

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Isomerization of Alkenes on Alumina and Thoria

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Investigation of catalytic dehydration of  $C_6-C_8$  alcohols has shown it to be an excellent method for the production of alkene hydrocarbons for the catalytic study of their vapors.<sup>1</sup> One of the facts brought out by this investigation is that olefins isomerize extensively when allowed to remain in contact with the active surfaces studied. Further work with the purified olefins themselves was thought desirable.

The apparatus for the catalytic studies<sup>2</sup> and for fractionation of the liquid products<sup>1</sup> have been described already. The procedures both for the passage of olefin and the separation and identification of the products were identical with those described. No drying of the hydrocarbons over calcium chloride was necessary, however, in the runs with pure olefins. The olefins used in the study of isomerization were the purified fractions resulting from the dehydrations and the isomerizations themselves. The catalysts used were prepared as previously noted.

**Experimental Results.**—To determine whether results on different samples of a catalyst can be compared with each other, ten different preparations of pure alumina were made. These were as follows: solutions of aluminum nitrate were prepared in the five strengths—1.5, 1, 0.5, 0.3 and 0.1 *N*. Aluminum hydroxide was precipitated by the addition of 15 *N* ammonia, rapidly and without stirring in the case of the 1.5 *N* aluminum nitrate solution (catalyst a), 0.1 *N* ammonia slowly with rapid stirring in the case of the 0.1 *N* solution of aluminum nitrate (catalyst b). The others were graded between. Two samples of each catalyst were made, one was heated to boiling before filtration, the other filtered and dried at 80° before final drying. The only effect found was on the particle size and appearance of the alumina itself. Isomerization was not affected. The results found for the two most contrasting catalysts are as follows.

TABLE I

Al<sub>2</sub>O<sub>3</sub>: Temperature 398°, Rate 3.1 cc./hr./10 g.

The runs were in the order hexanol-1 (a), hexene-1 (a), hexanol-1 (b), hexene-1 (b). The catalyst was dried by

passing dry nitrogen over it for 12 hours. This was done between hexanol-1 and hexene-1 the first time only. The second time the catalyst was allowed to be wet. Fractionation of products of hexanol-1 dehydration without any drying on calcium chloride show the same proportion of polymer. In this case it is impossible to separate the fractions because of azeotropic mixtures of water and hydrocarbons. The polymer is easily separated, because it has a much higher boiling point.

	Hexanol-1		Hexene-1	
	(a)	(b)	(a)	(b)
4-Methylpentene-2	2%	2%		
2-Methylpentene-1	1.1	1.5		
Hexene-1	22.0	23.7	5.9	6.3
3-Methylpentene-2- <i>t</i>	38.0	36.8	9.8	10.2
2-Ethylbutene-1	9.0	8.5	38.7	38.3
2-Methylpentene-2	6.0	6.2	27.7	27.9
Hexene-3	3.0	3.2	11.3	10.6
3-Methylpentene-2- <i>c</i>	2.0	1.8	5.3	5.2
Hexene-2	5.0	4.1		
Polymer	12.0	13.0	0	0

It may be seen that the mode of preparation of the pure alumina catalyst has no appreciable effect on the distribution of products. Catalyst (a) is made up of large glossy translucent chunks; (b) crumbles and is white. To be specially noted is the fact that there is no polymer formed in the runs with pure hexene-1, wet or dry. After two runs, the alumina is jet black from carbonization. This has no effect on the distribution of products. The products are found to be the same immediately after burning off the carbon with oxygen-bearing nitrogen and after ten runs without burning off the carbon.

Comparison of the products of dehydration of hexanol-1 and isomerization of hexene-1 at comparable rates of passage shows that the change of products from the dehydration with increase in rate is the result of progressive isomerization of the primary product hexene-1, and not to a change of mechanism of dehydration. Table II demonstrates this.

Hexene-1 shows the same products at 11.2 cc./hr. as hexanol-1 shows at 3.1; the same holds true for hexene at 22.5 cc. and hexanol-1 at 11.2 cc./hr./10 g. At the higher rates, hexene-1 tends to remain unchanged. The conclusion is that the alcohol is more strongly adsorbed than the olefin so that, at the faster rates, the proportion of material adsorbed changes so that the olefin does not remain on the surface long enough to isomerize.

(1) S. Goldwasser and H. S. Taylor, *THIS JOURNAL*, **61**, 1751 (1939).(2) S. Goldwasser and H. S. Taylor, *ibid.*, **61**, 1260 (1939).

At the slower rates, hexene-1 isomerizes more rapidly than the hexene-1 mixed with the alcohol since no surface is taken up by the alcohol or the product water. However, it is clear that the additional isomers produced at the slower rate of passage of alcohol are due to isomerization of the major primary product, hexene-1.

The course of isomerization as related to the structure of the olefin is summarized in Table III.

**Analysis of Results.**—(1) The first and most obvious conclusion concerning isomerization to be drawn from this table is that the straight chain olefin is the most unstable at these temperatures. Hexene-1 and heptene-1 give a large number of isomers on alumina. No other isomer gives any straight chain substance, however.

(2) On alumina at 398°, equilibrium is not reached from either the 2-methylpentene-2 side or the 3-methylpentene-2 side, since the per-

TABLE II  
Alumina at 398°: (a) is hexanol-1, (b) is hexene-1

Products	45.5		22.5		11.2		3.1	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
4-Methylpentene-2- <i>c</i> and - <i>t</i>	2		2		1.1		2	
2-Methylpentene-1	5.5		5		6.1		1.1	
Hexene-1	49.0	92	51	89	66.7	24	22	6.3
3-Methylpentene-2- <i>t</i>		8		9.2	7.1	36	38	10.2
2-Ethylbutene-1				1.8	2.3	13	9	38.3
2-Methylpentene-2						12	6	27.9
Hexene-3						8	3	10.6
3-Methylpentene-2- <i>c</i>						5	2	5.2
Hexene-2						2	5	
Polymer	18	0	20	0	16	0	12	0
Unchanged hexanol	24		20		0		0	

TABLE III  
ISOMERIZATION OF OLEFINS AS RELATED TO STRUCTURE, RATE = 3.12 Cc./Hr./10 G.

Substance	Cat.	T, °C.	Products													
			A	B	C	D	E	F	G	H	I	J	K	L	M	N
Hexene-1	Al <sub>2</sub> O <sub>3</sub>	398	38.3		28		10.2		6.3		11					0
Heptene-1				5.0		0		70		25		0				0
Hexene-1	ThO <sub>2</sub>	398	5				90									5
2-Methylpentene-2	Al <sub>2</sub> O <sub>3</sub>	398			62		35									3
2-Methylhexene-2				15		42		40								5
2-Methylpentene-2	ThO <sub>2</sub>	398	25		2		70									3
2-Methylhexene-2				20		3		72								5
3-Methylpentene-2- <i>t</i>	Al <sub>2</sub> O <sub>3</sub>	398	5		22		70									3
3-Methylhexene-2- <i>t</i>				2		10		82								6
3-Methylpentene-2- <i>t</i>	ThO <sub>2</sub>	398	19		7		70									4
3-Methylhexene-2- <i>t</i>				15		2		76								7
3-Methylpentene-2- <i>t</i>	ThO <sub>2</sub>	440	30		5		40						16		6	3
3-Methylhexene-2- <i>t</i>				20		8		45						11	9	7
3-Methylpentene-2- <i>t</i>	Al <sub>2</sub> O <sub>3</sub>	440	6		8		52						29		3	2
3-Methylhexene-2- <i>t</i>				3		5		63						18	7	4
2-Ethylbutene-1	ThO <sub>2</sub>	398	26		2		69									3
2-Ethylpentene-1				21		3		71								5
2-Methylpentene-2	Cr <sub>2</sub> O <sub>3</sub>	474	32% benzene, 65% unsatd.			3% satd.										
3-Methylpentene-2- <i>t</i>			32%			63%			5%							

A = 2-Ethylbutene-1      C = 2-Methylpentene-2      E = 3-Methylpentene-2-*t*  
 B = 2-Ethylpentene-1      D = 2-Methylhexene-2      F = 3-Methylhexene-2-*t*  
 G = Hexene-1      I = Hexene-3      K = 2-Methylpentene-1      M = Polymers  
 H = Heptene-1      J = Heptene-3      L = 2-Methylhexene-1      N = Isohexane

The primary fractionation data from which Table III, as well as Tables I and II, were constructed are given in Table IV which lists, from a given isomerization of a pure hexene or heptene, the volumes of liquid obtained at each "plateau" with the boiling range indicated.

TABLE IV  
 YIELDS AND FRACTIONATION DATA OF ISOMERIC HEXENES AND HEPTENES

Substance	Cat.	T, °C.	Volume distilled			Fractionation data
			Total	Plateaus	Intermediates	
Hexene-1	Al <sub>2</sub> O <sub>3</sub>	398	100	95	5	Cc.'s collected in plateaus of indicated boiling range 5.9 (63.5-63.6); 9.6 (65.6-65.7); 36.3 (66.6); 26.5 (67.1-.2); 10.4 (67.5-67.6).
Heptene-1			100	94	6	70.5 (91.2-91.3); 4.7 (93.9-94.0); 23.5 (94.9-95.0).
Hexene-1	ThO <sub>2</sub>	398	55	53	2	47.7 (65.6-65.7); 2.7 (66.6-66.7); 2.6 (over 150).
2-Methylpentene-2	Al <sub>2</sub> O <sub>3</sub>	398	70	68	2	23.8 (65.6-65.7); 42.2 (67.1-67.2); 2.2 (over 145).
2-Methylhexene-2			85	82	3	32.8 (93.1-93.2); 12.3 (93.9-94.0); 34.5 (94.4-94.5); 4.1 (over 160).
2-Methylpentene-2	ThO <sub>2</sub>	398	91	87	4	61.0 (65.6-65.7); 21.8 (66.6-66.7); 1.7 (67.1-67.2); 2.6 (over 150).
2-Methylhexene-2			79	75	4	54.8 (93.1-93.2); 15.0 (93.9-94.0); 2.2 (94.4-94.5); 3.7 (over 160).
3-Methylpentene-2- <i>t</i>	Al <sub>2</sub> O <sub>3</sub>	398	93	90	3	63.0 (65.6-65.7); 4.5 (66.6-66.7); 19.8 (67.1-67.2); 2.7 (over 150).
3-Methylhexene-2			59	56	3	46.5 (93.1-93.2); 1.1 (93.9-94.0); 5.6 (94.4-94.5); 3.4 (over 160).
3-Methylpentene-2- <i>t</i>	ThO <sub>2</sub>	398	76	73	3	51.1 (65.6-65.7); 13.9 (66.6-66.7); 5.1 (67.1-67.2); 2.9 (over 150).
3-Methylhexene-2			100	95	5	72.1 (93.1-93.2); 14.2 (93.9-94.0); 1.9 (94.4-94.5); 6.6 (over 160).
3-Methylpentene-2- <i>t</i>	ThO <sub>2</sub>	440	100	94	6	2.8 (60.1-60.2); 15.0 (61.9-62.0); 37.6 (65.6-65.7); 28.2 (66.6-66.7); 4.7 (67.1-67.2); 5.6 (over 150).
3-Methylhexene-2			89	85	4	5.8 (90.0-90.1); 9.5 (91.1-91.2); 38.3 (93.1-93.2); 17.0 (93.9-94.0); 6.8 (94.4-94.5); 7.7 (over 160).
3-Methylpentene-2- <i>t</i>	Al <sub>2</sub> O <sub>3</sub>	440	93	88	5	1.8 (60.1-60.2); 25.5 (61.9-62.0); 45.8 (65.6-65.7); 5.3 (66.6-66.7); 7.1 (67.1-67.2); 2.6 (over 150).
3-Methylhexene-2			97	91	6	3.6 (90.0-90.1); 16.4 (91.1-91.2); 52.3 (93.1-93.2); 2.7 (93.9-94.0); 4.6 (94.4-94.5); 6.4 (over 160).
2-Ethylbutene-1	ThO <sub>2</sub>	398	100	97	3	67.0 (65.6-65.7); 25.3 (66.6-66.7); 2.0 (67.1-67.2); 2.9 (over 150).
2-Ethylpentene-1			90	87	3	61.8 (93.1-93.2); 18.3 (93.9-94.0); 2.6 (94.4-94.5); 4.3 (over 160).

centages of products resulting are not the same from the two isomerizations. The same holds true for 2-methylhexene-2 and 3-methylhexene-2. On thoria, however, the composition of the isomerized liquid is practically the same starting from either the 2- or 3-methyl isomer. Therefore, isomerization is faster on thoria than on alumina. This agrees with the comparative rates of dehydration found for these two catalysts. That there is still some straight chain isomer left after passage over alumina and none over thoria also points to this conclusion. It is also to be noticed that the 7-carbon olefins isomerize slightly faster than the 6-carbon ones, as is evidenced by the fact that the isomers are closer to the composition found on thoria under the same conditions.

(3) The main isomerization observed is the migration of a methyl group across a double bond. The more stable of the two positions is the more centralized one. All 2-methyl compounds give the corresponding 3-methyl compounds in large

quantities. The reverse migration occurs only to a small extent.

(4) The isomer 2-ethylbutene-1 is the result of migration, not of a methyl group but of the double bond. The methyl group is in the same relative position as in the stable 3-methylpentene-2. Both 2-ethylbutene-1 and 2-ethylpentene-1 give the same composition of products over thoria as the 2- and the 3-methyl compounds. The similarity in composition of the products from isomerization of all these hydrocarbons indicates a reaction path conforming to a specific pattern.

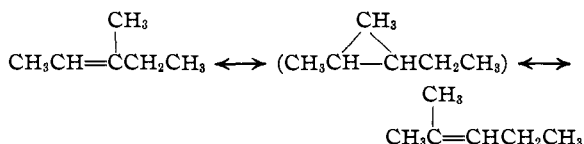
(5) Rise in temperature to 440° causes the double bond to shift to the end of the chain and considerable 2-methylpentene-1 and 2-methylhexene-1 are found. Decomposition has been enough to allow some hydrogenation of olefin. The same is true for both chromium and thorium oxides.

(6) Contrary to the findings concerning the

formation of polymer in the isomerization of a pure straight chain olefin, it is seen here that, while the straight chain olefin does not give any polymer on isomerization, there is some formed in all other cases.

(7) The formation of benzene from the 2-methylpentenes and 3-methylpentenes with chromic oxide catalyst points to the fact that there must be some isomerization to the straight chain taking place with consequent ring closure of the olefin. The only olefin for which any isomerization to the straight chain seems likely is the 2-methylpentene-1 isomer. If only a trace of hexene-1 or hexene-2 is formed from this isomer, benzene is formed immediately on the catalyst and the 2-methylpentene-1:hexene-1 equilibrium is displaced to the straight chain side. The results at 440° on thoria and alumina show the extent to which 2-methylpentene-1 is formed at higher temperatures. The fact that there is only 32% aromatic yield from the methylpentenes as compared with 95 to 100% from the hexenes is evidence of the comparative slowness of the isomerization to straight chain olefins even at the higher temperature of 474°.

**Mechanism.**—A mechanism which brings together several of the above findings concerning isomerization is, as in the case of the dehydration of alcohols described in a previous paper, the formation of an activated intermediate stage having the configuration corresponding to a 3-membered ring. That is, it is assumed that, on the surface of the catalyst, the following takes place



If this occurs, the products may be predicted exactly as in the case of the alcohols, and are found to agree exactly with those found. The

formation of polymer in the isomerization of the branched olefin points to the same type of activated intermediate found with the alcohols. That no compound such as 4-methylpentene-2 is found, as well as that 4-methylpentene-2 and its analogs do not isomerize, indicates that methyl groups migrate across double bonds only under these conditions.

At higher temperatures, where migration of a double bond is found to take place, 2-methylpentene-1 is formed from 2-methylpentene-2 by the same mechanism. The methyl group is again on the inside of the double bond. It is this type of reaction which gives hexene-1 as a product, which then immediately aromatizes on chromium oxide.

### Summary

1. Two different preparations of the same alumina catalyst have been shown to be comparable as to their effects on isomerization of alkenes.

2. Change in distribution of isomers produced with change in rate of passage of an alcohol over a dehydrating catalyst has been shown to be due to isomerization of the olefin products themselves.

3. The products of isomerization at 400° have been determined for several olefins and comparative rates of isomerization on thoria and alumina studied.

4. A mechanism postulating an intermediate 3-carbon ring structure similar to that proposed for the dehydration of alcohols has been found to account for the products of isomerization.

5. The order of stability of some olefins at 400° is as follows: 3-methylpentene-2-*t* > 2-ethylbutene-1 > 3-methylpentene-2-*c* > 2-methylpentene-2 > 2-methylpentene-1 > hexene-1. 3-Methylhexene-2-*t* > 2-ethylpentene-1 > 3-methylhexene-2-*c* > 2-methylhexene-2 > 2-methylhexene-1 > heptene-1.

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