

Fig. 3.—Plot of  $k_{\text{obsd.}}$  at 605  $m\mu$  vs. hexamethylbenzene concentration. Open circles represent experimental values; solid line calculated from equation 21.

Differentiation of this expression with respect to time gives

$$\frac{d\Delta A_{\lambda}}{dt} = d \left[ \epsilon_{\lambda,c} - \frac{1}{2}\epsilon_{\lambda,I_2} \left( 1 + \frac{1}{K_c [D]} \right) \right] \frac{dC_c}{dt} \quad (20)$$

which, by equation 4, equals  $-k_{\text{obsd.}} (\Delta A_{\lambda})^2$ .

Thus, by combining equation 20 with the rate of disappearance of the complex (equation 15), the observed rate constant becomes

$$k_{\text{obsd.}} = \frac{2k_c (K_c [D] + 1)}{d [K_c [D] (\epsilon_{\lambda,c} - \frac{1}{2}\epsilon_{\lambda,I_2}) - \frac{1}{2}\epsilon_{\lambda,I_2}]} \quad (21)$$

Values of  $k_{\text{obsd.}}$  calculated from this expression are compared in Figs. 3 and 4 (solid lines) with the experimentally determined values (open circles) at 605 and 646  $m\mu$ , respectively. For the calculations, the more reliable value of  $K_c$  from Fig. 1 (2.7 l. mole<sup>-1</sup>) was used for both wave lengths, although the particular value of  $\epsilon_{\lambda,c}$  used was that determined for the specific wave length.

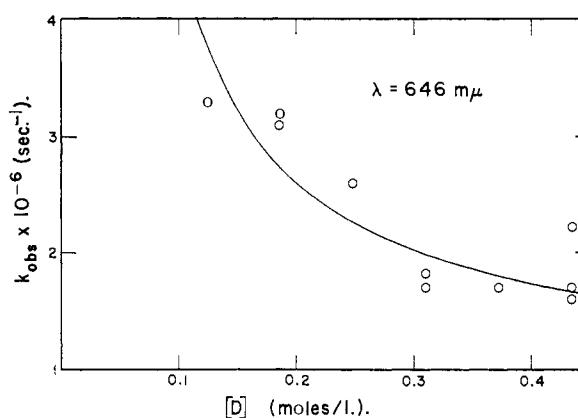


Fig. 4.—Plot of  $k_{\text{obsd.}}$  at 646  $m\mu$  vs. hexamethylbenzene concentration. Open circles represent experimental values; solid line calculated from equation 21.

It is clear that equation 21 correctly gives the observed qualitative behavior of  $k_{\text{obsd.}}$  with varying hexamethylbenzene concentration and appears to deviate badly only at the lowest concentrations of D, where experimental errors are quite large. It is concluded, therefore, that this interpretation in terms of a very rapid attainment of equilibrium between iodine atoms and D molecules to form DI complexes, together with the several simultaneous combination processes leading to  $I_2$ , provides a satisfactory and consistent picture of the observed kinetics. As pointed out, though, the assumption that all of the combination rate constants are the same can only be considered approximate, and more accurate measurements on  $k$  should show deviations from second order kinetics.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

## Alumina: Catalyst and Support. IX.<sup>1</sup> The Alumina Catalyzed Dehydration of Alcohols<sup>2,3</sup>

BY HERMAN PINES AND WERNER O. HAAG<sup>4</sup>

RECEIVED DECEMBER 19, 1960

There is no agreement in the literature with regard to the mechanism of catalytic dehydration of alcohols over alumina and not even with respect to the nature of olefinic hydrocarbons. It was demonstrated that the discrepancies result from different catalytic properties of the alumina catalysts used. Alumina catalysts can vary widely in their activity for double bond shift and for skeletal isomerization of olefinic hydrocarbons. These differences also influence the product distribution in the dehydration of alcohols. Dehydration was studied with aluminas having a whole spectrum of isomerization properties. The following alcohols were used: cyclohexanol, 2-butanol, 2-pentanol, 3-pentanol, 3,3-dimethyl-2-butanol (pinacolyl alcohol). The mechanism of the dehydration and of the accompanying isomerization is discussed.

Alumina is an excellent and widely used catalyst for the dehydration of alcohols.<sup>5</sup> In spite of this

(1) For paper VIII of these series see H. Pines and C. T. Chen, *Proceeding of the 2nd International Congress in Catalysis*, Paris, July 4-9, 1960.

(2) Paper 11 of the series "Dehydration of Alcohols." For paper I, see H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(3) Presented in part before the Division of Colloid Chemistry, American Society Meeting, San Francisco, April 13-18, 1958; and

fact there is no agreement in the literature with regard to the mechanism of this reaction or the nature of the olefinic products. For example, pure

before the Gordon Research Conferences in Catalysis, June 23-27, 1958, New London, N. H.

(4) Predoctoral Fellow, Universal Oil Products Company, 1956-1957; Tony Company, Chicago, Illinois 1957-1958.

(5) (a) A. A. Gregorieff, *J. Russ. Phys. Chem. Soc.*, **33**, 173 (1901). (b) V. N. Ipatieff, *ibid.*, **33**, 182 (1901); *Ber.*, **34**, 596, 3579 (1901).

1-olefins have been obtained from primary alcohols such as 1-butanol,<sup>6</sup> 1-pentanol,<sup>7</sup> 1-hexanol,<sup>8</sup> 1-heptanol<sup>9</sup> and 1-octanol.<sup>8b</sup> However, other authors found that alumina dehydrated primary alcohols to a mixture of olefins differing in the position of the double bond<sup>6b,10</sup> or even in the carbon skeleton.<sup>11</sup>

These and many similar discrepancies could result from different catalytic properties of the alumina catalysts used in different laboratories and/or from different reaction conditions.

It was recently shown<sup>12</sup> that alumina catalysts can vary widely in their activity for double bond shift and for skeletal isomerization of olefinic hydrocarbons. It was therefore of interest to investigate to what extent these differences would also influence the product distribution in the dehydration of alcohols, especially in the presence of water formed during the reaction. Cyclohexanol and 1-butanol were selected as test substances.

In connection with a study of the mechanism of the dehydration reaction it was desirable to determine the mode of elimination of the elements of water from secondary alcohols with respect to both the direction of elimination (Hofmann *versus* Saytzeff product) and the steric course (*cis versus trans*-olefin). With few exceptions<sup>13</sup> the data in the literature dealing with this subject are mostly of questionable value, since the often powerful olefin-isomerizing ability of most aluminas was not always recognized. Clearly, only the *primary* dehydration products can be mechanistically meaningful. Having at our disposal from our previous work<sup>12</sup> a series of alumina catalysts with a whole spectrum of isomerization activities, we studied the dehydration of the following secondary alcohols: cyclohexanol, 2-butanol, 2-pentanol, 3-pentanol and 3,3-dimethyl-2-butanol (pinacolyl alcohol). By proper choice of catalyst and reaction conditions, it was hoped to obtain the composition of the *primary* dehydration products, unchanged by secondary isomerization reactions.

While many catalysts were evaluated, only the data for a few typical alumina samples are given for simplicity: those obtained with the most "acidic" (P) and the most "non-acidic" (A) alumina, as well as with several commercial samples.

(6) (a) H. Pines, *J. Am. Chem. Soc.*, **55**, 3892 (1933). (b) V. N. Ipatieff, H. Pines and R. E. Schaad, *ibid.*, **56**, 2696 (1934). (c) C. Matignon, H. Moureu and M. Dode, *Compt. rend.*, **196**, 973 (1933); *Bull. Soc. Chim.*, (5), **2**, 1169, 1181 (1935). (d) J. C. Balaceanu and J. C. Jungers, *Bull. Soc. Chim. Belgique*, **60**, 476 (1957). (e) J. A. Norton, *Chem. Revs.*, **31**, 319 (1942).

(7) R. H. Ewell and P. E. Hardy, *J. Am. Chem. Soc.*, **63**, 3460 (1941).

(8) (a) R. G. Hay, C. W. Montgomery and J. Coull, *Ind. Eng. Chem.*, **37**, 335 (1945). (b) V. I. Komarevsky, S. C. Uhlick and M. J. Murray, *J. Am. Chem. Soc.*, **67**, 557 (1945). (c) T. W. Mears, A. Fookson, P. Pomerantz, E. H. Rich, C. S. Dussinger and F. L. Howard, *J. Research Natl. Bur. Standards*, **44**, 299 (1950).

(9) W. G. Appleby, C. J. Dobratz and S. W. Kapranos, *J. Am. Chem. Soc.*, **66**, 1938 (1944).

(10) (a) H. Adkins and S. H. Watkins, *ibid.*, **73**, 2184 (1951); (b) F. Asinger, *Ber.*, **75**, 1247 (1942); (c) T. W. Mears, A. Fookson, P. Pomerantz, E. H. Rich, C. S. Dussinger and F. L. Howard, *J. Research Natl. Bur. Standards*, **44**, 299 (1950).

(11) S. Goldwasser and H. S. Taylor, *J. Am. Chem. Soc.*, **61**, 1751 (1939).

(12) H. Pines and W. O. Haag, *ibid.*, **82**, 2471 (1960).

(13) E.g., H. J. Lucas, R. T. Dillon and W. G. Young, *ibid.*, **52**, 1949 (1930).

The results with other alumina preparations were found to fall in between those of (P) and (A). The catalyst used were well characterized with respect to surface area X-ray pattern, alkali content, amine chemisorption and catalytic activity for the conversion of olefins.<sup>12</sup>

### Experimental

The catalytic reactions were performed in a vertical flow reactor made of Pyrex glass. Product analysis was made by gas chromatography. The details of the experimental and analytical procedure have been described.<sup>12</sup>

**Catalysts.**—The preparation as well as the physical and catalytic properties of the catalysts have been reported in detail.<sup>12</sup> The figures in parentheses refer to the catalyst number in the previous publication.<sup>12</sup>

**Catalyst A** (No. 17)<sup>12</sup> was prepared from potassium aluminate by precipitation with carbon dioxide. It contained 1.0% of potassium. The catalyst showed good dehydration activity but very low activity for the double bond isomerization of olefins.

**Catalyst P** (No. 12)<sup>12</sup> was prepared from repeatedly distilled aluminum isopropoxide by hydrolysis with an ethanol-water mixture. The catalyst had been found to be very active for the skeletal isomerization of olefins.<sup>12</sup> It contained only 0.001% sodium.

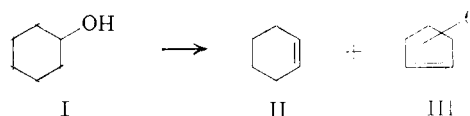
**Catalyst I** (No. 9-6)<sup>12</sup> was made by impregnating catalyst P with sodium hydroxide.

**Catalyst C** (No. 21)<sup>12</sup> was a commercial sample from the Harshaw Chemical Co. (AL-0104 T 1/8") containing 0.36% sodium.

**Catalyst D** (No. 24)<sup>12</sup> was obtained from the Houdry Process Corporation. (Hard Alumina, Grade 100) and contained 0.38% sodium.

### Results

**Cyclohexanol.**—The results from the dehydration of cyclohexanol (I) over various alumina catalysts are summarized in Table I. Over catalysts A, C and D (all containing small amounts of alkali), cyclohexene (II) was the only product in agreement with numerous reports in the literature<sup>14</sup> (exp. 1-3). However, the high purity alumina prepared from aluminum isopropoxide (P) gave a mixture containing up to 60% methylcyclopentenes (III), a result which does not seem to have been reported previously

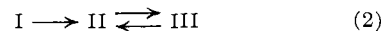


The relative proportion of III in the olefinic product increased with increasing temperature (exp. 4-6).

Two mechanistic pathways may be considered by which methylcyclopentene could be produced from cyclohexanol. In the first, II and III are formed from I in parallel reactions with or without consecutive interconversion of the olefins



The second possibility is that of a consecutive



with cyclohexene as a desorbed intermediate. In order to differentiate between the two reaction paths, the dehydration of I was performed at several different contact times. The product

(14) E.g., V. N. Ipatieff, *J. Phys. Chem. (U.S.S.R.)*, **38**, 92 (1966); K. Kochloeft and V. Bazant, *Chem. Listy*, **49**, 889 (1955).

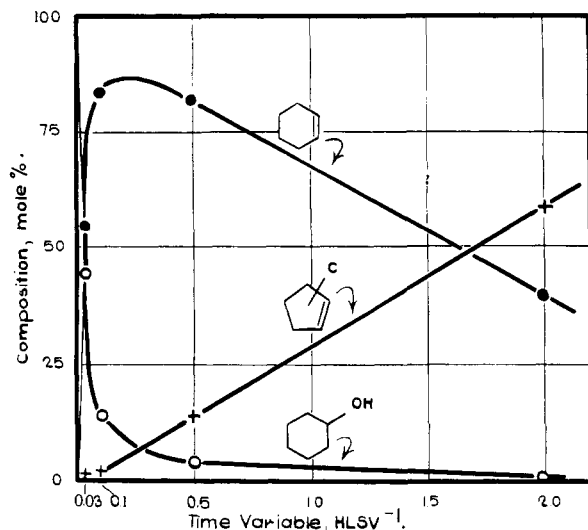


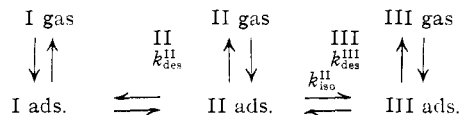
Fig. 1.—Dehydration of cyclohexanol over alumina P at 410° influence of contact time.

composition as a function of time (exp. 6–9, Fig. 1) strongly suggests a series reaction according to scheme 2, in which cyclohexanol is dehydrated to cyclohexene which in turn undergoes a slow skeletal isomerization to methylcyclopentenes. It was independently shown that II is converted to III under the same conditions over catalyst P (exp. 10)<sup>15</sup> while catalyst A and D were completely inactive and C gave only 0.9% of methylcyclopentene.<sup>11</sup> To further test scheme 2, the olefin composition was plotted against total amount of olefins produced (Fig. 2). Extrapolation to zero conversion indicates that the *primary* dehydration product consists of pure or nearly pure cyclohexene in agreement with (2).<sup>16</sup>

From a practical point of view, pure cyclohexene can thus be obtained from cyclohexanol most conveniently by choosing alkali containing alumina catalysts. When using pure alumina samples (or those containing halogens), the formation of methylcyclopentenes can be suppressed or minimized by employing lower temperatures or short contact times. The built-up of carbonaceous material on the catalyst surface, probably originating from the cyclopentenes, also was found to partially inhibit

(15) The relative ratio of methylcyclopentenes/cyclohexene = 9.8 seems to correspond to the thermodynamic equilibrium value, since an identical ratio was obtained when 1-methylcyclopentene was used as charge.

(16) This result also requires that the rate of desorption of II from the catalyst surface ( $k_{des}^{II}$ ) must greatly exceed that of the interconversion  $II \rightarrow III$  ( $k_{iso}^{II}$ ), assuming that the desorption rates of



the two olefins II and III are of similar value ( $k_{des}^{II} \approx k_{des}^{III}$ ). If  $k_{iso}^{II} \ll k_{des}^{II}$ , III desorbs almost simultaneously with II. The kinetic analysis, based on the gas phase species as the observable ones, would then register a *parallel* reaction 1, while the mechanistically significant reaction sequence would nevertheless be that of a *consecutive* reaction. This disguise, in which an actually consecutive reaction appears as a parallel one may also be encountered in cases of severe diffusion limitations.

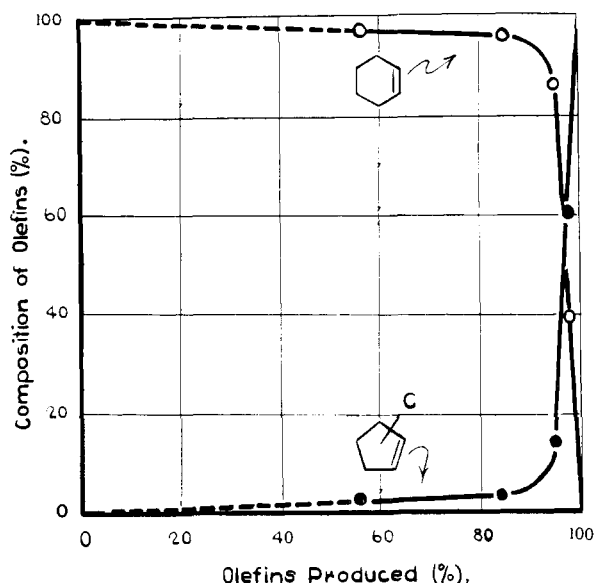


Fig. 2.—Dehydration of cyclohexanol over alumina P at 410°.

cyclohexene isomerization under conditions where no loss in dehydration activity was observable.

1-Butanol.—Similar results were obtained with 1-butanol (Table II). Again, alkali containing catalysts gave a high proportion of the expected

TABLE I  
EFFECT OF REACTION CONDITIONS AND ALUMINA TYPE ON THE DEHYDRATION OF CYCLOHEXANOL

Exp.	Catalyst	React. temp., °C.	HLSV <sup>a</sup>	Dehydration, %	Composition of olefins, %	
					CH <sup>b</sup>	MCP <sup>c</sup>
1	A	410	0.50	95	100	0
2	C	410	0.50	95	100	0
3	D	410	3.0	72	100	0
4	P	350	0.50	95	89	11
5	P	375	0.50	95	69	31
6	P	410	0.50	99	40	60
7	P	410	2.0	96	85.8	14.2
8	P	410	10	86	97.6	2.4
9	P	410	30	56	98.6	1.4
10 <sup>d</sup>	P	410	0.50		9.3	90.7

<sup>a</sup> HLSV, hourly liquid space velocity = volume of liquid charged per volume of catalyst per hour. <sup>b</sup> CH, cyclohexene. <sup>c</sup> MCP, methylcyclopentene; a mixture of all the endocyclic double bond isomers was obtained in a constant ratio of 3-methylcyclopentene/1- +4-methylcyclopentene = 0.31. <sup>d</sup> Charge, cyclohexene.

dehydration product, 1-butene, especially at lower temperature (exp. 11). It was accompanied, however, in all cases by some 2-butene (exp. 12–14). With the alkali-free high purity alumina the proportion of 2-butene was much higher and approached equilibrium values under more vigorous conditions (exp. 16–18).

The available data again indicate that the *primary* dehydration product from 1-butanol on all the alumina catalysts is the expected 1-butene. Dependent on the nature of the catalyst and the reaction conditions, this may then undergo further double bond shift or even skeletal isomerization to isobutylene (exp. 18). In agreement with this view is the observation that the 2-butenes produced during the dehydration of 1-butanol have a similar

TABLE II  
 DEHYDRATION OF 1-BUTANOL

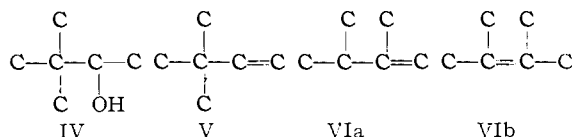
Exp.	Catalyst	Temp., °C.	HL-SV	Dehydration, %	Composition of <i>n</i> -butenes (%)			
					1-	<i>trans</i> -2	<i>cis</i> -2	<i>cis</i> / <i>trans</i>
11	A	350	0.50	82	97.3	0.7	1.6	2.3
12	A	410	.50	97	82.6	5.6	11.6	2.1
13	C	410	.47	95	80.0	8.0	12.0	1.5
14	D	410	.50	76	81.4	7.1	11.5	1.6
15 <sup>a</sup>	D	410	.90	..	86.9	5.3	7.8	1.5
16	P	350	8.50	47	86.3	4.3	9.4	2.2
17	P	350	2.10	94	61.8	14.6	23.6	1.6
18	P	410	0.50	95	25.2 <sup>b</sup>	41.7	33.1	0.79
	Equil. <sup>c</sup>	410			26.3	45.4	28.3	0.62

<sup>a</sup> Charge, 1-butene. <sup>b</sup> The reaction product consisted of 90% *n*-butenes and 10% isobutylene; no isobutylene was detected in the other experiments. <sup>c</sup> From the published data, J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946), by linear interpolation.

*cis/trans*-ratio as those obtained from the isomerization of 1-butene over the same catalyst (exp. 14 and 15). It will be noted that the 2-butenes are not formed in their relative equilibrium concentrations but in a stereoselective way favoring the *cis*-isomer.

**3,3-Dimethyl-2-butanol.**—In the dehydration of cyclohexanol and 1-butanol, the primary products were those expected from a removal of the elements of water from adjacent carbon atoms of the alcohol. The formation of isomeric olefins occurred in a step *subsequent* to the dehydration reaction.

This result cannot be generalized, however. The dehydration of pinacolyl alcohol (IV) over alumina D (350°, HLSV 0.5) gave only 41.7% 3,3-dimethyl-1-butene (V) and in addition 46.2% 2,3-dimethyl-1-butene (VIa) and 12.2% 2,3-dimethyl-2-butene (VIb). Under these conditions, V is not isomerized



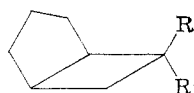
by this catalyst.<sup>12</sup> The catalytic dehydration of the neopentyl-type alcohol IV thus provides an example where skeletal rearrangement occurs *during* the dehydration step. In agreement with this conclusion is the recent finding that neopentyl alcohol itself is smoothly dehydrated over non-acidic alumina.<sup>1,17</sup>

In special cases rearrangement during dehydration is even more pronounced. Thus, the passage of *cis,cis*- and *trans,cis*-bicyclo-(3.2.0)-heptan-6-ol<sup>18</sup> (VII a and VII b, respectively) over the least isomerizing aluminas at our disposal gave a complex reaction mixture. The olefinic products are compared in Table III with those obtained from the pyrolysis of the borate esters.<sup>19</sup> At least fifteen different components were obtained, the major ones of which were identified by gas chromatography and are listed.

(17) H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(18) The two alcohols were kindly supplied by Dr. N. P. Cywinski.

(19) H. L. Dryden, B. E. Burgert and N. F. Cywinski, paper presented at the American Chemical Society Meeting, September, 1958, Chicago, Illinois, Abstract of papers 82 P.



VIIa, R = OH, R' = H  
 VIIb, R = H, R' = OH

Significantly different product distributions were obtained from the epimeric alcohols. For example, 3-vinylcyclopentene, the major single component from VII b, was absent in the product from VII a. The scarcity of the starting material and the complexity of the product obtained made a more detailed kinetic study not possible at this time.

TABLE III

DEHYDRATION OF BICYCLO-(3.2.0)-HEPTAN-6-OL AT 350°

Products	Product composition, weight, %				
	<i>cis-cis</i> (VIIa)		<i>trans-cis</i> (VIIb) <sup>c</sup>		
1,3-Cycloheptadiene	34	31	..	13	9
3-Vinylcyclopentene	33	..	80	29	42
1-Vinylcyclopentene	..	..	20	..	..
Norcarene	33	20	..	10	4
Others (no of compounds)	..	49(8)	..	49(12)	45(12)

<sup>a</sup> Borate ester, ref. 19. <sup>b</sup> Alcohol; catalyst C, HLSV, 1.2. <sup>c</sup> Alcohol; catalyst A; HLSV, 0.6.

**2-Butanol, 2- and 3-Pentanol.**—The results (Table IV) show again that the method of preparation of the alumina catalyst has a marked effect on the product distribution. Over the pure alumina (P) the olefinic products are nearly equilibrated (exp. 23 and 27). The alkali containing

TABLE IV

DEHYDRATION OF 2-BUTANOL, 2- AND 3-PENTANOL HLSV<sup>a</sup> = 0.5

Exp.	Catalyst	Temp., °C.	Alcohol <sup>b</sup>	Dehydration, %	Olefins produced, %			Ratio <i>cis/trans</i>
					1-	<i>trans</i> -2	<i>cis</i> -2	
22	P	280	2-B	90	38.4 <sup>c</sup>	32.0	29.6	0.92
23	P	350	2-B	93	21.5	46.2	32.3	0.70
24	D <sup>e</sup>	350	2-B	70	38.4	15.5	46.1	3.0
25	A <sup>e</sup>	350	2-B	85	40.3	15.1	44.6	3.0
26	I <sup>e</sup>	350	2-B	25	44.0	14.0	42.0	3.0
			327 Equilibrium <sup>d</sup>		21.2	49.7	29.1	0.59
27	P	350	2-P	79	14.2 <sup>c</sup>	57.5	28.3	0.49
28	D <sup>e</sup>	350	2-P	77	33.7	12.7	53.6	4.22
29	D <sup>e</sup>	410	2-P	76	28.3	25.2	46.5	1.84
30	D <sup>e</sup>	350	3-P	83	2.5	30.6	66.9	2.18
31	D <sup>e</sup>	410	3-P	75	5.8	35.7	58.5	1.64
			327 Equilibrium <sup>d</sup>		12.5	53.9	33.6	0.62

<sup>a</sup> Hourly liquid space velocity. <sup>b</sup> 2-B = 2-Butanol; 2-P = 2-Pentanol; 3-P = 3-Pentanol. <sup>c</sup> The *n*-olefins were normalized to 100%. The total olefinic product contained in addition to the olefins listed: exp. 22, 1% isobutylene; exp. 23, 2.5% isobutylene; exp. 27, 14.8% of a fourth compound, most likely 2-methylbutene. <sup>d</sup> J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946). <sup>e</sup> Alkali content, %: D, 0.38%; A, 1.0%; I, 1.5%.

catalysts (D,A,I), however, give kinetically controlled products. The very low activity of these catalysts for olefin isomerization had been ascertained independently and is also indicated by exp. 11 and 30, the latter giving only 2.5% of 1-pentene from 3-pentanol. It may therefore be concluded that the composition of the olefins produced at 350° is very nearly that of the *primary* dehydration products.

Experiments 24–26 show a small trend toward more 1-olefin as the catalyst becomes more basic. It was, therefore, desirable to determine the primary products from the alkali-free catalyst (P). They were obtained from a plot of product composition *versus* contact time and extra polation to zero time. (Fig. 3.) The experiments in Table IV indicates that the direction of elimination of water from 2-butanol is shifted more towards the end of the carbon chain as the alkali content of the catalyst is increased.

DIRECTION OF ELIMINATION OF WATER FROM 2-BUTANOL OVER VARIOUS ALUMINAS (350°)

Alumina catalyst	Alkali content, %	1-Butene in product, %	<i>cis/trans</i> 2-Butene
P	0.001	26.0	4.3
D	0.38	38.4	3.0
A	1.0	40.3	3.0
I	1.5	44.0	3.0

**Mechanism of Dehydration.**—The primary products obtained from 2-butanol (Table IV, Fig. 3) are of mechanistic significance and may be compared with other eliminations in the 2-butyl system.<sup>20</sup> The data shows that the direction of elimination does not follow the Hofmann rule<sup>21</sup> nor is it governed by statistical factors. The latter would predict 60% 1-butene and 40% 2-butene. The greater amount of 2-olefin and especially the unusual predominance of the *cis*-olefin over its *trans*-isomer rules out a concerted *cis*-elimination, in which steric factors invariably hinder the formation of *cis*-olefin. For example, the following ratios of *cis/trans*-2-butene are obtained on pyrolysis of 2-butyl compounds: acetate, 0.53<sup>22,23</sup>; xanthate, 0.45<sup>20</sup>; and amine oxide, 0.57,<sup>24</sup> whereas dehydration of 2-butanol over the alkali-free alumina (P) gave a *cis/trans*-ratio of 4.3 (Fig. 3).<sup>25</sup>

Apparently the transition state in the dehydration reaction does not resemble the olefinic product, and eclipsing of the 2,3-alkyl groups in 2-butanol does not occur in the transition state or else is over-compensated by other factors favoring the *cis*-isomer. Kinetic preference for *cis*- over *trans*-olefin in eliminations from acyclic compounds proceeding by any mechanism is extremely rare.<sup>26</sup> However, a similar high *cis/trans* ratio of 4.4 was observed in the isomerization of 1-butene over the same alumina catalyst P.<sup>27</sup> Although the close agreement of the ratio in dehydration and isomerization may be coincidental, it is suggested that both reactions proceed through the same intermediate, a sec.-butyl carbonium ion VIII.

(20) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(21) A. W. Hofmann, *Ann.*, **78**, 253 (1851); W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

(22) D. H. Froemdsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

(23) W. O. Haag and H. Pines, *J. Org. Chem.*, **24**, 877 (1959).

(24) A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).

(25) The equilibrium value *cis/trans*-2-butene is approximately 0.59 (Table IV).

(26) The only case of which we are aware is that of a slight preference for *cis*- over *trans*-2-butene and 2-pentene in the thermal decomposition of the quaternary ammonium hydroxides derived from 2-butyl and 3-pentyl amine, respectively.<sup>24</sup>

(27) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 2488 (1960).

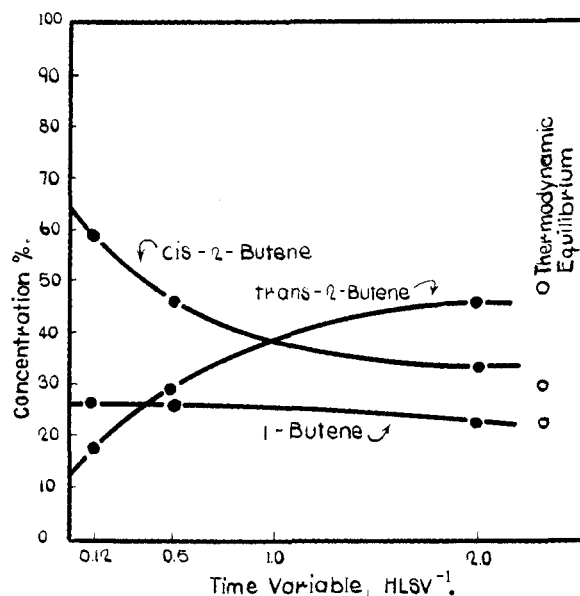
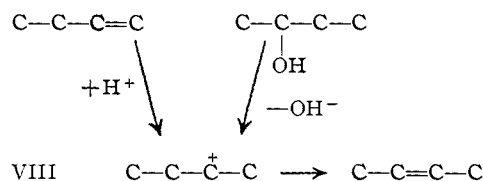
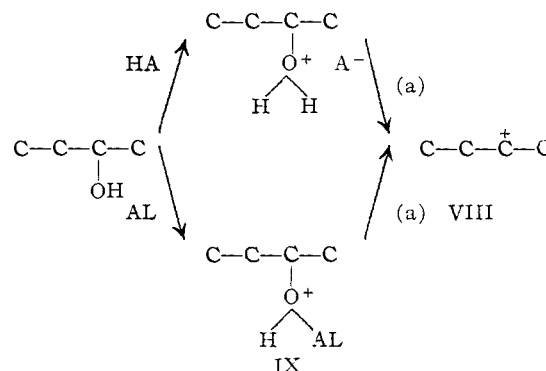


Fig. 3.—Distribution of butene as a function of contact time: 2-butanol over  $\text{Al}_2\text{O}_3$  (from isopropoxide) at 350°.



A likely precursor of VIII is an oxonium ion (IX), formed from the alcohol and either Brönsted (HA) or Lewis (AL) acid sites<sup>12</sup> on the alumina surface.



It is interesting to compare the dehydration reaction with eliminations in other onium compounds (Table V). Although the quite different reaction conditions do not allow a strict comparison, at least the strength of the base does not seem to have a large influence on the isomer distribution.<sup>23</sup> One observes a definite trend toward more 2-olefin as one passes from ammonium to sulfonium to oxonium compound. Thus, there is a gradual shift from Hofmann to Saytzeff product from which one can infer a corresponding change in mechanism from E2 (ammonium ion) to E1 (oxonium ion).<sup>29</sup> This

(28) H. C. Brown, I. Moritani and M. Nakagawa, *J. Am. Chem. Soc.*, **78**, 2190 (1956).

(29) B. V. Banthorpe, E. D. Hughes and Sir Christopher Ingold, *J. Chem. Soc.*, 4054 (1960).

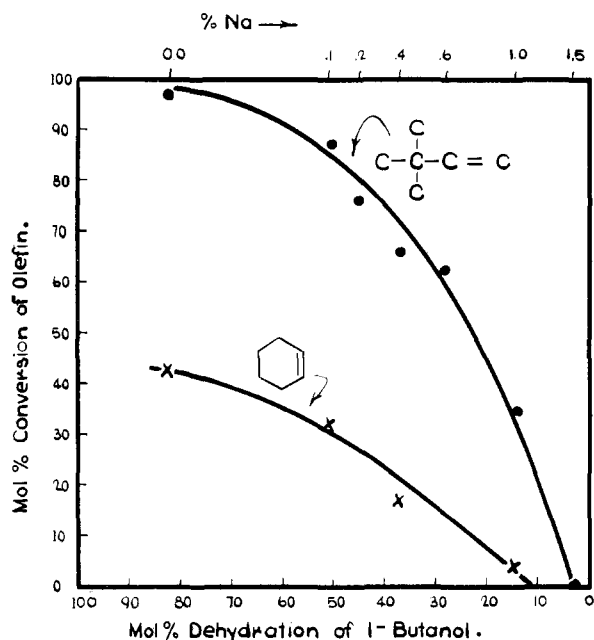


Fig. 4.—Dehydration and isomerization over aluminas impregnated with NaOH (350°, HLSV: 2.0).

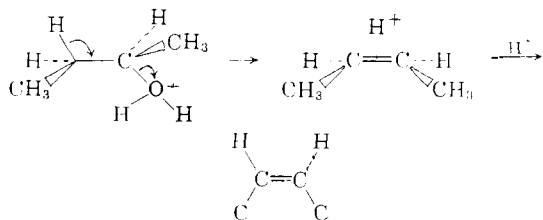
change towards unimolecular elimination may be expected from the decreasing stability of the onium ions.

TABLE V  
ELIMINATION IN THE 2-BUTYL SYSTEM C-C-C-C

R <sup>+</sup>	$\text{C}-\overset{\text{O}^+}{\text{N}}-\text{C}$	$\text{C}-\overset{\text{O}^+}{\text{S}}-\text{C}$	$\text{H}-\overset{\text{O}^+}{\text{C}}-\text{H}$	$\text{H}-\overset{\text{O}^+}{\text{C}}-\text{H}$
Anion or catalyst	OH <sup>-</sup>	OEt <sup>-</sup>	1 <sup>a</sup>	P <sup>b</sup>
% 2-butene	5.4	26	56	72
<i>cis/trans</i> <sup>c</sup>	1.45	<sup>d</sup>	3.0	4.3
Ref.	24	30 <sup>e</sup>		<sup>e</sup>

<sup>a</sup> Alumina I, impregnated with sodium hydroxide (1.5% Na). <sup>b</sup> Alumina P, alkali + free. <sup>c</sup> Ratio *cis/trans*-2-butene. <sup>d</sup> Said to be "mostly *trans*." <sup>e</sup> This paper.

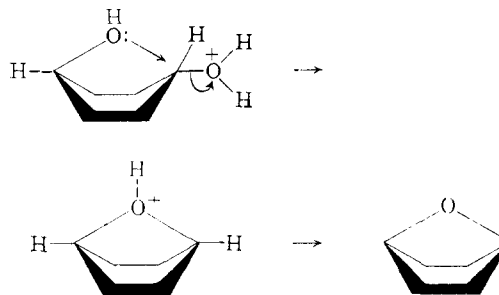
Unimolecular ionization reactions in the absence of a polar solvent such as required for IX → VIII on the surface of a catalyst are somewhat difficult and can be expected to depend strongly on anchimeric assistance



The assistance of neighboring hydrogen in the formation of carbonium ions has been repeatedly

(30) E. D. Hughes, C. K. Ingold, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2007 (1948).

observed.<sup>31</sup> The existence of proton-olefin complexes was suggested as being responsible for the unusually high *cis-trans* ratio.<sup>27</sup> Neighboring methyl participation may account for the skeletal rearrangement during the dehydration of pinacolyl alcohol mentioned above. A synthetic application of this tendency for anchimeric assistance of ionization may be found in the preparation of 1,4-epoxycyclohexane IX from *trans*-1,4-cyclohexanediol.<sup>32</sup> In polar media such as sulfuric acid or hydrobromic acid the solvent competes successfully with the back side approach of the hydroxyl group,



and no 1,4-epoxide is formed, but only normal dehydration to olefins occurs.<sup>32</sup>

With aluminas containing alkali the proportion of 1-butene in the product increased (Table IV), the details of these reactions are under investigation.

The proposed oxonium-carbonium-ion sequence includes the dehydration of alcohols over alumina under general acid catalyzed dehydrations. Acid sites on the surface are believed to be the active centers<sup>12</sup> which differ primarily in their strength from those on silica-alumina and other "acid" oxides. A very different view has been stated recently<sup>33</sup>; the opinion was expressed "that the mechanism of action and the nature of the active centers for the alcohol-dehydration reaction differs from those in the case of hydrocarbon conversion."<sup>33</sup> Our own results, however, support the contrary. When a high-purity alumina is impregnated with increasing amounts of sodium hydroxide, its activity for the dehydration of 1-butanol decreases from 82% (0.001% Na) to 3% (1.5% Na). Significantly, the activity of the same catalysis for the skeletal isomerization of cyclohexene and 3,3-dimethyl-1-butene decreases likewise (Fig. 4). This paralleled loss in activity is apparent with as little as 0.1% Na which corresponds to one sodium atom per 1000 Å.<sup>2</sup> surface. We take this as evidence that the same, "acid" centers are involved in the dehydration as are in the olefin isomerization reactions.

(31) See footnote 38 of ref. 27.

(32) R. C. Olberg, H. Pines and V. N. Ipatieff, *J. Am. Chem. Soc.*, **66**, 1096 (1944).

(33) K. V. Topchieva, K. Yun-Pin and I. V. Smirnova, in "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 799.