Anal. Calcd. for $C_{24}H_{19}O_4N$: C, 74.77; H, 4.97. Found: C, 74.71; H, 4.88.

Reductions with aluminum isopropylate, palladized charcoal and with platinum proved unsatisfactory due mainly to the insolubility of the starting material and its primary reduction products. Reductions with sodium and alcohol apparently produced some toluene, but no pure material could be isolated from the reduction mixtures.

Acknowledgment.—The authors wish to express their gratitude to Messrs. Walter S. Ide, James E. Murphy and Samuel W. Blackman for the microanalyses here reported.

Summary

The primary and secondary amino alcohols of the 2-hydroxy and 2-methoxy-5-methylphenethyl and phenylisopropylamine series have been prepared.

TUCKAHOE 7, NEW YORK RECEIVED OCTOBER 10, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. I. Effect of Olefins upon the Isomerization of *n*-Butane in the Presence of Aluminum Halide–Hydrogen Halide Catalyst

BY HERMAN PINES AND R. C. WACKHER

The catalytic isomerization of butanes has been in the last few years, a subject of extensive study.[1]

The reactants and catalysts used in the experiments were not completely free of extraneous contaminants which are usually inherent in the reagents used or in the technique of operation.

Recently, Leighton and Heldman[2] and Heldman[3] have carried out the isomerization of *n*-butane under more careful experimental conditions, using high vacuum apparatus. These authors studied the kinetics of isomerization of butane and, in accordance with the observation of previous investigators,[1,4] found that aluminum bromide–hydrogen bromide is an effective isomerization catalyst.

An attempt to study the kinetics of butane isomerization was made by the present authors. The experiments were carried out in sealed tubes, using a high-vacuum technique for the purification of the reagents and for charging and discharging the products. This study had to be abandoned, however, because the results obtained were erratic owing to some impurities in *n*-butane which were not separated by fractional distillation. It was noticed that when apparently pure *n*-butane was further purified by passing it over aluminum chloride granules and then redistilled, no isomerization of this *n*-butane in the presence of aluminum bromide–hydrogen bromide took place.

It was found that in order to cause the isomerization of *n*-butane under relatively mild conditions it was necessary to add various compounds which are ordinarily present as impurities in the commercial butane isomerization processes. Olefins, air and water individually or collectively act as promoters for the isomerization of *n*-butane. These compounds may serve as a source of, or may cause the formation of, carbonium ions, which seem to be required to promote the isomerization of paraffins.

The present paper is limited to the effect of olefins upon the isomerization of *n*-paraffins; the effect of air and water upon this reaction will be discussed in succeeding papers of this series.

The addition of 0.01% of *n*-butenes to *n*-butane was sufficient to cause the isomerization of *n*-butane in the presence of aluminum chloride–hydrogen chloride at 100°. The effect of olefin concentration upon the isomerization of *n*-butane in the presence of aluminum bromide–hydrogen bromide and aluminum chloride–hydrogen chloride was studied. In the absence of olefins which may serve as a source of carbonium ions aluminum halide–hydrogen halide does not cause the isomerization of butane, unless the experimental conditions are conducive to the formation of decomposition products. This can be accomplished either by raising the temperature of reaction or by increasing the amount of hydrogen halide introduced. The data obtained in this investigation are not in agreement with the experimental results obtained by Heldman[3] who, most likely, did not purify the butane sufficiently to remove impurities which might act as a source of, or initiate the formation of, carbonium ions.[5]

Experimental

Materials.—Aluminum bromide was prepared by the action of bromine on aluminum foil in a stream of dry nitrogen. The product was partially purified by distillation in a stream of dry nitrogen and sealed into small, weighed ampoules according to the general method developed by A. Stock.[6] Final purification was carried out

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[1] (a) C. W. Montgomery, J. H. McAteer and N. W. Franke, THIS JOURNAL, **59**, 1768 (1937); (b) G. C. A. Schuit, H. Hoog and J. Verheus, *Rec. Trav. Chim.*, **59**, 793 (1940); (c) B. Moldavskii and T. Nizovkina, *J. Gen. Chem.*, *U. S. S. R.*, **9**, 1652 (1939); (d) C. W. Montgomery, J. H. McAteer and N. W. Franke, paper presented before the Petroleum Division of the American Chemical Society, April 3–7, 1939, Baltimore, Md.

[2] P. A. Leighton and J. D. Heldman, THIS JOURNAL, **65**, 2276 (1943).

[3] J. D. Heldman, *ibid.*, **66**, 1786 (1944).

[4] V. N. Ipatieff and H. Pines (to Universal Oil Products Co.), U. S. Patent 2,283,143 (May 12, 1942).

[5] For the discussion of the mechanism of isomerization see the paper by H. S. Bloch, H. Pines and L. Schmerling, THIS JOURNAL, **68**, 153 (1946).

[6] Alfred Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1934.

in vacuo as described under "Apparatus and Procedure."

Aluminum Chloride.—Givaudan aluminum chloride was first purified by melting at 180–190° under 100 atmospheres of hydrogen pressure in a glass liner placed in a steel bomb. It was found that after cooling, aluminum chloride sublimed to the top of the liner and formed large white crystals. This product was powdered and stored in air-tight containers until final purification *in vacuo* as described under "Apparatus and Procedure."

***n*-Butane.**—Chemically pure *n*-butane—obtained from Phillips Petroleum Co.—containing less than 0.2% isobutane and less than 0.01% olefins was further purified of its olefin content by passing it over granular aluminum chloride at room temperature and at atmospheric pressure at approximately a one-space velocity. Any evolved hydrogen chloride was removed by passing the exit gas through soda-lime and solid potassium hydroxide. This procedure resulted in a reduction of the olefin content to less than 0.0001%, determined by titrimetric analysis,[7] while the isobutane content was still less than 0.2%. The product was stored in a steel bomb until final purification in the high vacuum apparatus.

***n*-Butenes.**—Chemically pure *n*-butenes—obtained from Phillips Petroleum Co.—were used as received, except for final purification in the high-vacuum apparatus.

Hydrogen bromide, prepared by the reaction of bromine with tetralin, was freed of the last traces of water and bromine, upon introduction into a 5-liter glass storage vessel attached to the high-vacuum apparatus, by passing through naphthalene, two Dry Ice–acetone traps, and phosphorus pentoxide. The vapor pressure of the pure product was 465 mm. at −78.1°. Because of the slight reaction between hydrogen bromide and mercury that resulted from their standing in contact in the light, a final purification step in the vacuum apparatus was made before the hydrogen bromide was measured out for each experiment in the high-vacuum apparatus.

Hydrogen chloride was prepared by the reaction of sulfuric acid and sodium chloride. The product was purified by the method used for hydrogen bromide, with storage in a 5-liter glass vessel attached to the high-vacuum apparatus. The vapor pressure of the pure hydrogen chloride was 194 mm. at −106°.

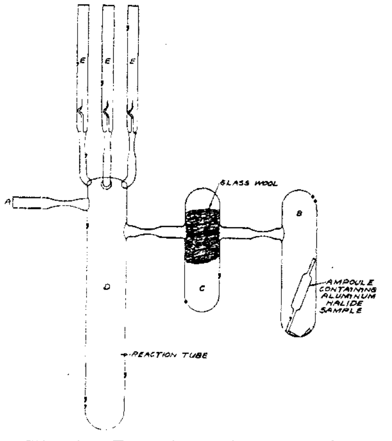

Fig. 1.—Reaction tube assembly.

Apparatus and Procedure.—The use of high-vacuum equipment was resorted to in this work in order that the reaction might be studied in the complete absence of extraneous substances. With the exception of the reaction tube and gas buret, the apparatus was essentially the same as that developed by A. Stock[6] and others. A sketch of the general features of this apparatus is shown in Fig. 3. The use of the Stock type of mercury seal valves ensured that the materials, from the time of their final purification until removal from the reaction tube, came in contact only with glass and mercury.

The reaction tube is shown in Fig. 1. The main tube D has a capacity of 95 cc. At the start of an experiment it was sealed at A to the end of a series of traps, or fractionation line of the vacuum apparatus, through a Stock valve, and then evacuated and flamed. Dry air was then admitted; the top of tube B was opened, and the aluminum halide was inserted. The top of the tube was resealed, and with the tube in Dry Ice–acetone, the whole was evacuated to less than a millimeter of mercury. Some hydrogen halide still remained dissolved in the aluminum halide under these conditions. Most of the hydrogen halide was removed, during the first stage of sublimation, from tube B to tube C by allowing the mercury in the Stock valve to rise only enough to permit the hydrogen halide to escape under approximately 5–10 mm. pressure. Tube B was then sealed off; the reaction tube was evacuated to approximately 0.1 mm. of mercury, and the aluminum halide was sublimed from tube C to the reaction tube D with the Stock valve closed. After sealing off tube C and with the Stock valve still closed, the aluminum halide could be accumulated in the bottom of the reaction tube by immersing the bottom in Dry Ice while flaming the upper portion. The reaction tube containing the pure white aluminum halide was finally evacuated to about 10^{-3} mm. of mercury previous to the addition of other substances.

The *n*-butane was next added to the reaction tube. *n*-Butane from the storage cylinder was condensed in a glass tube equipped with a ground joint and weighed, while stoppered, to the nearest 0.01 g. It was then transferred to the fractionation line and further purified by several alternate freezings in liquid nitrogen, by pumping and melting to eliminate dissolved air, and by distillation from Dry Ice–acetone to eliminate moisture. From the fractionation line, it was again distilled from Dry Ice–acetone temperatures to the reaction tube. Calculations indicated that the amount of water that might be present in the purified butane was of the order of 0.004 mole per cent., which, experiments showed, was not sufficient to influence the reaction.

n-Butenes were weighed out and added in the same

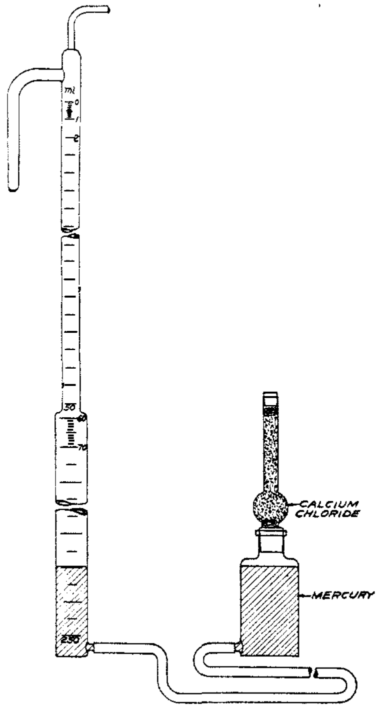

Fig. 2.—Gas buret for high vacuum apparatus.

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[7] "UOP Laboratory Test Methods for Petroleum and its Products," Universal Oil Products Co., Chicago, Ill. Method G-158-4.

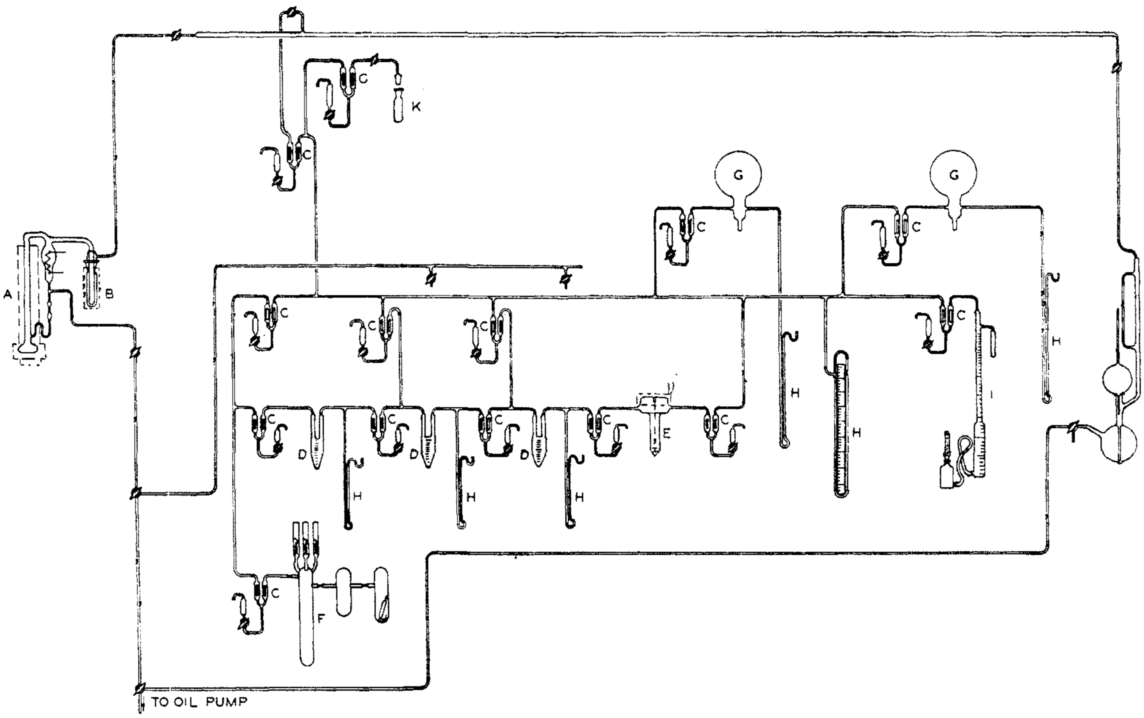

Fig. 3.—High vacuum isomerization apparatus: A, mercury vapor pump; B, Dry-Ice trap; C, stock valves; D, traps of fractionation line; E, still with electrical stirrer; F, reaction tube; G, storage vessels; H, manometers; I, gas buret; J, McLeod gage; K, weighed butane for introduction.

manner as the *n*-butane except in those cases involving quantities too small for accurate weighing. In the latter case, the *n*-butene was measured volumetrically after distillation from Dry Ice–acetone temperature in the calibrated gas buret shown in Fig. 2.

The hydrogen halides, drawn from their storage vessels, were further purified by several distillations from Dry-Ice temperature, measured volumetrically in the gas buret, and added by the usual technique to the reaction tube. The reaction tube was always kept at low temperatures until the final substance was added, and the tube was sealed off and transferred to the thermostat.

The thermostats employed were of two types. For use at the lower temperatures, a 50-gallon water thermostat was equipped with a rotating wheel on which the reaction tube could be attached. The temperature could be easily controlled to ±0.5° by use of tap water in a cooling coil and a calrod heater actuated by a simple mercury contact through an ionic relay.

The reactions at 100° and above were carried out in an Ipatieff-type bomb, into which the sealed glass reaction tube was placed; either butane was added or nitrogen pressure was applied as a compensating pressure medium. The bomb was immersed in an oil-bath heated by electric elements surrounding the bath. Temperatures were controlled within ±3–4° by a Minneapolis-Honeywell thermoregulator. The bomb or its contents were not agitated. Reaction times were considered from time of immersion in the oil-bath until withdrawal from the oil-bath. The bomb could be cooled with wet ice sufficiently to permit removal of the tube within fifteen minutes.

In all experiments, the reaction tubes, upon removal from the thermostats, were immediately put in Dry Ice, resealed to the vacuum line with one of the tubes E (Fig. 1), and the volatile contents were distilled off. Distillation was continued until no further material was obtained upon pumping at low pressures with the reaction tube at room temperature. When the products were removed from the apparatus they were passed through a potassium hydroxide solution and then analyzed by low-temperature distillation on a Podbielniak Super-cal fractionating column. In those cases containing large amounts of material boiling above butane range, the products were directly distilled upon removal from the reaction tube and the small quantities of hydrogen halide were determined, for correction purposes, in the lighter gases.

The apparatus and experiments were designed so that a sufficient quantity of butanes was available for analysis by low temperature distillation, inasmuch as it was believed that this procedure would give the most reliable analysis. The quantity of butane used was of the order of 7 g. Because the small ampoules of aluminum bromide contained slightly different amounts, the weights of *n*-butane and hydrogen bromide, which could be measured accurately, were varied so that a constant molar ratio was maintained. This also applied in the case of the aluminum chloride experiments although more constant amounts of the latter could be weighed out. In both cases, the weight of aluminum halide used was taken after subtracting the slight amount of residue in tube A after sublimation. No account was taken of the small amount of hydrogen halide pumped off as experience had shown this to be only 0.01–0.02 g.

Discussion of Results

Effect of Olefins upon the Isomerization of *n*-Butane Catalyzed by Aluminum Bromide–Hydrogen Bromide.—The effect of olefins upon the isomerization of *n*-butane is given in Table I.

TABLE I

EFFECT OF OLEFINS UPON THE ISOMERIZATION OF *n*-BUTANE CATALYZED BY ALUMINUM BROMIDE–HYDROGEN BROMIDE

Experiment no.	1	2	3	4
Mole % of *n*-butenes in butane	0	0.03	0.08	0.58
% of isobutane produced	0.2	2.1	19.3	65.6

Table II

Effect of Olefins upon the Isomerization of n-Butane Catalyzed by Aluminum Chloride–Hydrogen Chloride

Experiment no.	5	6	7	8	9	10	11	12	13	14	15
Mole % n-butenes in butane	0	0.013	0.05	0.09	0.28	2.49	5.22	9.44	17.4	25.8	34.5
Composition of the hydrocarbon layer after reaction, mole %											
Propane	0	0	0	0	0	0.2	6.5	11.1	5.5	1.6	1.6
n-Butane	99.9	87.6	87.0	82.8	72.3	44.9	36.1	32.2	32.0	41.0	48.3
Isobutane	<0.1	11.8	12.6	16.9	26.8	51.0	49.3	48.4	48.4	41.5	33.5
Pentanes +	0.1	0.6	0.4	0.3	0.9	3.9	8.1	8.3	14.1	15.9	16.5
Isobutane in the butane fraction, mole %	0	11.9	12.7	17.0	27.0	53.2	57.8	59.9	60.2	50.4	41.0
Wt. % of hydrocarbons combined with the catalyst based on wt. of olefins added	0	0	0	0	0	33	53	...	50	51	44

The experiments were carried out in sealed tubes of 25-cc. capacity and at a temperature of 25 ± 0.1°. The duration of each experiment was fifteen hours. The reaction tubes were charged with 6.54 to 7.34 g. of n-butane, 2.81 to 3.14 g. of aluminum bromide and 56.3 to 61.0 cc. at normal temperature and pressure of hydrogen bromide. The molar ratio of n-C_4H_{10}:$AlBr_3$:HBr was 100:9.3:2.2. The product was a clear homogeneous solution.

It was found that, at the studied conditions, chemically purified n-butane free from sources of carbonium ions did not isomerize to isobutane. The addition of three parts of n-butenes per ten thousand parts of butane was sufficient to start the isomerization, while in the presence of 5.8 parts of olefins per one thousand parts the yield of isobutane was very large. The amount of side products formed during the isomerization was less than 0.3%. In the case of added olefins, a small amount of an oily product insoluble in the hydrocarbons was formed.

Isomerization of n-Butane Catalyzed by Aluminum Chloride–Hydrogen Chloride.—Because aluminum chloride is a weaker catalyst than aluminum bromide, the experiments were carried out at 100° instead of at 25° as in the case of the latter. The degree of isomerization, which is a function of the amount of olefins present, is shown in Table II. The reaction was carried out in a 95-cc. capacity sealed tube at 100° during a period of twelve hours. The amount of reagents used in each experiment was: n-butane, 7.20 to 7.25 g.; aluminum chloride, 1.47 to 1.51 g.; hydrogen chloride, 0.265 to 0.270 g. The molar ratio of the reagents used was: 100:5.86:3.05. The concentration of n-butenes based on the charged butane varied from 0 to 34.5%.

Table II shows that when olefins are absent, isomerization of purified n-butane does not proceed under the above-described conditions. The addition of one part of olefins per ten thousand parts of n-butane is sufficient to cause the isomerization. When the concentration of olefins in n-butane increases to 2.49% or higher, appreciable amounts of side reactions occur, as evidenced by the formation of propane and higher boiling hydrocarbons, which might have resulted from the interaction of isobutane formed with the added olefin.[8,9] It will be noted that in the presence of added olefins, the catalyst forms a complex with hydrocarbons. The hydrocarbons which are combined with aluminum halide amount to from 33 to 53% by weight of the added olefins. When the concentration of added olefins is from 2.5 to 17.4%, based on butane present, the content of isobutane in the butane fraction reaches 80–90% of the equilibrium composition.[10]

Effect of Temperature.—The isomerization of n-butane proceeds also in the absence of added olefins if the temperature of reaction is high enough. This can be explained by the fact that aluminum chloride–hydrogen chloride, because it is a cracking catalyst,[11] may cause the formation of carbonium ions *in situ* to promote the isomerization of butane to isobutane. The degree of isomerization, however, is greater when olefins

Table III

The Effect of Temperature upon the Isomerization of n-Butane Catalyzed by Aluminum Chloride–Hydrogen Chloride

Experiment no.	5	6	17	8	18
Temperature, °C.	100	125	150	100	125
Charge, mole %					
$AlCl_3$	8.91	9.26	9.50	9.21	9.14
HCl	5.87	3.24	3.19	5.86	3.37
n-C_4H_{10}	100	100	100	100	100
n-C_4H_8	....	....	....	0.09	0.101
Analyses, %					
Propane	....	0	3.3	0	0
Isobutane	0.1	16.3	62.4	16.9	22.2
n-Butane	99.9	83.1	31.8	82.8	76.9
Pentanes	0.1	0.6	2.5	0.3	0.9
HCl recov. based on HCl charged	98	95	97	....	.....

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(8) V. N. Ipatieff, A. V. Grosse, H. Pines and V. I. Komarewsky, This Journal, **58**, 913 (1936).

(9) H. Pines, A. V. Grosse and V. N. Ipatieff, *ibid.*, **61**, 640 (1939).

(10) Herman Pines, B. Kvetinskas, L. S. Kassel and V. N. Ipatieff, *ibid.*, **67**, 631 (1945).

(11) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, 1941, Chap. 4, pp. 68–73.

are added. The experimental data are tabulated in Table III. The amounts of reagents used are of the same order as given in Table II.

Effect of Hydrogen Chloride.—The experimental data, summarized in Table IV, disclose that the isomerization of *n*-butane proceeds in the absence of added olefins if the concentration of hydrogen chloride is high enough. This is demonstrated in Experiments 5 and 19. If the temperature of isomerization is increased to 150°, it is possible to control the degree of isomerization by varying the amount of hydrogen chloride introduced. In the presence of a large excess of hydrogen chloride, cracking occurs, as is evidenced by the side reactions.

TABLE IV

EFFECT OF HYDROGEN CHLORIDE CONCENTRATION UPON THE ISOMERIZATION OF *n*-BUTANE

Experiment no.	5	19	20	21	22
Temperature, °C.	100	100	150	150	150
Charge, based on 100 moles of butane charged					
$AlCl_3$	8.91	8.84	9.18	9.50	9.05
HCl	5.87	17.6	0	3.19	7.12
n-C_4H_{10}	100	100	100	100	100
Analyses, mole %					
Propane	....	....	....	3.3	57.9
Isobutane	0.1	14.1	11.1	62.4	23.4
n-Butane	99.9	85.0	88.2	31.8	13.8
Pentanes +	0.1	0.9	0.7	2.5	4.4
HCl recovered, mole %	98	....	....	97	57

Although Expt. 20 was effected in the absence of hydrogen chloride, it is to be noted that the practical operations are always conducted in the presence of hydrogen chloride since this permits the use of lower temperatures and shorter contact time, with high yields of isobutane, and lengthens the active life of the catalyst.

Acknowledgment.—The authors wish to thank Professor V. N. Ipatieff for the encouragement given and interest shown during the progress of the work and Mr. Frank L. Hayes for the construction of the vacuum apparatus.

Summary

The isomerization of *n*-butane in the presence of aluminum chloride–hydrogen chloride and aluminum bromide–hydrogen bromide catalyst has been studied using high vacuum technique. It was found that under certain conditions paraffinic hydrocarbons do not undergo isomerization by means of aluminum halide–hydrogen halide catalyst unless olefins are present or probably formed *in situ*. It was assumed that the olefins function as a source of carbonium ion.

The addition of one part of olefin per ten thousand parts of *n*-butane is sufficient to promote isomerization. The effect of olefins, temperature, and concentration of hydrogen chloride upon the degree of isomerization is given.

RIVERSIDE, ILLINOIS RECEIVED APRIL 5, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. II.[1] Effect of Oxygen upon the Isomerization of *n*-Butane and *n*-Pentane in the Presence of Aluminum Bromide and Aluminum Chloride

BY HERMAN PINES AND R. C. WACKHER

In a previous paper[1] of this series it has been shown that under certain conditions aluminum halide–hydrogen halide does not catalyze the isomerization of butanes or pentanes unless traces of olefins are added as such or formed *in situ*. This study has been extended in order to investigate various other factors which might influence the isomerization of paraffinic hydrocarbons. Since air is one of the constituents which might be present as an impurity during the isomerization, the effect of small amounts of oxygen upon the course of isomerization of butanes and pentanes has been investigated. The catalyst used for this reaction was aluminum chloride or aluminum bromide. The former, being only slightly soluble in the hydrocarbons, was deposited in some experiments on charcoal in order to increase the active surface of the catalyst. The high vacuum technique, described previously, was used for the purification of the reagents and the charging and discharging of the reaction tube.

It was found that *n*-pentane does not undergo isomerization when agitated at 25° for 257 hours with aluminum chloride deposited on charcoal. In the presence of about 0.013 mole per cent. of oxygen, however, added as air, 93% of the pentane underwent both isomerization and disproportionation after ninty-six hours of agitation, resulting in the formation of isobutane, isopentane and higher boiling hydrocarbons. A similar result was obtained when 0.016 mole per cent. of oxygen, in the form of air, was added to *n*-pentane containing aluminum chloride–charcoal catalyst, and the mixture was exposed for twelve hours to sunlight without agitation. The effectiveness of oxygen as a promoter for isomerization is noted from Expt. 3 in Table I. The introduction of 0.007 mole per cent. oxygen was sufficient to isomerize *n*-pentane to isopentane using aluminum chloride as a catalyst. After nine hours of exposure to sunlight without agitation, about 40% of *n*-pentane underwent isomerization accompanied by disproportionation of the pentane

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[1] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595 (1946).