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INTRAMOLECULAR HYDROGEN SHIFT AS A MECHANISM FOR THE ISOMERIZATION OF 1-BUTENE OVER CALCIUM OXIDE

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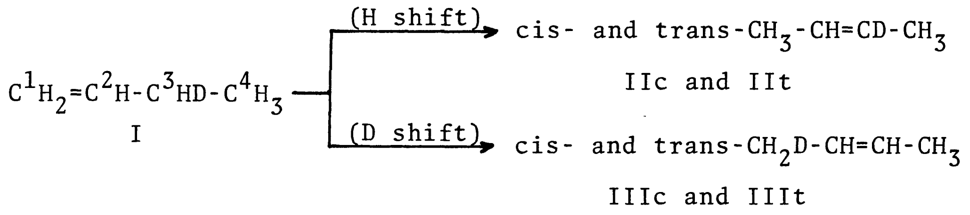
Isomerization of 1-butene-3-d_1 was studied over CaO and $MgSO_4$. Small decrease in deuterium content and little formation of d_2 species, as well as the existence of 2-butene-1-d_1, show that the reaction over CaO proceeds via intramolecular 1,3 hydrogen shift. Results with $MgSO_4$ were consistent with a carbonium ion mechanism, which involves surface proton transfer to butene.

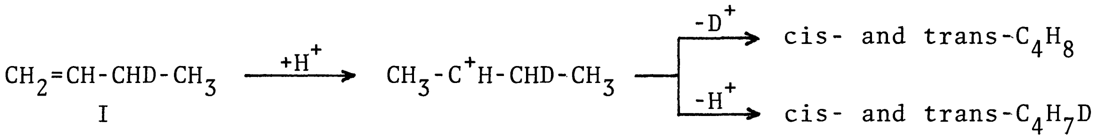
It has recently been reported that alkali-earth oxides are very active catalysts for butene isomerization when evacuated in situ at high temperature.[1,2) Over these catalysts the isomerization of 1- to cis-2-butene and the reverse are very rapid. From the measurement of basicity and the characteristic selectivity, the reaction has been suggested to proceed via allylic carbanion.[1-3) Shannon et al.[4) observed that only small isotope mixing took place between cis-2-C_4H_8 and C_4D_8 when isomerized over MgO at extremely low temperature (-68°C), while appreciable mixing is expected by a carbonium ion mechanism.[5) They suggested that butene isomerizes over MgO by a mechanism that is effectively intramolecular. Intramolecular mechanism has previously been suggested by Hall and co-workers for butene isomerization over Al_2O_3.[6) In base-catalyzed homogeneous isomerization, it has been shown that the reaction proceeds by intramolecular hydrogen shift, probably via an allylic intermediate.[7) Thus, it is of general interest to determine the reaction mechanism of the present system and compare it with other catalyst systems.

We studied the isomerization of 1-butene-3-d_1 (CH_2=CH-CHD-CH_3) (I) at 0°C over CaO, of which the base strength distribution has previously been determined.[8) The results indicated as described below an intramolecular 1,3 hydrogen shift.[9) The same reaction over magnesium sulfate supported on silica (Mg-S), a protonic acid catalyst, was also examined for comparison purpose.[10)

Isomerization by intramolecular hydrogen migration from C^3 to C^1 will produce 2-butenes, II and III, without loss of deuterium.



But in a mechanism which contains effective hydrogen transfer between catalyst and butenes, the deuterium content of isomerized 2-butenes may decrease considerably. For example, in the case of a carbonium ion mechanism,



$$\underset{\text{I}}{CH_2{=}CH{-}CHD{-}CH_3} \xrightarrow{+H^+} CH_3{-}C^+H{-}CHD{-}CH_3 \begin{cases} \xrightarrow{-D^+} \text{cis- and trans-}C_4H_8 \\ \xrightarrow{-H^+} \text{cis- and trans-}C_4H_7D \end{cases}$$

Calcium oxide was prepared by the calcination of calcium carbonate at 900°C for 20 hr and evacuated in situ at 400°C for 1 hr prior to reaction. Mg-S which was prepared as described elsewhere[10)] was evacuated at 80°C for 1 hr prior to reaction. Reaction apparatus was a closed circulating system, having a volume of 150 cc, connected to a vacuum line. Butene pressure was 10-20 mmHg. Deuterium content of butenes was analyzed by mass spectrometry after gas chromatographic separation. 1-Butene-3-d_1 was prepared by the dehydrobromination of 2-bromobutane-3-d_1.[11)] It contained 92% of d_1 species, the rest being 1-butene-d_0. The position of deuterium was exclusively at carbon 3, as determined by the microwave spectrometry.[12)]

Most of 2-butenes formed from 1-butene-3-d_1 was cis-2-butene (cis/trans ≑ 8) in agreement with the literature.[1,2)] The deuterium distribution in starting 1-butene and in isomerized cis-2-butene is given in Table 1.

Table 1 Distribution of Deuterium in Starting 1-Butene and in cis-2-Butene Formed from the Isomerization of 1-Butene-3-d_1 over CaO at 0°C

1-Butene		cis-2-Butene		
$CH_2{=}CH{-}CHD{-}CH_3$	92.0%	$CH_3{-}CH{=}CD{-}CH_3$	66.5%	86.0%
$CH_2{=}CH{-}CH_2{-}CH_3$	8.0	$CH_2D{-}CH{=}CH{-}CH_3$	19.5	
		$CH_3{-}CH{=}CH{-}CH_3$	14.0	

Conversion of 1-butene was 9%. d_1% of the remaining 1-butene was 91.5%. d_2-species was little formed (less than 1%), so that <u>inter</u>molecular hydrogen exchange by any mechanism does not exist significantly. Results with Mg-S are given in Table 2. It is to be noted that the decrease of d_1% during isomerization over CaO was fairly small (92%→86%), in striking contrast to that over Mg-S where it decreased almost to 50%. This result indicates that the isomerization proceeds mostly via intramolecular mechanism over CaO. It was observed that d_1% of isomerized cis-2-butene varied from 80 to 86% upon changing pretreatment of CaO.

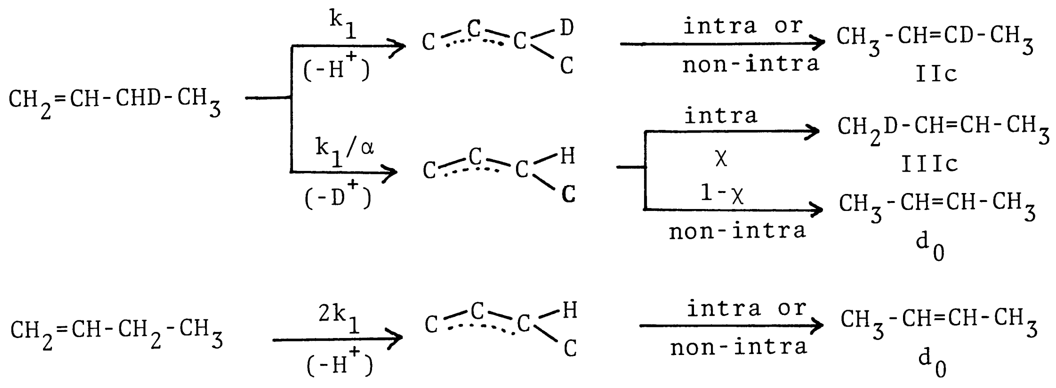
The intramolecular hydrogen (or deuterium) migration may be confirmed by the existence of cis-2-butene-1-d_1 (IIIc). It was determined by use of microwave spectrometry that 22.7% of cis-2-butene-d_1 was 1-d_1 (IIIc) and the rest was 2-d_1 (IIc). The greater amount of IIc than IIIc may be ascribed to kinetic isotope effects. If the reaction proceeds exclusively by the intramolecular mechanism, the ratio of IIc to IIIc is equal to the kinetic isotope effect. But, in this

Table 2 Distribution of Deuterium in Butenes Obtained from Isomerization of 1-Butene-3-d_1 over Mg-S at 60°C

	Composition %		d_1 % *)	
	Run 1	Run 2	Run 1	Run 2
1-Butene	85.5	83.3	93.0	91.0
trans-2-Butene	5.9	6.4	55.0	56.0
cis-2-Butene	8.6	10.3	57.5	57.5

*) Small amount of d_2-species was neglected.

case, as there was loss of deuterium, IIc contains not only products formed by intramolecular mechanism, but also, to a minor extent, those formed by mechanisms other than the intramolecular mechanism. With the assumptions that the reaction proceeds via an allylic carbanion species and that the proton or deuteron abstraction is rate-determining, the results may more quantitatively be treated with the following reaction scheme.



where α is the kinetic isotope effect of the proton abstraction and χ is the fraction of the isomerization via intramolecular mechanism. The relative rates of the formation of IIc, IIIc and d_0-species become $0.92k_1$, $0.92\chi k_1/\alpha$ and $\{(0.92)(1-\chi)/\alpha + (0.08)(2)\}k_1$, respectively. Using data in Table 1, α and χ are calculated to be 3.0 and 89%, respectively. Thus the isomerization over CaO proceeds mostly (80-90%) via intramolecular 1,3 hydrogen shift, as in the case of base-catalyzed homogeneous isomerization. Isotope effect in the latter system was reported to be 4.4.7) That of about 3.5-4.0 was reported for Al_2O_3.5)

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