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The Rearrangement of 1-Butene-1-^{14}C over the Chromia-Alumina Catalyst[1)]

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An investigation of the radioactive carbon rearrangement in the dehydrogenation reaction to produce radioactive 1, 3-butadiene from 1-butene-1-^{14}C over the chromia-alumina catalyst was carried out under various conditions. The extent of the carbon-14 rearrangement from the 1-position in the 1-butene to the 2-position in the 1, 3-butadiene produced in the reaction was large at higher temperatures. The existence of four-membered ring intermediates on the catalyst was suggested as a possible mechanism for the rearrangement.

An extensive study of the mechanism for the dehydrogenation of butane and butenes over the chromia-alumina catalyst has been carried out by Balandin and his co-workers.[2-4)] They have shown that the dehydrogenation of a mixture consisting of 50% *n*-butane and 50% 1-butene labeled with carbon-14 over the catalyst at 600°C gave radioactive 1, 3-butadiene of the same specific activity as that of 1-butene in the starting mixture. About one-third of the 1-butene was apparently converted to 1, 3-butadiene, with very little of the butane being dehydrogenated to either butenes or butadiene.

An investigation of the dehydrogenation and aromatization of straightchain alkane over the chromia-alumina catalyst by Pines and his co-workers has shown that ring intermediates on the surface of the catalyst were involved in the transition state.[5)] Therefore, the formation of butadiene from butenes might also be considered to involve not only dehydrogenation reaction between the adjacent positions but also one between distant positions, *e. g.*, between the 1- and 3-positions, or between the 1- and 4-positions. The latter mechanism, which may be thermodynamically unfavorable at moderate temperatures, may be expected to involve some skeletal rearrangement in the butadiene produced.

The present study, therefore, was undertaken in order to determine the position of carbon-14 in the butadiene produced in the dehydrogenation of 1-butene-1-^{14}C, and to obtain better information concerning the dehydrogenation mechanism of butenes.

Experimental

Material. The *n*-butane, 1-butene, *trans*-2-butene, *cis*-2-butene and 1, 3-butadiene (c. p. grade) were purchased from the Matheson Co. The 1-butene-1-^{14}C (0.200 mc/2.7 mg) and ethylene-1-^{14}C (0.100 mc/0.93 mg) were obtained from the New England Nuclear Corp.; they were diluted with non-radioactive 1-butene and ethylene respectively to moderate radioactivities by using a vacuum system.

Catalyst. The chromia-alumina catalyst was obtained from the Houdry Process and Chemical Co. The catalyst is designated as type A-50 and has intrinsic acidity. It contains about 20% chromia on alumina. The catalyst is in the form of cylindrical pellets, 2.5 mm in diameter and 6 mm in length. Furthermore, it has the following characteristics: surface area 55 m^2/g, total pore volume 0.31 m*l*/g, pellet density 1.42 g/m*l*, calculated average pore diameter 225 Å.[6)]

Dehydrogenation Reaction. Prior to its placement in the reactor, 1-butene-1-^{14}C with a large amount of helium (93—98 vol%) was heated by passing it through a stainless-steel-tube preheater (6 mm in diameter, 3 m in length) which was kept at lower temperature than the reactor (about 50°C). The reactor was made from a quartz tube, 1.5 cm in diameter, in which 28 g of the above-mentioned chromia-alumina catalyst was charged; it was heated by an electric furnace. The flow rate was determined by a wet gas meter. The gaseous products were collected in a U-tube cooled

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with liquid nitrogen and were then analyzed by a gas chromatograph.

Carbon-14 Position Determination. For the determination of the position of carbon-14 in the 1, 3-butadiene produced, the 1, 3-butadiene was converted to the adduct of the maleic anhydride of 1-phenyl-1, 3-butadiene (I), and then to benzoic acid (II), using the sequence of reactions shown in Fig. 1.[7-10]

The isotope effect of carbon-14 in this process could be neglected, in view of Rapp's results.[8]

Synthesis of 1-Phenyl-4-chloro-2-butene-1, 4-$^{14}C_1$. Aniline (25.4 g) was dissolved in concentrated hydrochloric acid (67.6 m*l*) and diazotized with an aqueous solution (25 m*l*) of sodium nitrite (19 g) below 0°C. The radioactive 1, 3-butadiene produced in the dehydrogenation reaction was separated by gas chromatography and dissolved in acetone (200 m*l*) containing non-radioactive 1, 3-butadiene (25.8 m*l*, in liq.). The solution was poured into a cupric chloride (8 g) and calcium oxide (7.5 g) aqueous solution (15 m*l*) placed in a 500 m*l* round-bottomed flask equipped with a dry-ice reflux condenser and a dropping funnel. The cold solution of the diazo compound was vigorously stirred, drop by drop, into the above mixture below 0°C. The reaction product was then extracted with ether and vacuum-distilled. 1-Phenyl-4-chloro-2-butene-1, 4-$^{14}C_1$, 23.6 g, bp 110°C/10 mmHg (Ref. 11, 107—112°C/12 mmHg) was thus obtained.

The Adduct of 1-Phenyl-1, 3-butadiene-1, 4-$^{14}C_1$ with Maleic Anhydride. The adduct of maleic anhydride was prepared by the method described in the literature.[12] The product was recrystallized several times from a benzene-ligroin (1 : 1) solvent until the specific activity of the compound reached a constant value, mp 120—122°C (Ref. 12, 120°C).

Oxidation of the Adduct to Benzoic Acid. The adduct (2.36 g) was added to an aqueous solution (150 m*l*) of potassium hydroxide (2.5 g) and potassium permanganate (17 g). The mixture was then heated with stirring for 8 hr at 90°C. The reaction product was extracted with ether, washed with water, and dried with calcium chloride. After the ether had been distilled off, the crude material was recrystallized repeatedly with water until it reached a constant specific activity.

Radioactivity Counting. The radioactivity of the gas products of the dehydrogenation reaction was determined by a counting-rate meter (Nuclear Chicagio Corp., Model 1620) after analysis by gas chromatography. In order to confirm the radioactivity, each component was also dissolved separately into a known amount of toluene-solution-dissolved scintillators after gas counting. The radioactivity of each toluene solution was measured by a liquid scintillation spectrometer (Nuclear Chicago Corp., Model 701).

The radioactivity of the final products in the carbon-14 position determination was measured by a liquid scintillation spectrometer.

The extent of the carbon-14 rearrangement from the 1-position in the 1-butene to the 2-position in the 1, 3-butadiene was calculated by the following equation:

$$0.5(1-R)=[\mathrm{II}]/[\mathrm{I}] \qquad (1)$$

Where R is the ratio of the sum of the radioactivity in the 2- and 3-positions to the total radioactivity in the 1-phenyl-1, 3-butadiene. [I] and [II] are the specific activities of the adduct of maleic anhydride and the benzoic acid respectively.

Results and Discussion

Before the carbon-14 rearrangement experiment, the characteristics of the dehydrogenation reaction and the rate of the isomerization reaction between 1-butene and 2-butenes were examined.

Dehydrogenation Reaction. The dehydrogenation of 1-butene-1-^{14}C over the catalyst at 485—675°C produced mainly *n*-butane, *trans*-2-butene, *cis*-2-butene, 1, 3-butadiene, and unreacted 1-butene. Table 1 shows some typical results. The butadiene formation increased with an increase in the reaction temperature. The carbon deposition also increased at higher temperatures. "The relative activity" of the product denotes the relative specific activity of each product when the specific activity of unreacted 1-butene-1-^{14}C, was taken as 1.00. If these products were produced *via* an intermolecular recombination reaction, the specific activities of *n*-butane and 1, 3-butadiene should be different from that of the feed material. However, Table 1 indicates that all the C_4-compounds in the products have almost the same specific activity as that of the feed material. Therefore, the intermolecular recombination reaction cannot be considered in these reactions.

Isomerization Reaction. An equilibrium mixture of *n*-butane, 1-butene-1-^{14}C, *trans*-2-butene, *cis*-2-butene, and 1, 3-butadiene was allowed to react over the catalyst. The results are shown in Table 2. The chemical composition of the reaction mixture did not change much in either run. The relative activities of *trans*-2- and *cis*-2-butene increased from 0.167 and 0.140 at 220°C to 0.976 and 1.01 at 520°C respectively. These results indicate that the isomerization reaction was fast enough to reach equilibrium at 520°C. On the other hand, the relative activity of 1, 3-butadiene was smaller than those of 2-butenes at 220°C and 520°C. This suggests that the isomerization is much faster than the dehydrogenation, even at 520°C.

Carbon-14 Rearrangement. The radioactivity distribution in the 1, 3-butadiene obtained in the runs of Table 1 was investigated by the process shown in Fig. 1. Table 3 and Fig. 2 indicate the data of the carbon-14 rearrangement. The radioactivity of each product can be considered to

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TABLE 1. CHEMICAL YIELD AND RELATIVE ACTIVITY IN DEHYDROGENATION OF 1-BUTENE-1-^{14}C OVER CHROMIA-ALUMINA CATALYST

React. temp., °C	485		500		675	
	Yield, %[a]	Relative[b] activity	Yield, %	Relative activity	Yield, %	Relative activity
C_2-Hydrocarbon	0	—	0.2	—	1.1	—
Propylene	0.1	—	—	—	5.6	0.85
n-Butane	0.1	1.18	0.3	1.18	0.3	0.90
1-Butene	36.6	1.00	22.8	1.00	8.1	1.00
trans-2-Butene	29.0	1.16	33.0	0.960	8.3	0.95
cis-2-Butene	25.0	1.15	30.8	0.970	7.2	0.91
1, 3-Butadiene	9.5	1.02	12.9	0.740	69.3	0.85
Total	100.3		100.0		99.9	
W. H. S. V.[c] (g/hr/cat.g.)	0.323		0.379		0.659	

a) Total yield of the gaseous products was 75—80 (vol%) based on 1-butene fed.
b) Ratio of the specific activity, when the activity of 1-butene was taken as 1.00.
c) Weight hourly space velocity.

TABLE 2. ISOMERIZATION OF BUTENES IN EQUILIBRIUM MIXTURE OVER CHROMIA-ALUMINA CATALYST

React. temp., °C	Starting mixture %	220[a]			520[b]		
		Reaction product %	Δ[c] %	Relative[d] activity	Reaction product %	Δ %	Relative activity
n-Butane	4.8	4.9	+0.1	0.007	4.8	0	0.104
1-Butene	25.5	21.6	−3.9	1.00	22.8	−2.7	1.00
trans-2-Butene	38.8	39.0	+0.2	0.167	28.4	−10.4	0.976
cis-2-Butene	26.3	29.5	+3.2	0.140	25.6	−0.7	1.01
1, 3-Butadiene	4.7	4.8	+0.1	0.040	18.4	+13.7	0.727
Total	100.1	99.8			100.0		

a) He : Hydrocarbon = 97.5 : 2.5, W. H. S. V. = 0.37
b) He : Hydrocarbon = 96.0 : 4.0, W. H. S. V. = 0.37
c) Increased amount (%) from the starting mixture.
d) Specific activity of 1-butene-1-^{14}C was taken as 1.00.

TABLE 3. DETERMINATION OF CARBON-14 REARRANGEMENT IN THE 1, 3-BUTADIENE

Reaction temperature °C	Substance	Number of recryst.	Specific activity μc/mol	Carbon-14 rearrangement %
485	Adduct (I)	2	20.2 ±0.2	5.7±0.8
485	Adduct (I)	3	19.6 ±0.2	
485	Benzoic acid (II)	2	9.33±0.08	
485	Benzoic acid (II)	3	9.34±0.08	
490	Adduct (I)	1	2.58±0.03	6.9±1.1
490	Adduct (I)	2	2.58±0.03	
490	Benzoic acid (II)	1	1.20±0.01	
490	Benzoic acid (II)	2	1.19±0.01	
500	Adduct (I)	1	6.81±0.07	9.8±0.9
500	Adduct (I)	2	6.70±0.07	
500	Benzoic acid (II)	1	3.04±0.03	
500	Benzoic acid (II)	2	3.05±0.03	
675	Adduct (I)	1	22.7 ±0.3	22.8±1.1
675	Adduct (I)	2	22.5 ±0.3	
675	Benzoic acid (II)	1	8.73±0.12	
675	Benzoic acid (II)	2	8.75±0.12	

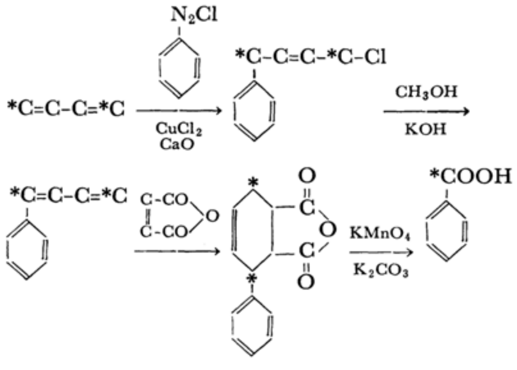

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Fig. 1. Carbon-14 position determination in the butadiene.

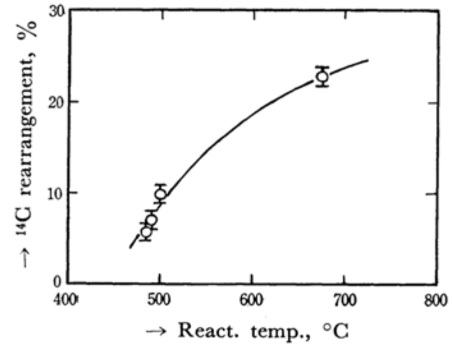

Fig. 2. Carbon-14 rearrangement.

reach a constant value after several recrystallizations of the product. The degree of carbon-14 rearrangement, R, was calculated by means of the Eq. (1). This rearrangement increased roughly with an increase in the temperature.

The following possible mechanisms for the carbon-14 rearrangement may be considered: (a) the recombination of molecular fragments produced during the pyrolysis of butenes, (b) the formation of a three-membered ring intermediate, (c) the formation of a cyclobutane-type intermediate, and (d) the formation of a cyclobutene-type intermediate. These four possibilities will be discussed below.

From the above discussion, it may be seen that the dehydrogenation took place mainly through an intramolecular reaction. However, a small amount of C_2-hydrocarbon was detected in the reaction products shown in Table 1. Therefore, the recombination of ethylene and methyl moieties produced by the pyrolysis of butenes might produce butenes and butadiene, resulting in carbon-14 rearrangement:

$$^{14}C{=}C{-}C{-}C \rightleftarrows \begin{bmatrix} ^{14}C{=}C\cdot & \cdot C{-}C \\ \downarrow\uparrow & \\ \cdot ^{14}C{=}C & \cdot C{-}C \end{bmatrix} \rightarrow C{=}^{14}C{-}C{-}C$$

With this in mind, ethylene and propylene were allowed to react under these rearrangement conditions. The results showed that no significant amount of 1, 3-butadiene was produced. Furthermore, a mixture of 1-butene and ethylene-1-^{14}C (1 : 1), under rather severe dehydrogenation conditions (755°C), produced scarcely any radioactive butadiene (Table 4). Accordingly, this mechanism cannot explain the present results.

Table 4. Dehydrogenation of a mixture of 1-butene and ethylene-1-^{14}C over chromia-alumina at 755°C

Gaseous products	Yield vol%	Relative activity[a]
Ethylene	33.2	1.00
Propylene	1.7	0.19
n-Butane	1.5	0.25
1-Butene	8.0	0.00
trans-2-Butene	5.5	0.00
cis-2-Butene	4.8	0.00
1, 3-Butadiene	45.2	0.008
Total	99.9	

a) Specific activity of ethylene-1-^{14}C was taken as 1.00.
Weight hourly space velocity was 0.323 g/hr/cat.g.
Feed gas; He : Hydrocarbon = 98.2 : 1.8

Pines and his co-workers showed that the dehydrogenation of hydrocarbons over acidic chromia-alumina produced a large amount of skeletally-rearranged products, presumably *via* a carbonium ion mechanism, while that over non-acidic chromia-alumina produced less skeletally-rearranged products, probably by a free radical mechanism.[5] Since the catalyst used in our experiment was acidic, as was reported by the supplier, the carbonium ion mechanism explaines the present results more plausibly. The dehydrogenation at the 1- or 3-position of butenes might give a cyclopropane-type intermediate, followed by a cleavage of the bond between the 1- and 3-positions or the 2- and 3-positions (Fig. 3). This mechanism would involve a carbon-14 rearrangement. On the other hand, the cleavage of the bond between the 1- and 2-positions, which is almost equal as possible as the other two bond cleavages, would produce isobutylene. In practice, no detectable amount

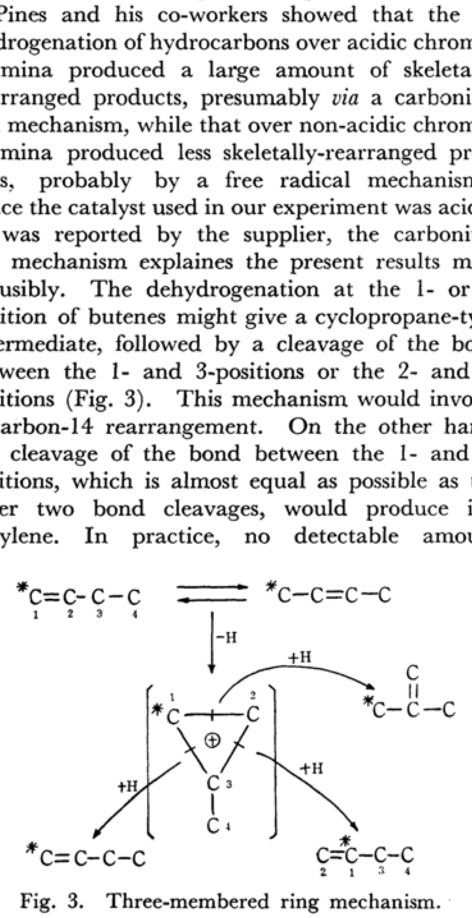

Fig. 3. Three-membered ring mechanism.

of isobutylene was obtained in our reaction products.

However, the isobutylene produced might preferably have undergone further dehydrogenation and carbonization on the surface of the catalyst as compared with other C_4-hydrocarbons. In order to investigate this possibility, synthetic mixtures of isobutylene and 1-butene were prepared and passed over the catalyst at various temperatures. Table 5 shows the experimental results. These results indicate that isobutylene was not particularly reactive under the present dehydrogenation reaction conditions as compared with 1-butene. If isobutylene was produced according to the (b) mechanism, it should be detectable under the carbon-14 rearrangement conditions. Accordingly, the (b) mechanism is not consistent with the results obtained.

TABLE 5. DEHYDROGENATION OF MIXTURES OF ISOBUTYLENE AND 1-BUTENE OVER CHROMIA-ALUMINA CATALYST.[a]

React. temp., °C	550	600	620	650
Starting mixture, %				
1-Butene	49.8	49.8	58.1	58.1
Isobutylene	50.2	50.2	41.9	41.9
Main gaseous product, %				
Propylene	1.1	—	3.7	10.2
1-Butene	13.4	12.7	12.9	9.7
Isobutylene	46.7	48.6	41.7	39.4
trans-2-Butene	13.1	12.3	12.1	8.7
cis-2-Butene	11.5	10.5	10.3	7.4
1, 3-Butadiene	14.2	15.9	19.3	24.6
Total	100.0	100.0	100.0	100.0

a) The mixture was diluted with helium (95 vol%). Weight hourly space velocity was 0.550 (g/hr/cat.g).

The last remaining mechanism for the rearrangement involves the formation of four-membered ring intermediates. The dehydrogenation of butenes at the 1- or 4-position would make a cyclobutane-type intermediate on the catalyst. The cleavage of the bond between the 2- and 3-positions or the bond between the 3- and 4-positions could produce the carbon-14 rearrangement.

Another possible mechanism is that 1, 3-butadiene is initially produced by dehydrogenation from butenes, and then is further dehydrogenated at the 1- and 4-positions to form a cyclobutene-type intermediate on the catalyst (Fig. 4). Such an intermediate could also cleave the bond between the 2- and 3-positions and produce carbon-14-rearranged 1, 3-butadiene.

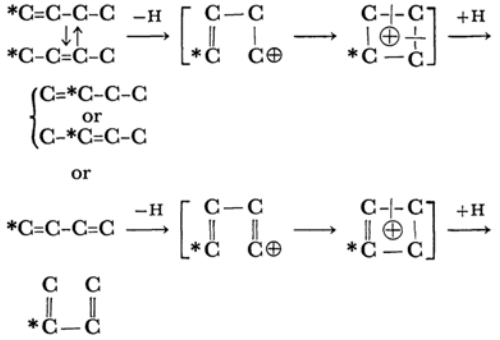

Fig. 4. Four-membered ring mechanism

Although these two four-membered ring intermediates have not yet been identified, the present experimental results suggest the existence of the intermediates on the surface of the catalyst. The (c) and (d) mechanisms are not distinguishable in the present work. Further study must be undertaken in order to elucidate the mechanism of the carbon-14 rearrangement in more detail.

Summary

1. The dehydrogenation reaction of 1-butene over the chromia-alumina catalyst takes place through an intramolecular reaction.

2. The isomerization reaction of 1-butene to *trans*-2- and *cis*-2-butene is much faster than the dehydrogenation reaction.

3. A carbon-14 skeletal rearrangement has been found in the dehydrogenation reaction of 1-butene-1-^{14}C. The rearrangement increases with an increase in the temperature.

4. The four-membered ring intermediates have been suggested as a possible mechanism for the rearrangement.

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