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Summary

A study of the effect of non-electrolytes upon the rate of setting of gelatin gels has been carried out.

Small concentrations of non-electrolytes in-

crease setting time, this effect becoming a maximum at 0.02-0.03 molar.

Concentrations of non-electrolyte exceeding 0.1 molar cause gels to set more rapidly than in the absence of non-electrolytes.

Comparison with results of diffusion experiments leads to the conclusion that the slower setting gels have a more open structure.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Catalytic Dehydration of C₆-C₈ Aliphatic Alcohols

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An apparatus for the study of vaporized hydrocarbons and its application to the dehydrogenation of cycloöctene were described in a previous paper.¹ In seeking a good source of aliphatic hydrocarbons, it was found that certain alcohols were available in comparatively large quantities. Catalytic dehydration of these alcohols in this same apparatus proved to be an excellent source of alkenes and provided certain information concerning the mechanisms of dehydration and isomerization.

The separation of the pure isomers resulting from the dehydration of an alcohol was accomplished by the use of a modification of the Podbielniak column together with a special head which permits controlled reflux ratio.

Apparatus.—The column proper is shown in Fig. 1. It consists simply of a Pyrex tube, A, 1.5 meters long and 4.5 mm. i.d., flared at both ends to fit in a 1.8-meter long 16-mm. tube, B, which has a 16-mm. ground joint at one end and is ring-sealed at 1 and 2 at both ends. The space between the two tubes is evacuated through a side tube with the column at about 150°, the necessary heat being provided electrically with 12.2 meters of no. 20 chromel wire wound externally. About 6.1 meters of no. 20 chromel are wound spirally on a rod of such size that, when the spiral is stretched to six or seven turns per inch (2.5 cm.), it fits snugly inside the center tube of the column. This is the Podbielniak type packing. It does not allow reflux liquid to run down the column but causes it to travel down in a spiral path. More time is thus afforded for equilibrium to be set up and separation is excellent. The hold-up is small and the amount of liquid reaching the head without flooding is much larger than can be secured with the helical glass packing. A 200° thermometer, C, graduated in tenths of one degree is tied with asbestos directly to the column so that the

bulb of the thermometer touches the evacuated jacket about one-third from the bottom. Just above the ground joint and also 1.5 meters up the column are wound asbestos strips so that the column is tightly supported inside a 1.5-meter 35-mm. Pyrex tube.

The head, D, which is described by J. H. Simons,² is sealed on just above the outermost insulating jacket and fitted with a thermometer, E, which is calibrated at 0, 56.7 and 100°. This head is a total condensing variable take-off type and has the advantage that it will accurately control reflux ratio, that it allows accurate and direct temperature measurement, and that hot hydrocarbon vapors can in no way come in contact with any contaminating surfaces. It can be adjusted for total return so that, in adjusting the column for operation, there is no loss.

Heating of the liquid is supplied by a small electrical heater, F. Either a 100-cc. or 200-cc. flask, G, with interchangeable ground joints may be used. The receivers are 30 cm. long 12-mm. tubes immersed in an ice-bath so that the outlet tube, H, from the head is at a lower level than the

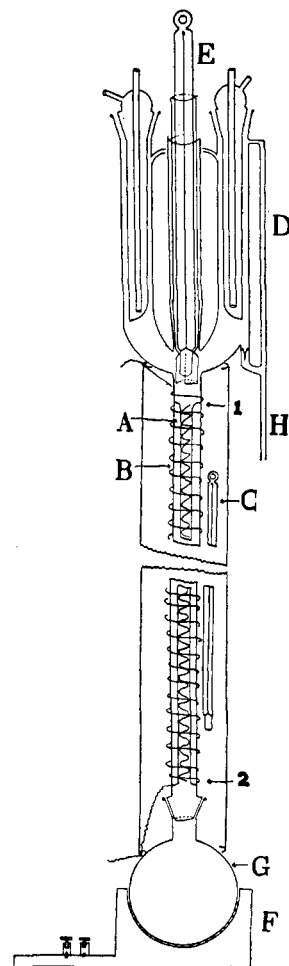


Fig. 1.—Fractionation apparatus.

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

(2) J. H. Simons, *Ind. Eng. Chem., Anal. Ed.*, **10**, 29 (1938).

surface of the ice, eliminating as far as is possible loss from evaporation during a distillation.

The catalytic apparatus used in this study of dehydration is identical with that previously described.¹ When the rate of passage of alcohol was 20 cc. per hour or more, the central buret tube used was 12 mm. o.d.

Materials.—The alcohols used were commercial products supplied by E. I. du Pont de Nemours and Company and by Carbon and Carbide Chemical Corporation. They were purified by careful distillation in the column described. The maximum impurity in any one of the alcohols proved to be about 3%. The heptanol-4 used was synthesized as follows.

A manganous oxide was prepared by passing methanol vapors over manganous carbonate *in situ* at 400°. The temperature was then raised to 450° and butyric acid passed over it. The heptanone-4 formed was separated by fractional distillation. This was then reduced by passing its vapors mixed with hydrogen over a nickel catalyst at 150°. Repetition of passage and distillation gave a pure heptanol-4; sp. gr. d_{20}^{20} , 0.820, refractive index n_D^{20} 1.4325, b. p. (760 mm.) 155.4°.

The properties of the other purified alcohols were:

	Sp. gr. d_{20}^{20}	n_D	B. p., °C. (760 mm.)
Hexanol-1	0.8189	1.4161	156.4
2-Ethylbutanol-1	.8328	1.421	148.9
2,4-Dimethylpentanol-1	.819		157
2,4-Dimethylpentanol-3	.8288	1.4226	140
2-Ethylhexanol-1	.833		184.6

The catalysts used in the investigation were alumina, chromic oxide gel and thoria. Uranium oxide was found to be inactive for dehydration. The preparation of chromic oxide gel has been described previously. Alumina was prepared by precipitating aluminum hydroxide from a 1.5 *N* aluminum nitrate solution with concentrated ammonia, vigorously stirred and filtered on a Büchner funnel. When dried at 100° the particles obtained were glassy, large and non-crumbling. Several other methods were tried for this preparation, including precipitation from dilute solutions and heating before filtration. The method cited proved to be the most convenient in preparation and handling, and also the most active in dehydration. The thoria catalyst used was prepared by the method of Kramer and Reid.³ It consists of thoria supported on pumice in the proportion 1:3 and is prepared by the ignition of thorium nitrate under carefully controlled conditions.

Procedure.—The procedure for the passage of an alcohol over a catalyst is identical with the procedure described for the dehydrogenation of cycloöctene. It is very convenient to collect the product in a pig of 100-cc. capacity, used only for the alcohols. The liquid condensed separates into two layers, water and hydrocarbon. To determine extent of dehydration, the water layer is drawn off and weighed, and the volume of the hydrocarbon layer measured. The specific gravity of the alcohols is about 0.82, the hydrocarbon about 0.69. For 100 cc. of alcohol dehydrated, there should be 96 cc. of hydrocarbon and 14.1 cc. of water. This method of estimation is quite

accurate. The hydrocarbon is then dried over calcium chloride for two hours, then placed over a new batch of calcium chloride in a second flask and allowed to stand for twelve hours. This eliminates any unchanged alcohol as well as water. Traces of water show up as a cloudiness in the first drops refluxing in the fractionation. When this occurs, the column must be opened and dried thoroughly.

For the fractionation of the dry hydrocarbon mixture, the procedure will be described in detail. The mixture is placed in a 200-cc. flask fitted with a ground joint and attached to the column. The heater is placed under the flask and its temperature adjusted so that the liquid will begin to boil in about half an hour. The valve in the head is turned so that all vapors will pass to the non-exit side and the condenser on the other side adjusted so that all condensate will return to the column. The rheostats in series with the heating coil around the vacuum jacket are adjusted from time to time so that the temperature shown by the thermometer in the outer jacket keeps pace exactly with that in the head. The purpose of this and the vacuum jacket is to make the column as-adiabatic as possible, so that heat exchange will take place only between the refluxing liquid and the vapors coming up the column. As soon as the column is operating properly, that is, about 30 drops of liquid are returning to the column every five seconds, with no flooding, the condenser on the exit side is adjusted so that one drop is collected in the receiver every five seconds. As the distillation is in progress, a plot is made with the number of drops as the abscissa and the temperature of the head as ordinate. The receiver is changed at the beginning and end of each horizontal part of the curve, there resulting two portions of liquid for each constant boiling fraction, one of a nearly pure hexene isomer, the other of a mixture consisting of the two isomers between the boiling points of which the mixture distils. Total reflux is used for five minutes at the end of each horizontal part in order to make the break sharper. Throughout the distillation, outer jacket temperature must be the same as, or 1° lower than, the temperature of the head. The receivers are of known volume and the amount of each fraction may be ascertained without undue transfer of liquid.

Specific gravities, correct to the third decimal place, and Hanus numbers are taken for each fraction. The Hanus number determination is used to determine the purity of the fraction with respect to non-olefins, and the fraction corresponding to a horizontal part of the curve is then identified by comparison with a table of boiling points and specific gravities of hydrocarbons, as described in the next section. The absolute amount of the various isomers in a mixture is determined by extrapolation of the horizontal and rising parts of the curve. The meeting point of the lines gives the amount of the pure fraction. The slopes of the vertical lines are those of the tangents to the distillation curve at the points of inflection. It must be understood that, even for the fractions corresponding to the horizontal parts of the curve, absolute purity is not obtained. The main constituent of a given fraction is present, however, in amounts greater than 95%. The fractionation, from which the data in Table II are taken, is shown in abbreviated form in Fig. 2, and demonstrates

(3) Kramer and Reid, *THIS JOURNAL*, 43, 880 (1921).

the method of extrapolation. The validity of the method was checked by the fractionation of known mixtures, in which case complete substantiation was found.

The amount of the liquid to be placed in the distilling flask was determined by that component of the mixture which was present in smallest amounts, since to get a good flat in the curve required about 0.75 cc. In all cases, 100 cc. of an alcohol or more was dehydrated, and 100 cc. of the dry hydrocarbon mixture fractionated, so that, as a rule, volumes were equal to percentages. In certain cases where material was scarce and the composition of the resultant mixtures was known qualitatively by previous experience, a 20-cc. sample was sufficient, and a 10-cc. sample of a two-component mixture was sometimes sufficient.

Identification of Fractions.—The first satisfactory compilation of the physical properties of pure hydrocarbons has appeared only recently. The compilation was made by G. L. Eaton.⁴ The table is comprehensive and lists specific gravities, etc., for every pure hydrocarbon known. No complete tabulation of octene isomers is available.

To illustrate difficulty in identification, the following may be cited. Fractionations continuously gave a cut at 65.6–65.7° and no further cut to 66.2°. There appeared to be no isomer boiling at the lower temperature recorded in the literature. However, one of the isomers of 3-methylpentene-2 was reported as boiling at 65.7–66.2°. By the elimination of the fractions which were known with some certainty, it was decided that the fraction boiling at 65.7° must be 3-methylpentene-2 and further work was carried out on this basis. A paper by van Risseghem,⁵ which has appeared recently, in which was described the isolation of several pure hexene isomers identified by chemical means and checked with infrared spectra, records that the isomer variously reported as boiling at 65.7–66.2° is *trans*-3-methylpentene-2 and that its true boiling point is 65.7°. This concordance may be used to emphasize the confidence that may be placed in the fractionations obtained.

While most boiling points reported are uncorrected, transformations of values found at one pressure to another pressure for purposes of comparison are necessary. According to an article on conversion factors in the same treatise,⁴ the following facts are found.

B. p. at 760 mm., ° C.	0	50	100	150
Corr. per mm. for b. p. at 760 = 50 mm.	0.035	0.040	0.046	0.051

Most hexene isomers boil in the range 60 to 70°. The correction on a normal day will amount to 0.4°, which is as much as the difference between two isomers to be separated. Pressure variations corresponding to as much

as 0.6° have been found in interrupted distillations of a given cut.

With a distillation curve corrected to 760 mm., it was found that the sequence of the fractions together with their boiling points could be correlated readily with the

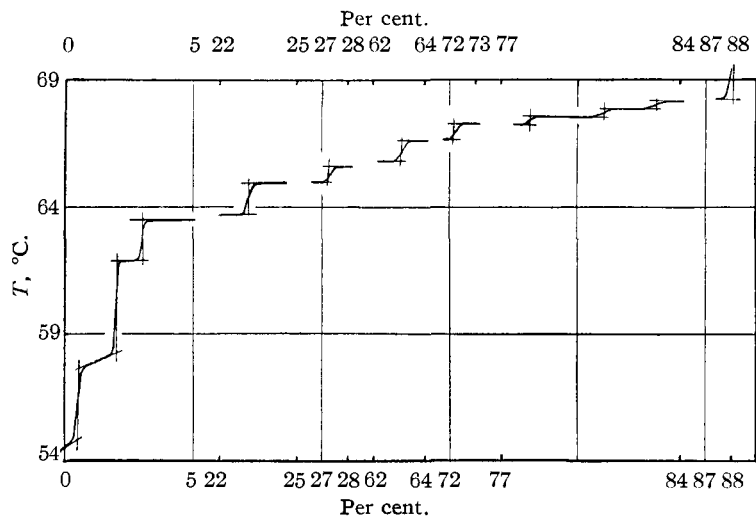


Fig. 2.

boiling point sequence of the isomeric olefins in question. A correlation with specific gravities served as additional check. If the specific gravities fell in the sequence which the fractions required when the identifications were made from the boiling point, identification was assumed to be adequate for the purposes of the present study, a procedure which is common in other work of this type. Accordingly, we have, in the succeeding data, labelled the respective cuts with the name of the alkene having the corresponding boiling point. Substances of a type other than hydrocarbon can confuse identification, but the use of specific gravities eliminates this possibility. In certain cases, where there was a good quantity of isomer available, dibromo derivatives were prepared as a further check. For example, the dibromo derivative prepared from the hexene identified as hexene-1, gave a product: b. p. 77–77.5° (15 mm.) and sp. gr.^{13,5} 1.596, whereas the literature shows this derivative to have: b. p. 77–78° (15 mm.) and sp. gr.^{13,5} 1.59625.

The possibility of the formation of azeotropic mixtures was considered. In sixty or more fractionations of mixtures of pure hexene isomers, containing every possible combination of such isomers, save one to be mentioned, no fractions were found which did not correspond exactly with tabulated isomers in all properties. Only in one case, with mixtures containing both hexene-1, b. p. 63.5–64.0°, and *trans*-3-methylpentene-2, b. p. 65.7–66.0°, was there evidence for a constant boiling mixture at 65.0°. However, no more than 4% of the total multicomponent mixture came off in this form.

Table Ia was used for the identification of the hexenes. Similar tables, Tables Ib and Ic, were used for the heptenes and the octenes.

Table II shows a typical fractionation. The

(4) G. L. Eaton, "Science of Petroleum," Vol. II, Oxford University Press, Oxford, 1937, p. 1302, etc.

(5) H. van Risseghem, *Bull. soc. chim. Belg.*, **47**, 47 (1938)

percentage data given are deduced from Fig. 2, by the method of extrapolation given. All percentages in the tables following are deduced in a similar manner from the fractionation curves (see Figs. 3-7). The close checks found for the observed and the calculated values of specific gravities and unsaturation attest both the purity and the correctness of method.

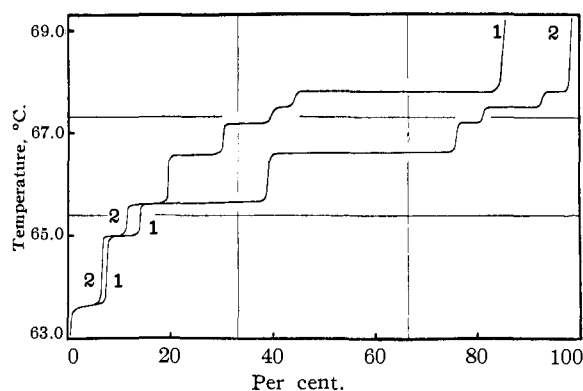


Fig. 3.—Distillation curves of dehydration products on alumina at 398° from 2-ethylbutanol-1: 1, fast speed; 2, slow speed.

Observed B. p., °C.	Sp. gr. ²⁰ ₄	Indicated hexene isomer	Lit. data B. p., °C.	Sp. gr. ²⁰ ₄
63.5-63.7	0.673	Hexene-1	63.5-63.7	0.6732
65.6-65.8	.694	3-Methylpentene-2- <i>t</i>	65.6-65.8	.6940
66.6	.689	2-Ethylbutene-1	66.6	.6897
67.2	.690	2-Methylpentene-2	67.2	.6904
67.5	.720	Hexene-3	67.5	.7190
67.8	.696	3-Methylpentene-2- <i>c</i>	67.8	.6956

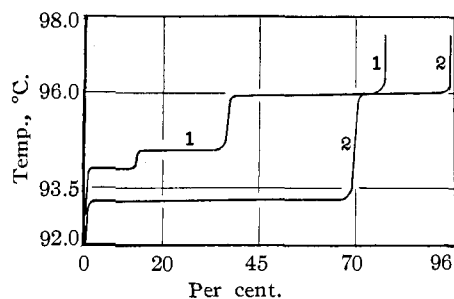


Fig. 4.—Distillation curves of dehydration products on alumina at 398° from heptanol-4: 1, fast speed; 2, slow speed.

Observed B. p., °C.	Sp. gr. ²⁰ ₄	Indicated heptene isomer	Lit. data B. p., °C.	Sp. gr. ²⁰ ₄
93.1-93.2	0.712	3-Methylhexene-2	93.1-93.3	0.7120
93.9-94.0	.707	2-Ethylpentene-1	93.9-94.3	.7079
94.5-94.6	.709	2-Methylhexene-2	94.4-94.6	.7089
95.8-95.9	.704	Heptene-3	95.8-96.1	.7043

Experimental Results

(A) **Effect of Rate on Products of Dehydration.**—Purified hexanol-1 was passed over a preparation of alumina at 398°. The rate of

TABLE Ia

Isomeric hexenes	B. p. 760 mm. (range) °C.	Sp. gr. ²⁰
3,3-Dimethylbutene-1	41.2	0.6529
4-Methylpentene-1	53.6-53.9	.6646
3-Methylpentene-1	53.6-54.0	.6700
4-Methylpentene-2- <i>c</i>	54.2-55.2	.6702
2,3-Dimethylpentene-2	56.0	.6803
4-Methylpentene-2- <i>t</i>	57.7-58.5	.6709
2-Methylpentene-1	61.5-62.0	.6817
Hexene-1	63.5-64.1	.6732
3-Methylpentene-2- <i>t</i>	65.7-66.2	.6940
2-Ethylbutene-1	66.2-66.7	.6897
2-Methylpentene-2	67.0-67.2	.6904
Hexene-3- <i>t</i>	67.3-67.5	.7170
3-Methylpentene-2- <i>c</i>	67.6-68.2	.6956
Hexene-2	67.9-68.1	.6813
Hexene-3- <i>c</i>	70.0-71.2	.7190
2,3-Dimethylbutene-2	73.0	.7280

TABLE Ib

Isomeric heptenes	B. p. 760 mm. (range) °C.	Sp. gr. ²⁰ ₄
4,4-Dimethylpentene-2	76.0	0.6881
3,3-Dimethylpentene-1	76.9	.6961
2,3,3-Trimethylbutene-1	80.0	.707
2,4-Dimethylpentene-1	80.9-81.3	.6937
2,4-Dimethylpentene-2	82.6	.6947
3-Methylhexene-1	84.0	.6953
2,3-Dimethylpentene-1	84.1-84.3	.7054
5-Methylhexene-1	84.7	.6936
4-Methylhexene-2 (1)	85.1-85.6	.6981
5-Methylhexene-2 (1)	85.6-86.1	.7020
3,4-Dimethylpentene-2	86.2-86.4	.7126
2-Methylhexene-3	86.4-86.9	.6942
4-Methylhexene-2 (2)	87.1-87.6	.7007
4-Methylhexene-1	87.2-87.5	.6969
3-Methyl-2-ethylbutene-1	88.7-89.1	.7186
5-Methylhexene-2 (2)	91.1-91.6	.6990
2-Methylhexene-1	91.1-91.5	.7000
3-Methylhexene-2	93.1-93.3	.7120
2-Ethylpentene-1	93.9-94.3	.7079
2-Methylhexene-2	94.4-94.6	.7089
3-Ethylpentene-2	94.8-94.9	.7172
Heptene-1	94.9	.6993
2,3-Dimethylpentene-2	95.1	.719
Heptene-3	95.8-96.1	.7043
Heptene-2	98.1-98.4	.7034

TABLE Ic

Isomeric octenes	B. p. 760 mm. °C.	Sp. gr. ²⁰ ₄
5,5-Dimethylhexene-3	100.1	0.7408
2,4,4-Trimethylpentene-1	102.6	.711
2,4,4-Trimethylpentene-2	104.5	.7211
4,4-Dimethylhexene-2	105.6	.7202
6-Methylheptene-1	111.5	.7124
2-Methylheptene-3	120.4	.7314
4-Methylheptene-3	120.4	.724
Octene-1	123	.7155
2-Methylheptene-2	125.2	.816

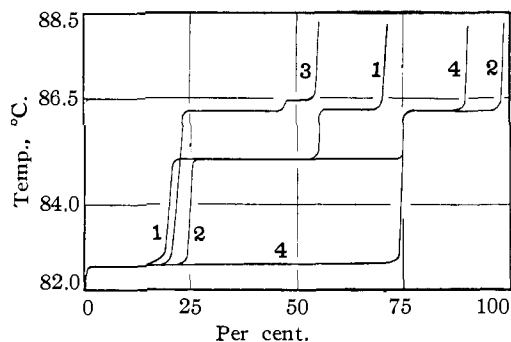


Fig. 5.—Distillation curves of dehydration products on alumina at 398° from 2,4-dimethylpentanol-1: 1, fast speed; 2, slow speed and 2,4-dimethylpentanol-3; 3, fast speed; 4, slow speed.

Observed B. p., °C.	Sp. gr. ²⁰ ₄	Indicated heptene isomer	Lit. data B. p., °C.	Sp. gr. ²⁰ ₄
82.6	0.695	2,4-Dimethylpentene-2	82.6	0.6947
85.1-85.2	.701	4-Methylhexene-2	85.1-85.6	.7007
86.2-86.3	.712	3,4-Dimethylpentene-2	86.2-86.4	.7126
86.4-80.5	.694	2-Methylhexene-3	86.4-86.9	.6942

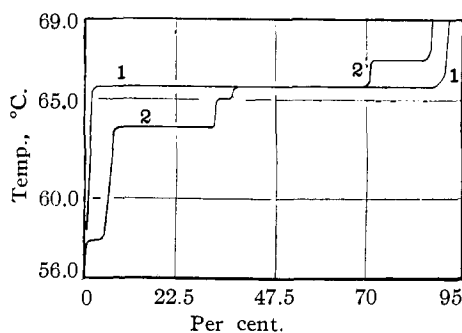


Fig. 6.—Distillation curves of dehydration products on thoria at 398° from hexanol-1: 1, slow speed; 2, fast speed.

Observed B. p., °C.	Sp. gr. ²⁰ ₄	Indicated hexene isomer	Lit. data B. p., °C.	Sp. gr. ²⁰ ₄
57.8-58.1	0.670	4-Methylpentene-2- <i>t</i>	57.7-58.5	0.6709
63.5-63.6	.673	Hexene-1	63.5-63.7	.6732
65.6-65.7	.694	3-Methylpentene-2- <i>t</i>	65.6-65.8	.6940
66.6	.689	2-Ethylbutene-1	66.6	.6897

flow was controlled to 1%. The results are recorded in Table III, together with a set of data for a 10% UO₂-90% Al₂O₃ catalyst available from other work.

(1) The first and most obvious thing about Table III is that the primary products are shown to be hexene-1, 2-methylpentene-1, 4-methyl-

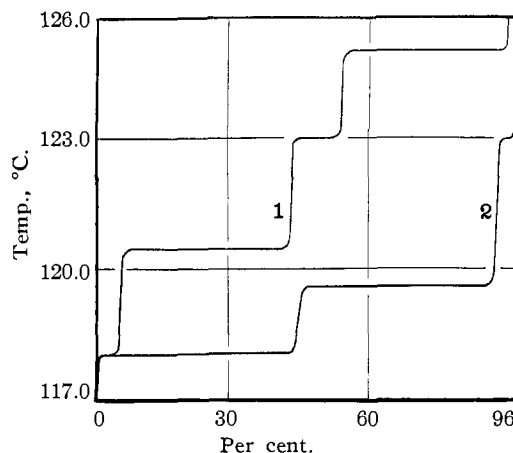


Fig. 7.—Distillation curves of dehydration products on thoria at 398° from 2-ethylhexanol-1: 1, slow speed; 2, fast speed.

Observed B. p., °C.	Sp. gr. ²⁰ ₄	Indicated isomer	Lit. data B. p., °C.	Sp. gr. ²⁰ ₄
118.1	?			
119.6	?			
120.4	0.724	4-Methylheptene-3	120.4	0.724
123.0	.717	Octene-1	123	.7155
125.0-125.1	.816	2-Methylheptene-2	125.2	.816

pentene-2, and, surprisingly, a small amount of 2-methylpentane. (2) As the rate becomes slower, the actual amount of hexene in the mixture increases at the expense of unchanged hexanol. The hexene-1 in turn decreases and other hexene isomers appear. That this is due to direct

TABLE II

DEHYDRATION OF HEXANOL-1 ON ALUMINA, 3.12 Cc./HOUR AT 398°

B. p., °C.	Compound	%	Sp. gr. (obsd.)	Sp. gr. (lit.)	Unsaturation (Obsd.)	Unsaturation (Calcd.)
54.6-55.0	4-Methylpentene-2- <i>c</i>	0.5	0.670	0.6702		
57.7-58.5	4-Methylpentene-2- <i>t</i>	1.5	.671	.6709		
61.9	2-Methylpentene-1	1.1	.682	.6817	0.00391	0.00394
63.5-63.7	Hexene-1	20.0	.673	.6732	.00389	.00390
65.0	Mixture	4.0				
65.6	3-Methylpentene-2- <i>t</i>	36.0	.694	.6940	.00399	.00400
66.6	2-Ethylbutene-1	9.0	.689	.6897		
67.2	2-Methylpentene-2	6.0	.690	.6904	.00398	.00399
67.5	Hexene-3	3.0	.720	.7190		
67.8	3-Methylpentene-2- <i>c</i>	2.0	.696	.6956		
68.0-68.1	Hexene-2	5.0	.680	.6813		
Over 150	Polymer	12.0	.762			

The micro-pipet used for Hanus no. contained 0.2638 cc.

TABLE III

Products	Rate of passage, in cc./hr./10 g. catalyst, %				3.1 (10% UO ₂ - 90% Al ₂ O ₃)
	45.5	22.5	11.2	3.1	
4-Methylpentene-2- <i>c</i>				0.5	
4-Methylpentene-2- <i>t</i>	2	2	1.1	1.5	5
2-Methylpentane	1	3	2.0	0.0	0
2-Methylpentene-1	5.5	5	6.1	1.1	8
Hexene-1	49.0	51	66.7	22.0	40
3-Methylpentene-2- <i>t</i>			7.1	38.0	28
2-Ethylbutene-1			2.3	9.0	
2-Methylpentene-2				6.0	
Hexene-3				3.0	
3-Methylpentene-2- <i>c</i>				2.0	
Hexene-2				5.0	
Polymer	18.0	20	16.0	12.0	17
(Ether in polymer)	(1)	(0.5)	(0)	(0)	
Unchanged hexanol-1	24.0	20	0.0	0.0	
Total	99.5	101	101	100.1	98
Major products, corrected	} hexene-1	64	66	22	
for unchanged hexanol		} polymer	24	16	12

isomerization of hexene-1 on the alumina surface will be shown in a later paper. The same is the case with 2-methylpentene-2, as is shown in the table. (3) The faster the passage, the more unchanged hexanol and polymer is found. An ether is found in the polymer only in the case of most rapid passage. Slower pas-

The polymer discussed is a yellow oily liquid with a boiling range of 200–250°. This and the specific gravity point to a dodecalene. A Hanus number determination corresponds exactly with that calculated for a dodecalene.

(B) Effect of Catalyst on Products of Dehydration.—

TABLE IV
PURIFIED HEXANOL-1 PASSED AT 3.1 CC./HR./10 G. CATALYST AT 398°

Products	Al ₂ O ₃ (a)	Al ₂ O ₃ (b)	ThO ₂	Catalyst, %		Cr ₂ O ₃
				10% UO ₂	100% UO ₂	
4-Methylpentene-2- <i>c</i>	0.5	0.5				
4-Methylpentene-2- <i>t</i>	1.5	1.5		5		23.4 benz.
2-Methylpentene-1	1.1	1.6		8		37 olef.
Hexene-1	20.0	21.0		40		37.6 sats.
Mixture	4.0	3.5		2		
3-Methylpentene-2- <i>c</i>	36.0	35.0	90	28		
2-Ethylbutene-1	9.0	8.5				
2-Methylpentene-2	6.0	6.2				
Hexene-3	3.0	3.2				
3-Methylpentene-2- <i>t</i>	2.0	1.8				
Hexene-2	5.0	4.1				
Polymer	12.0	13.0	10	17		
Hexanol					100	

sage allows any ethers formed to decompose. (4) Correcting for unchanged hexanol, it is seen that the amount of polymer formed is a function of the unchanged hexanol. The amount of hexene formed does not change, but slower rate allows its isomerization. (5) The results found for 10% uranyl on alumina lie between the results from the two slowest rates on pure alumina. This is due to a screening of alumina surface by inactive uranyl, as will be shown.

This table yields the following conclusions. (1) Mode of preparation of aluminum oxide does not significantly change dehydration. Four different pure aluminas were tried. (2) Isomerization proceeds much more rapidly on thoria. All intermediate isomers have disappeared. All hexene-1 has isomerized to 3-methylpentene-2. (This will be elaborated in a later paper.) (3) 100% uranium oxide produces no dehydration, either at 400 or at 500°. The catalyst preparation

proved to be active for dehydrogenation, however. No preparation of pure uranium dioxide was found that dehydrated. (4) As was shown in section (A), the 10% uranyl catalyst on alumina gives products which are the same as though a faster rate were used over pure alumina. (5) The reaction with chromic oxide is a different type from the others. Not only is there dehydration but dehydrogenation. Benzene is formed

from the hexene-1 and some of the olefins formed are hydrogenated at this comparatively low temperature. Water vapor when mixed with olefin over chromic oxide causes oxidation of the olefin so that considerable carbon dioxide is evolved.

The effect of rise of temperature is slight, except to decrease decomposition. In the case of chromic oxide, however, an increase to 460° gives excellent dehydrogenating conditions. The ma-

TABLE V
EFFECT OF RATE AND CATALYST ON PRODUCTS OF DEHYDRATION

Products	Hexanol-1		2-Ethylbutanol-1		Heptanol-4		2,4-Dimethylpentanol-1		2,4-Dimethylpentanol-3	
	f	s	f	s	f	s	f	s	f	s
Alumina at 398°										
4-Methylpentene-2- <i>c</i>		0.4								
4-Methylpentene-2- <i>t</i>	2	1.5								
2-Methylpentene-1	5	1								
Hexene-1	51	22	11	9						
3-Methylpentene-2- <i>t</i>		38	9	30						
2-Ethylbutene-1		9	10	37						
2-Methylpentene-2		6	10	5						
Hexene-3		3	4	12						
3-Methylpentene-2- <i>c</i>		2	43	5						
Hexene-2		5								
2-Methylhexene-2					22					
Heptene-3					40	25				
2-Ethylpentene-1					15					
3-Methylhexene-2						70				
4-Methylhexene-2							35	49		
2-Methylhexene-3									5	
2,4-Dimethylpentene-2							20	24	17	20
3,4-Dimethylpentene-2							15	24	30	75
Polymer	20	12	4	2	18	5	10	3	8	5
Ether	0.5	0	0.6	0	0	0				
Unchanged	20	0	3	0	5	0	20	0	40	0
Decomposed (off-gas)	0.2	0.5	0.3	0.7	0.2	0.4	0.3	0.6	0.2	0.6

Products	Hexanol-1		Products	2-Ethylhexanol-1	
	f	s		f	s
Thoria at 398°					
4-Methylpentene-2- <i>t</i>	5		Octene-1	12	2
Hexene-1	30		2-Methylheptene-2	40	
3-Methylpentene-2- <i>t</i>	35	90	4-Methylheptene-3	40	
2-Methylpentene-2	15		B. p. 118.1°	5	46
			B. p. 119.6°		46
Polymer	15	10		5	5
Unchanged	0	0		2	0
Decomposed	0.8	1.5		0.4	1.1

Products	320°	380°	Hexanol-1 398°	420°	460°	Heptanol-4 410°	2,4-Dimethyl- pentanol-1 400°
	Cr ₂ O ₃ , 3.11 cc./hr./10 g.						
Aromatic		17	25	33	46	40	5
Olefin (liq.)		24	37	51	49	50	20
Saturate		58	38	15	5	10	25
Polymer							50
Unchanged	100 (hexanol-1 unchanged on 100% UO ₂ at 400, 500°)						

f = 22.5 cc./hr./10 g. catalyst. s = 3.1 cc./hr./10 g. catalyst.

lor product is benzene, and the saturates drop to 5%. There is no water in the exit gas, it being entirely converted to hydrogen and carbon dioxide.

To determine whether there are analogous effects with change in rate of passage with other alcohols, the primary products of decomposition were determined in the cases of several other alcohols.

Table V gives the percentage decomposition of the hydrocarbon layer resulting from the dehydration of several alcohols at a slow and a rapid rate. Figures 3, 4, 5, 6 and 7 record the distillation curves obtained with the products from the six-, seven- and eight-carbon alcohols indicated. The correlation of the "flats" in the curves and the specific gravities is made with data, for the isomer indicated, obtained from Tables Ia, b, and c. In every case, save for the two unidentified octenes, this correlation leads to the designation of the isomer as given below each curve. It is from such distillation curves that the data in Table V were deduced.

From Table V, it is seen that the following are the primary products of dehydration on alumina gel.

- (1) Hexanol-1: hexene-1; 2-methylpentene-1; 4-methylpentene-2.
- (2) 2-Ethylbutanol-1: hexene-1; 3-methylpentene-2; 2-ethylbutene-1; 2-methylpentene-2; hexene-3.
- (3) Heptanol-4: heptene-3; 2-ethylpentene-1; 2-methylhexene-2.
- (4) 2,4-Dimethylpentanol-1: 4-methylhexene-2; 2,4-dimethylpentene-2; 3,4-dimethylpentene-2.
- (5) 2,4-Dimethylpentanol-3: 2-methylhexene-3; 2,4-dimethylpentene-2; 3,4-dimethylpentene-2.
- (6) 2-Ethylhexanol-1: 2-methylheptene-2; 3-methylheptene-2; 4-methylheptene-4; octene-3.

The only one of these cases in which there is any doubt as to the primary products is that of hexanol-1 on thoria. The fastest rate used still gave 100% dehydration.

Analysis of Results

Production of Oily Polymer.—The polymer is produced in larger quantity at the faster rates. This is the case with both alumina and thoria. As was pointed out in the detailed table of effect of rate of passage on the products of hexanol dehydration, the amount of polymer depends on the amount of hexanol in the vapor. Although the concentration of hexene-1 is as large at 11.2 cc./hour as at 22 cc./hour, the amount of polymer has fallen sharply and there is no hexanol left unchanged. To confirm this, purified hexene-1

was passed over a thoroughly dry alumina. Although every other condition was the same, there was no polymer formed. Water vapor mixed with hexene-1 likewise had no effect. This points definitely to an intermediate in the dehydration reaction which can either polymerize or give olefin. Evaporation without drying shows that the amount of polymer is not changed by calcium chloride used in drying.

Formation of Ethers.—Ethers are known to be very unstable on dehydration catalysts at temperatures over 350°. The presence of an ether was found only in the products from the two most rapid passages of hexanol-1.

Distribution of Products.—Table III in section (A) shows that isomerization occurs as passage of alcohol becomes slower, the olefins having both greater availability of surface and more time on the surface. The straight chain olefin, hexene-1, seems to be the least stable at the temperature and passes to the various isomers tabulated. The other primary products are more stable, 2-methylpentene-2 also tending to disappear, however. This, also, is confirmed by passage of the pure isomer. The isomer 3-methylpentene-2-*trans* seems to be the most stable and the percentage of this increases as the rate decreases further. In the rapid dehydration of 2-ethylbutanol-1 (Table V), 3-methylpentene-2-*cis* appears as the major primary product. In the slower passage the same effects of isomerization appear. Again 2-methylpentene-2 and the straight chain hexene-1 disappear, as does the major product. Again, 3-methylpentene-2-*trans* appears as the major secondary product. In the dehydration of hexanol-1 on thoria, it is evident that both dehydration and isomerization occur much more rapidly than on alumina since, even at the fastest rate, there is no unchanged alcohol and the major products appear to be 3-methylpentene-2 and hexene-1. All the hexene-1 which has isomerized has gone to this 3-methylpentene-2 isomer and at the slower rate there is nothing in addition but polymer.

The three 7-carbon alcohols dehydrated show somewhat similar behavior. Heptene-3, the straight chain major product from heptanol-4, isomerizes to branched chain isomers which in turn give 3-methylhexene-2, while 2-methylhexene-2 goes directly to 3-methylhexene-2-*trans*, as is shown if the pure isomer is passed over alumina at various rates of speed. This is exactly analogous to hexanol-1. The other two 7-carbon

alcohols are different in that there is no straight chain primary product. The migration of a methyl group across a double bond toward the center of the molecule, which is the trend observed above, is prevented for either of two reasons. The length of the hydrocarbon chain is such that either the double bond is one carbon removed from the side chain or migration across the bond makes the side chain no more central. For both 2,4-dimethylpentanol-1 and 2,4-dimethylpentanol-3 the primary and secondary products are the same, the percentages changing with the amount of unchanged alcohol in the vapor.

Amount of Unchanged Alcohol.—From the results on alumina, it would seem that ease of dehydration is in the order:

Unchanged alcohol	2-Ethylbutanol-1 3 (primary)	> heptanol-4 5 (secondary)	> hexanol-1 20 (primary)	> 2,4-dimethylpentanol-1 20 (primary)	> 2,4-dimethylpentanol-3 40 (secondary)
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where the numbers are the amount of unchanged alcohol resulting from dehydration under comparable conditions.

While it has generally been found that the comparative rates of dehydration of alcohols are in the order primary, secondary, tertiary, this does not hold here.

Discussion.—From the results above, it is possible to derive a mechanism which affords a very convenient picture and proves itself useful in understanding dehydration of higher alcohols.

Mechanism.—Models for the above five alcohols were constructed to scale. To investigate what possible hydrogens could be involved with the hydroxyl group in dehydration, the models were contorted in every way possible. Those hydrogens which could actually touch the oxygen of the hydroxyl group were taken as possibilities. The hydrogens on carbons 3, 4 and 5 of heptanol-4 are inaccessible, but the hydrogens on 1, 2, 6, and 7, are all equally accessible. In hexanol-1, only the hydrogens on carbon 2 are inaccessible, those in fact which are usually supposed to be involved. In the case of 2,4-dimethylpentanol-1 only the hydrogens on carbon 2 are entirely inaccessible. Similarly with the others. Assuming that by elimination of water in these various possible ways, there is formed a sort of activated ring involving 3, 4, 5 or 6 carbons, as the case may be, a series of reactions may be predicted. The predictions are made in the following manner.

Each bond in the hypothetical ring is in turn

broken and a free radical intermediate indicated which satisfies its valence requirements internally, giving rise to an olefin. That such predictions are valid is shown by Egloff in his book "Reactions of Pure Hydrocarbons,"⁶ in which are enumerated the reactions of many cyclic hydrocarbons under various conditions, together with the products formed. While the reactions of such hydrocarbons at high temperatures may produce a bewildering array of products, such a method of prediction accounts for all in an orderly fashion. The formation of 5- and 6-membered rings in any quantity was early ruled out because catalytic pyrolysis of such substances produces characteristic products: comparatively high boiling homologs of cyclohexene in the case of the

6-membered ring; various gaseous hydrocarbons from the 5-membered ring. Both of these cases could have been detected easily but were found in none of the investigations under discussion.

The reason for this non-formation of the larger, more stable, rings may lie in the fact that the alcohols used were too short-chained to allow such rings to be formed except by the reaction of the hydroxyl group with primary hydrogens. The great difference in reactivity between primary and secondary hydrogens is well exemplified by the cyclization of the hydrocarbons on chromic oxide. *n*-Octane, when dehydrogenated on chromic oxide, does not give ethylbenzene as the major product as might be supposed, but according to Moldavski,⁷ gives 90% *o*-xylene and only 10% ethylbenzene. This together with the facts that octane is easier to aromatize than heptane and heptane than hexane means that two secondary hydrogens are removed more easily than one primary and one secondary, while one primary and one secondary are removed more easily than two primary hydrogens.

Forming the hypothetical 4- and 3-membered rings with the five alcohols discussed, certain conclusions result. It will be noted that 2,4-dimethylpentanol-3 does not allow the formation of a 4-membered ring, while 2,4-dimethylpentanol-1 allows two different 3-membered rings,

(6) G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1937, pp. 689-696.

(7) Moldavski and Kamusher, *Compt. rend. Acad. Sci. U. S. S. R.*, **1**, 355 (1936).

TABLE VI

Alcohol			Found	Hydrogens available				
	4-Carbon ring	3-Carbon ring		3-Ring		4-Ring		
				<i>p</i>	<i>s</i>	<i>p</i>	<i>s</i>	<i>t</i>
2-Ethylbutanol-1	$\begin{array}{c} \text{4-Carbon ring} \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CH}_2 \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{3-Carbon ring} \\ \text{CH}_3\text{CH}_2\text{CH}-\text{CHCH}_3 \\ \\ \text{CH}_2 \end{array}$						
	Hexene-2 3-Methylpentene-2	Hexene-3 3-Methylpentene-2 2-Methylpentene-2 2-Ethylbutene-1	Hexene-3 3-Methylpentene-2 2-Methylpentene-2 2-Ethylbutene-1	0	4	6	0	0
Heptanol-4	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2 \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2 \\ \\ \text{CH}_2 \end{array}$						
	Heptene-3 2-Ethylpentene-1 3-Methylhexene-2	Heptene-3 2-Ethylpentene-1 3-Methylhexene-2 2-Methylhexene-2	Heptene-3 2-Ethylpentene-1	0	4	6	0	0
Hexanol-1	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}-\text{CH}_2 \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2 \\ \\ \text{CH}_2 \end{array}$						
	Hexene-1 2-Ethylbutene-1 3-Methylpentene-2	Hexene-1 2-Methylpentene-1 2-Methylpentene-2	Hexene-1 2-Methylpentene-1 4-Methylpentene-2	0	2	0	2	0
2,4-Dimethylpentanol-1	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH} \\ \\ \text{CH}_3-\text{CHCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CHCH}-\text{CHCH}_3 \\ \\ \text{CH}_2 \end{array}$						
	2,2-Dimethylpentene-3 2,4-Dimethylpentene-2	2,4-Dimethylpentene-2 2,3-Dimethylpentene-3 4-Methylhexene-2	2,4-Dimethylpentene-2 2,3-Dimethylpentene-3 4-Methylhexene-2	3	2	0	0	1
2,4-Dimethylpentanol-3	Impossible	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}-\text{CHCH}_3 \\ \\ \text{CH}_2 \end{array}$		12	0	0	0	0
		4-Methylhexene-2 2,3-Dimethylpentene-3 2,4-Dimethylpentene-2	2-Methylhexene-3 2,3-Dimethylpentene-3 2,4-Dimethylpentene-2					

only one of which involves a secondary hydrogen, however. It also may be seen that, when only one carbon in the 3- or 4-membered ring is substituted, there are only two scissions which are different; when two carbons are substituted, there are three; if the two substitutions in the 4-membered ring are different, there are three. It will be remembered that if these rings were actually formed, the momentary presence of the oxygen and a hydrogen atom in the ring makes 3- and 4-membered rings into 5- and 6-membered rings, respectively.

While, in general, the products are similar from both types of ring, they are different enough in some cases to allow discrimination. The case of butanol-1 is a good example. The 4-membered ring allows formation only of butene-1 and butene-2. The 3-membered ring allows these two and also isobutene. This latter actually is found as one of the products of dehydration with iodine⁸

(8) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 40.

as catalyst. This also points to the comparative ease of removal of a secondary hydrogen as compared with a primary.

Table VI shows the assumed 3- and 4-membered rings and their products for the five alcohols discussed. Under the alcohol considered are shown the hypothetical 3- and 4-membered rings resulting from dehydration together with the products to be expected from them. The column "Found" gives the primary products actually found. The column "Hydrogens available" indicates the number of hydrogens bound to carbon available for the formation of each ring and the class of hydrogen: primary, secondary and tertiary.

The exact agreement of the primary products found and those predicted from the 3-membered ring is apparent. In hexanol-1, there is one product which is not accounted for in either way, but the 3-membered ring still gives the better agreement. The tabulation of the hydrogens available brings to light an important corollary.

Ease of Dehydration.—Under the discussion of the amount of unchanged alcohol, it was shown that the order of ease of dehydration was not that expected. In Table VII are listed the number of hydrogens available in the same order as found for ease of dehydration.

TABLE VII

Order found	2-Ethyl- butanol-1	Hep- tanol-4	Hex- anol-1	2,4-Di- methyl- pentanol-1	2,4-Di- methyl- pentanol-3
Order found	3	5	20	20	40
3 ring, s	4	4	2	2	0
3 ring, p	0	0	0	3	12
4 ring, s	0	0	2	0	0
4 ring, p	6	6	0	0	0

Table VII shows the exact correlation between the number of secondary hydrogens available for the formation of the 3-membered ring by the elimination of water, and the ease of dehydration. The most difficult to dehydrate is 2,4-dimethylpentanol-3, as is shown by the large amount of unchanged alcohol after a passage. There are no hydrogens available except primary ones, in a position for 3-ring formation. At the slower passage, dehydration involving the primary hydrogens takes place, and complete dehydration is made possible by the large number of such hydrogens available.

The products of dehydration as reported by other workers conform to this proposed mechanism of dehydration. To be noted in this connection is the paper by Cramer and Glasebrook⁹ which has appeared since the completion of the work in this paper. The dehydration of 2,2-dimethylbutanol-3 was found to give several products, namely, 2,2-dimethylbutene-3, 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, which are the products to be expected from the mechanism proposed above.

Conclusion

Evidence from three sources thus points to an activated intermediate stage having the configuration corresponding to a 3-membered ring. (1) The most strongly adsorbed substance in the system involved in the dehydration of an alcohol is the alcohol itself, by reason of its hydroxyl group. The formation of larger amounts of polymer when alcohol vapor is present in larger quantities indicates that the alcohol is flushing something from the surface. This substance, which produces olefins if allowed to remain on the surface, may be displaced as polymer by alcohol or, displaced as

active intermediate, may polymerize in the vapor phase. The presence of some polymer even at the slowest rates indicates that flushing by alcohol still exists on a portion of the catalyst, probably at the point of entrance to the catalyst. Pure olefin, with or without water vapor, gives no polymer whatsoever on alumina and thoria surfaces.

(2) Ease of dehydration is shown to be correlated with the number of secondary hydrogens on the carbon second from that having the hydroxyl group. The elimination of water in this position causes the formation of an activated intermediate stage with the configuration of a 3-membered ring, and this in turn breaks down.

(3) The products which are predicted from the reactions of pure hydrocarbons, assuming that this activated cyclopropane configuration is formed, correspond exactly with those found to be the actual primary products of dehydration. The effects of various catalysts on the products may be summarized as follows. Alumina tends to break all the bonds of the ring more or less indiscriminately and to give all the products possible. The proportions of the various products give the relative frequency of the various scissions. This fits with other observations that alumina opens bonds in those rings which are strained. Thoria is less general in its action and tends to break one bond selectively. This is illustrated in the alcohols studied by other workers. Chromium oxide introduces the further complication of dehydrogenation. The olefin gives aromatization instead of isomerization, but, in this case, poisoning of the catalyst prevents ready determination of the nature of the olefin products.

Summary

1. An apparatus and a procedure have been described which allow the separation of isomers resulting from the dehydration of an alcohol.
2. The effects of rate of passage and change of catalyst have been investigated and interpreted.
3. Ease of dehydration and structure of the alcohol have been correlated and ease shown to be dependent on the availability of secondary hydrogen atoms on the carbon beta to that with the hydroxyl group.
4. The conclusion is derived that there is an activated intermediate stage in dehydration that has the configuration corresponding to a 3-membered ring.

(9) Cramer and Glasebrook, *THIS JOURNAL*, **61**, 230 (1939).