is the main reaction. In the presence of oxygen, added to the gas stream, C_5H_8 was the main product, much less C_4H_6 being produced. The presence of oxygen however slowed down the over-all decomposition rate. The results are summarized in Table II.

TABLE I

Dehydrogenation and decomposition of butene-1

Diluting gas	% Reaction* (after 22 min)	Dehydrogenation selectivity, %	Main products†			Catalyst
			Butadiene	Propylene	Ethylene	
Moist N_2	43.4	44.5	14.5	16.0	7.8	ZnO + 1% Ga
Steam + N_2	41.0	41.4	14.8	16.7	7.6	ZnO + 1% Ga
Moist N_2 + 27 mm O_2	40.0	39.0	12.2	12.2	7.9	ZnO + 1% Ga
Dry N_2	62.9	29.6	13.0	21.7	20.0	ZnO + 1% Ga
Steam + N_2	26.0	23.5	5.5	12.3	4.3	Zn metal
Dry N_2	54.1	22.0	11.0	19.6	15.4	Zn metal

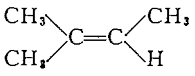
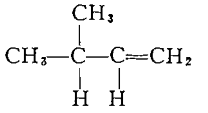
*Isomerization is not taken into account in evaluating % reaction.
†Expressed as percentages of the total carbon in the products.

2-Methyl Butene-2

2-Methyl butene-2 produces mainly C_5H_8 and C_4H_8 with only very small amounts of C_4H_6. The results are summarized in Table II. The results show that double-bond isomerization to give 3-methyl butene-1 does not occur, otherwise the products of decomposition of the latter hydrocarbon would also be found. This was confirmed by gas chromatographic analysis.

TABLE II

Dehydrogenation and decomposition of 3-methyl butene-1 and 2-methyl butene-2 on ZnO + 1% Ga

Olefin	Diluting gas	% Reaction* (after 22 min)	Dehydrogenation selectivity, %	Main products†				
				C_5H_8	C_4H_8	C_4H_6	C_3H_6	C_2H_4
	Steam + N_2	30.0	48.0	13.1	9.4	1.1	3.0	3.0
(2-Methyl butene-2)	Steam + N_2 + 44 mm O_2	42.5	41.2	12.6	8.4	—	9.4	—
 $CH_3\text{—}\overset{CH_3}{\underset{H}{C}}\text{—}\underset{H}{C}\text{=}CH_2$	Steam + N_2	82.8	9.7	5.0	9.0	21.0	11.5	21.5
(3-Methyl butene-1)	Steam + N_2 + 29 mm O_2	56.0	22.1	12.4	10.0	10.2	8.4	8.4

*Isomerization is not taken into account in evaluating % reaction.
†Expressed as percentages of the total carbon in the products.

As the amount of butadiene produced by the decomposition of 2-methyl butene-2 was very small even after about 20 recycles, it appeared that the butene produced in this reaction was mainly the unreactive isobutene. Gas chromatographic analysis of the C_4H_8 fraction showed that the butene consisted of 75% isobutene, 25% *trans*-butene-2, and no *cis*-butene-2 or butene-1.

DISCUSSION

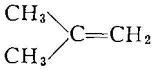
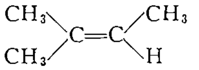
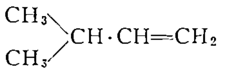
The processes studied in the present work involve dissociation of C—H and C—C bonds at the surface of the catalyst. In general C—C bonds in hydrocarbons are considerably weaker than C—H bonds and this factor alone would favor cracking over dehydrogenation. Selectivity to dehydrogenation is in general determined by the ability of a particular catalyst to dissociate preferentially the C—H bonds. This in general depends not only on the properties of the catalyst but also on the reaction conditions, such as temperature, contact time, etc. The present experiments were carried out at a single temperature and under conditions which might have favored the cracking processes and somewhat exaggerated their importance. Thus, over a period of time there was some accumulation of metallic zinc on the colder parts of the reaction vessel. For these reasons some of the results were independently checked (3) under similar conditions but with certain additional precautions. The ratio of the dead volume to the catalyst volume in the reaction zone was also reduced. Some differences were observed, particularly a tendency for reduction of cracking relative to dehydrogenation. In the case of 2-methyl butene-2, for example, only isoprene and 2-methyl butene-1 were formed. The main features of the reactions, however, remained very similar. The present results will, therefore, be discussed as obtained under the particular experimental conditions employed. Further study of these processes on the same and some other catalysts at various temperatures is in progress.

The reactions of the individual olefins studied show some characteristic differences. It is known from infrared studies of chemisorbed olefinic hydrocarbons (4) that there are under certain conditions and on some metals at least three and perhaps more than three points of contact (with the necessary corresponding dissociative chemisorption of hydrogen atoms). On hydrogenation–dehydrogenation catalysts the processes of dissociative and associative chemisorption, dehydrogenation and hydrogenation, and of desorption with isomerization or polymerization, are closely related. The predominance of one or the other of these processes depends on the surface concentrations of adsorbed species (in particular that of hydrogen) and on the rates of their formation by adsorption and of their mutual interactions and desorption, both of which are functions of temperature and the nature of the catalyst. The extent of dissociative "stripping" of hydrogen atoms and of the number of contacts with the surface may, therefore, vary widely with the conditions. The kinetic differences observed in the present work should be contrasted with the identical infrared spectra of chemisorbed isomeric *n*-hexenes (4). The adsorbed complexes in the case of 3-methyl butene-1 and 3-methyl butene-2, for example, cannot be identical under conditions of the present work.

In order to explain in a consistent manner the products of dehydrogenation and isomerization observed in the present work a sequence of dissociative processes, following energetically favorable paths, is postulated. This incorporates dissociative chemisorption of the weak C—C and C—H bonds in β position to the double bonds. On the present catalyst at 615° C the weaker β C—C bonds appear to be broken more readily than the stronger β C—H bonds, although this may vary with the type of catalyst used and the temperature. Thus, in the case of butene-1 the breakage of β C—H and β C—C bonds may lead to the formation of butadiene and propylene, respectively. These two compounds are formed in approximately equal amounts in spite of the fact that there are two β C—H bonds and only one β C—C bond indicating that the latter break more readily. In 3-methyl butene-1 there are two β C—C bonds and only one β C—H bond and the reaction involves predominantly cracking to lower hydrocarbons, with butadiene as the main product. The presence of two weak β C—C bonds also explains the high reactivity of this compound. On the other hand, 2-methyl butene-2 possesses no β C—C bonds but only the stronger β C—H bonds, and is consequently much less reactive and direct dehydrogenation is the main reaction. The very low reactivity of isobutene can be partly explained in the same manner, but the main factor appears to be that a conjugated system of double bonds to form C_4H_6 is impossible without rearrangement to a straight chain carbon skeleton. As a result any dissociative chemisorption is eventually followed by recombination with the initially dissociated H atoms to regenerate isobutene. The dependence of the over-all reactivity under comparable conditions and of the selectivity to dehydrogenation of these olefins on the number of β C—C and β C—H bonds is shown in Table III.

TABLE III

Comparison of the reactivity and selectivity to dehydrogenation with the number of β C—C and β C—H bonds in the olefins

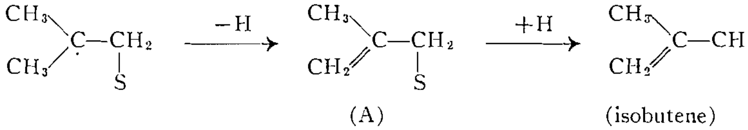
Olefin	% Reaction* (after 22 min)	Dehydrogenation selectivity,* %	Number of β C—C bonds	Number of β C—H bonds
 $(CH_3)_2C{=}CH_2$	Small	—	None	6
 $(CH_3)_2C{=}CH(CH_3)$	30.0	48.0	None	9
$CH_3{\cdot}CH_2{\cdot}CH{=}CH_2$	41.0	41.4	1	2
 $(CH_3)_2CH{\cdot}CH{=}CH_2$	82.8	9.7	2	1

*Isomerization is not taken into account in evaluating % reaction.

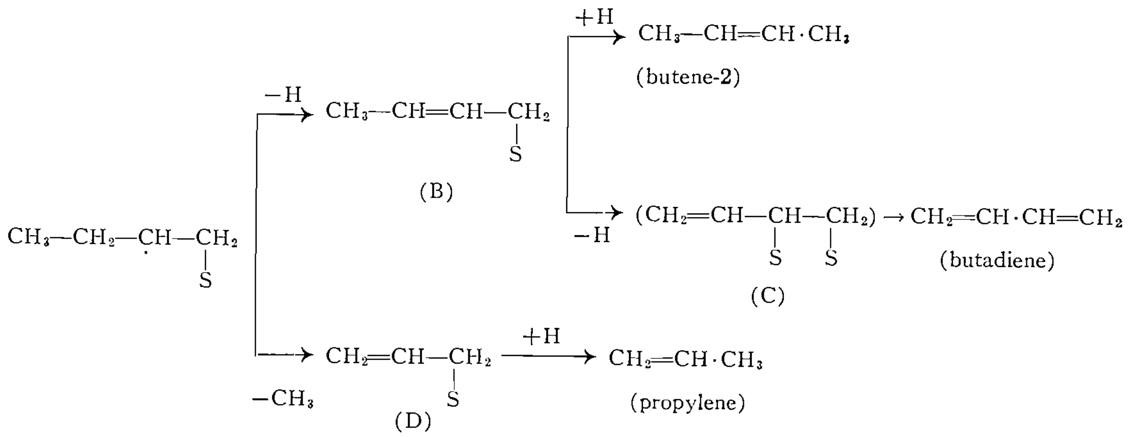
The dissociation of the bonds in β position to the double bond may constitute the initial step in the catalytic process (a purely dissociative mechanism), or the dissociation may be preceded by an initial interaction of the catalyst with the double bond (a combined associative–dissociative mechanism). The two possibilities are in many respects very similar and are difficult to distinguish experimentally. Both lead to the formation of chemisorbed allyl or substituted allyl radicals. In the purely dissociative mechanism the double-bond shift can be visualized as occurring through a 1,3 switch in the position of attachment of the allylic radical to the surface, and the dissociative process can then be further propagated through the breakage of bonds β to the shifted double bond, with formation of dienes. Some energetic restrictions have to be imposed to accommodate, for example, the lack of isomerization of 3-methyl butene-2 to 3-methyl butene-1.

In the combined associative–dissociative mechanism the energetic restrictions can be introduced by assuming an "orientation" in the initial interaction of the catalyst with the olefin. It can be assumed that (*a*) the initial attachment to the surface takes place at the "less-substituted" of the two carbon atoms of the olefinic double bond, (*b*) a C—H or a C—C bond in β position to the original double bond is broken and a new double bond is formed, (*c*) if there are C—H (or C—C) bonds in β position to the new double bond, these may be broken in turn and dienes formed, (*d*) alternatively and simultaneously recombination may take place with chemisorbed H atoms to regenerate the olefin but with the double bond shifted one position. This is represented for the olefins of interest in connection with the present work in the following scheme.

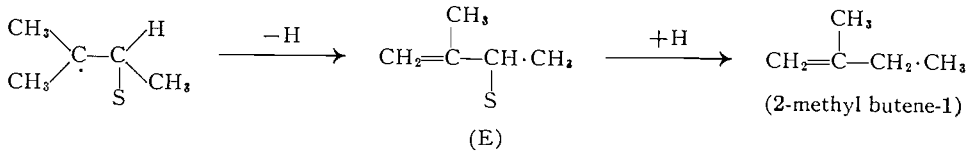
Isobutene



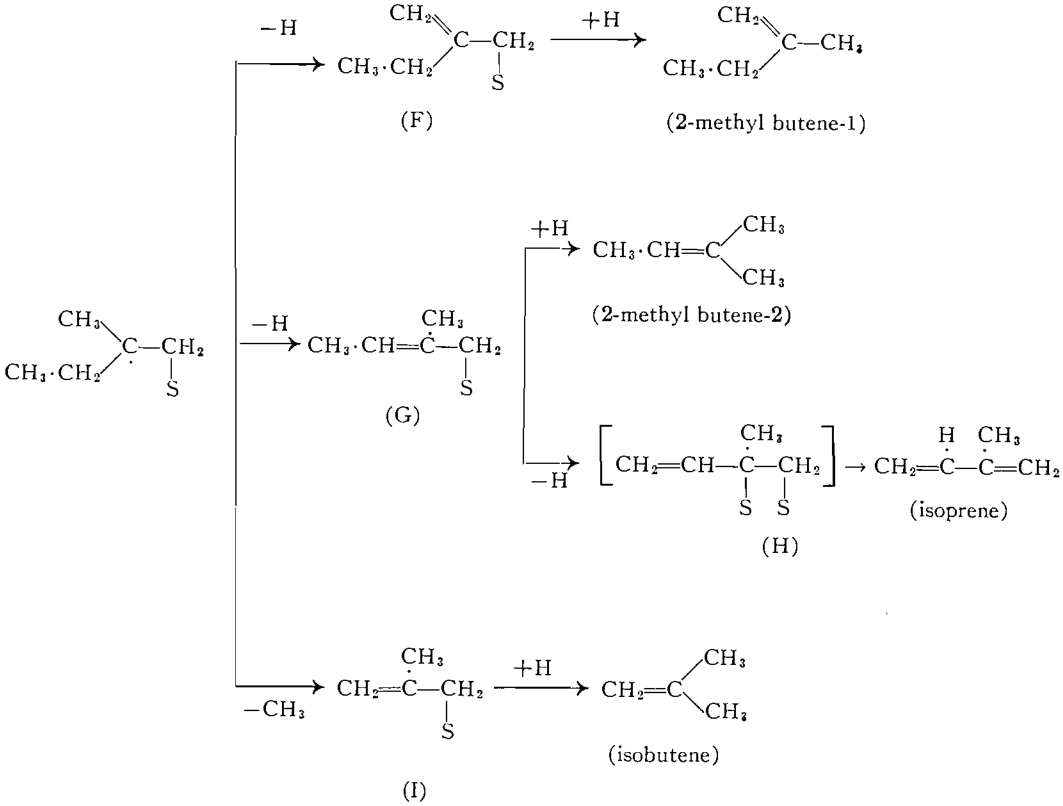
Butene-1



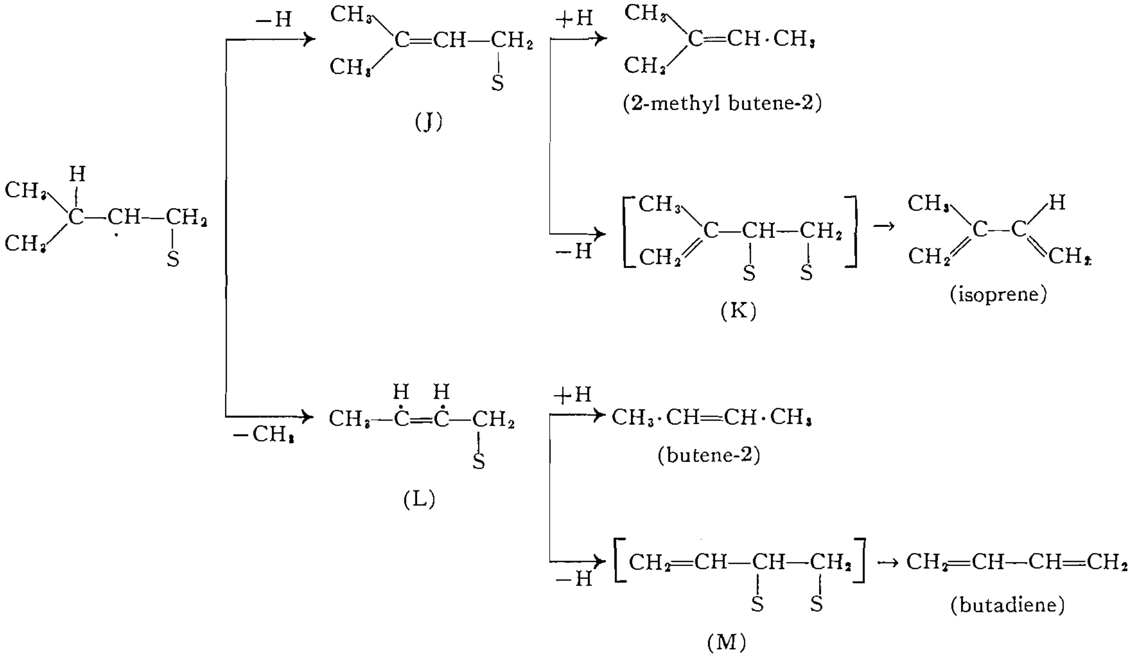
2-Methyl Butene-2



2-Methyl Butene-1



3-Methyl Butene-1



The products predicted in this scheme for various olefins by consistent application of the mechanism summarized in the four points given above agree well with the observed products if, for the moment, the formation of the cracking products ethylene and propylene is disregarded in most cases. Thus, no isomerization of 2-methyl butene-2 to 3-methyl butene-1 is predicted, although the double bond should shift in the opposite direction to form 2-methyl butene-1. This last compound should then produce isoprene and isobutene, which are the main products formed. No butadiene is predicted nor is it formed to any extent. On the other hand, in the case of 3-methyl butene-1, isoprene, butadiene, and butene-2 (but only a trace of butene-1 or isobutene (3)) are all formed in substantial amounts. Furthermore, the primary isomerization product is 2-methyl butene-2, as predicted, rather than 2-methyl butene-1 (3).

In the proposed scheme of reactions no cracking into ethylene and propylene (with one exception) is considered. This type of cracking can be formally explained in a consistent manner by assuming that in the intermediates (B), (G), (J), and (L) the incipient new double bond may break. In the case of the intermediates such as (A), (D), etc. where an analogous split would liberate CH_2, this cracking probably does not occur to any extent. Thus, isobutene is stable, 3-methyl butene-1 forms large amounts of propylene and ethylene, while 2-methyl butene-2 forms very little of these compounds.

The dissociative and associative mechanisms of olefin chemisorption have been the subject of numerous studies and discussions. The difficulty of unambiguous differentiation between the two (and the "hydrogen-switch" mechanism) is well recognized (5) .The number of points of contact indicated for the complexes (A), (B), etc. and their positions in the olefin molecules are necessarily arbitrary. In the case of the complexes (C, H, K, M) preceding dienes the formal application of the associative mechanism leads to 1,2-diadsorbed species with a double bond in 3 position, as shown in the above scheme. The purely dissociative mechanism discussed earlier, on the other hand, leads to 1,4-diadsorbed molecules with a double bond in 3 position. Formation of transitory double bonds in chemisorbed hydrocarbons, somewhat similar though not identical with those depicted here, was recently postulated by Burwell *et al.* (6) in order to explain racemization of (+)3-methylhexane occurring concurrently with H—D exchange on some metal surfaces.

The condition of the catalytic surface appears to play an important role in determining the relative extents of cracking, dehydrogenation, and isomerization. Thus in the reaction of butene-1 over-all reaction increased but the amount of butadiene formed remained unaltered in the absence of moisture, as shown in Table I. The presence of moisture seems to be essential in suppressing the cracking. The role of moisture may be to prevent the exposure of the Zn atoms by covering the surface with hydroxyl groups. The promotion of cracking by Zn is perhaps due to the relatively strong bond between this metal and CH_3 (7), which is stronger than the corresponding bond with hydrogen.

The sensitivity of the catalytic surface to the ambient atmosphere reflected itself in a strong increase in conductivity, almost to that of metallic zinc as soon as any hydrocarbon was admitted to the system. This held true even when oxygen was present in the gas phase, in spite of the normally observed decrease in conductivity of *n*-type semiconductors as the partial pressure of oxygen is increased.

Under dry conditions appreciable quantities of benzene (up to 14% after 35 to 40 recycles) were formed from butene-1. While the mechanism of formation of benzene is not understood, it is likely that it results from recombination of acetylenic residues. A mixture of butadiene and ethylene failed to yield any benzene under similar reaction conditions.

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