Some preliminary experiments were made to measure the equilibrium in the reaction

$$NO(g) + NO_2(g) + H_2O(g) \longrightarrow 2HNO_2(g)$$

without first determining the absorption coefficient of nitrous acid gas. An attempt to solve for the absorption coefficient and the equilibrium constant simultaneously was not successful. Results obtained indicated that considerably more work would have to be done in order to select the proper range of concentrations and that the absorption coefficient of nitrous acid gas would have to be measured directly. However, it is worth noting that the absorptions of the two compounds, nitrous and nitric acid, are sufficiently differentiated in the 1.4μ region to make feasible the measurements of the concentrations of each in the presence of the other.

This research was initiated under the supervision of Dr. Oliver R. Wulf and it is a pleasure to acknowledge his assistance in the earlier stages of this work. To Lola S. Deming the author is indebted for most of the calculations involved.

Summary

A direct determination was made of the equilibrium constant for the reaction $H_2O(g) + NO_2(g) + {}^1/_2O_2(g) \rightarrow 2HNO_3(g)$, using the infrared absorption at 1.4μ of nitric acid vapor as a method of analysis. Agreement with the calculations of Forsythe and Giauque is within limits of error. Transmission values of nitric acid and nitrous acid in the 1.4μ region are given.

BELTSVILLE, MD. RECEIVED AUGUST 9, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

The Catalytic Isomerization of Paraffin Hydrocarbons. I. Butanes[1]

BY PHILIP A. LEIGHTON AND JULIUS D. HELDMAN[2]

The catalyzed isomerization of *n*-butane has been a subject of considerable interest and application in recent years. The rearrangement is achieved at relatively low temperatures with the aid of a Friedel–Crafts type catalyst, usually aluminum chloride, plus a "promoter" such as hydrogen chloride.[3]

Montgomery, McAteer and Franke[4] have shown that aluminum bromide, which is soluble in the lower paraffin hydrocarbons, will catalyze the isomerization of liquid *n*-butane at room temperature.

Very little is known regarding the actual mechanism of the catalyzed isomerization. It warrants careful study from a fundamental standpoint because of its importance, because of its chemically clean-cut character, and because it offers a good starting point for the general understanding of halide catalysis.

The first possibility considered was that of a homogeneous gas phase isomerization. When aluminum chloride, hydrogen chloride and *n*-butane were mixed as vapors at 130° or above, no isomerization of the alkane could be observed, although extensive carbonization occurred in one experiment. Because of the difficulty of handling aluminum chloride as a vapor, boron trifluoride was substituted for it. In nine experiments, over widely varying temperatures (up to the threshold of pyrolysis of the butanes) and with substantial amounts of boron trifluoride and hydrogen chloride present, no detectable reaction occurred.

Kinetic studies of the liquid phase isomerization, which was briefly checked for homogeneity in Pyrex tubes, were then undertaken. It was found in earlier "qualitative" experiments that extremely small traces of water or hydrogen bromide exert a promoter effect on the catalyst. For quantitative rate experiments it was necessary to devise a technique for the introduction of pure, dry aluminum bromide and hydrogen bromide in known amounts into the reaction bomb tubes.

Experimental

All work was done on the vacuum bench with a pumping system capable of producing a vacuum of 10^{-5} mm. or better.

Hydrogen bromide was made either by the addition of water to phosphorus tribromide or the dehydration of a 48% solution of the acid by excess phosphorus pentoxide. The product in each case was purified by several distillations from dry-ice to liquid air with subsequent pumping off of the residue. There was apparently no difference between the products made by the two methods.

Aluminum Bromide.—The anhydrous catalyst was prepared by direct combination of the elements, using an excess of aluminum. The product was distilled three times in vacuum. It was a heavy crystalline mass with a faint pink tinge. In the qualitative experiments it was quickly transferred in air into the reaction tubes. After several runs, it became obvious that some hydrogen bromide was always produced by reaction of the catalyst with air moisture and that it was impossible to reproduce rate measurements with aluminum bromide handled in air. The further purification and handling of the catalyst is described under the procedure in quantitative experiments.

Butanes.—The hydrocarbons were the gift of the Shell Development Company. The stated analyses were as

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[3] For a review of work in this field, see Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, N. Y., 1942.

[4] Montgomery, McAteer and Franke, (a) THIS JOURNAL, **59**, 1768 (1937); (b) papers presented before the Petroleum Division of the American Chemical Society, Part I, Baltimore Meeting, April 3–7, 1939, p. M-1.

follows: *n*-butane, 99.8%, traces of air and *i*-butane, less than 0.01% olefins and 0.00(5)% sulfur; *i*-butane, 99.7%, traces of air, and *n*-butane, less than 0.01% olefins and 0.00(5)% of sulfur, *ca.* 0.1% propane. The products were distilled into glass storage bulbs containing phosphorus pentoxide, thoroughly degassed, and stored at dry-ice temperature.

The storage flasks led to two bulbs of known volume terminating in capillary leads. A known amount of butane could be transferred to a reaction vessel by filling one of the bulbs with hydrocarbon at −78° and distilling into the vessel. The size of the doses was directly determined by weighing the butanes so transferred. The results of the volume and weight calibration of the transfer pipets are

	P_1	P_2	P_1/P_2
Vol. of pipet to standard mark	2.142 ml.	0.919 m.	2.33
Wt. to fill pipet at −78°			
n-Butane	1.454 g.	0.620 g.	2.35
i-Butane	1.435 g.	0.615 g.	2.33

The constancy of the ratio of volume or weight in P_1 to P_2 serves as a check on the calibrations.

Qualitative Experiments.—Aluminum bromide was weighed by difference into a reaction vessel of about 3 ml. volume with an extension of 7-mm. tubing. The vessel was then sealed to the outer cone of a ground joint and attached to the vacuum line. It was never possible completely to eliminate water vapor from contacting the bromide.

The system was then evacuated and hydrogen bromide and butane distilled into the reaction tube, the hydrogen bromide being prepared as needed. The vessel was sealed off *in vacuo* while frozen in liquid air, warmed, shaken to dissolve the aluminum bromide, and then thermostated at the desired temperature.

In all runs, almost all the solid dissolved, but traces of a white pasty material were left on the cell wall. This was probably hydrated alumina or a basic aluminum bromide resulting from the reaction of the catalyst with traces of water vapor introduced in transferring. All solutions were clear and colorless.

After a run, the tube was immersed in liquid air and the order of the remaining pressure usually estimated by the type of glow produced by a Tesla coil. In all runs tested, the *maximum* residual pressure was of the order of 10^{-1} to 10^{-2} mm.

While the vessel was still frozen, the extension was broken open and sealed to a train of potassium hydroxide pellets and phosphorus pentoxide. The system was evacuated and the reaction products distilled back and forth through the potassium hydroxide and phosphorus pentoxide. The resulting clear hydrocarbon was then analyzed as later described.

Quantitative Experiments.—For the rigid control of variables, it was necessary to develop methods for complete exclusion of extraneous moisture, for handling anhydrous aluminum bromide in a vacuum, and for transferring pure hydrogen bromide quantitatively. Fifty reaction vessels were sealed to a manifold; each vessel was constricted close to the seal. The manifold led to a 25-ml. bulb which was connected to a glass-nosed enclosed iron core for breaking a sealed-off capillary inlet to the vacuum line.

The aluminum bromide previously prepared was placed in a bulb, sealed in series with two other bulbs, the last of which was joined to the manifold bulb. The system was attached to the vacuum line *via* a long side-arm and thoroughly pumped. The reaction tubes and glass leads were then flamed to the highest temperature feasible and pumped for six hours. The side-arm was sealed off.

The catalyst was distilled from bulb to bulb, discarding generous fractions in each container, which was then sealed off and drawn away. The final product in the last bulb, approximately 25 g., was a perfectly colorless-to-white, highly refracting rhombohedral crystalline mass. After transfer of all the bromide needed into the reaction tubes, a small sample was distilled into some connecting tubing and sealed *in vacuo*. The melting point of this sample was 97.5–97.6°.[5]

By manipulation of two Tirrill burners, the catalyst was distilled into the reaction tubes in amounts varying from about 10 to 300 mg. After the distillation was completed, the capillary seal was broken and the tubes pumped as a further precaution. No gas could be detected.

The amount of hydrogen bromide added was controlled by using two "dosers." The gas was allowed to fill these at known pressure, that of hydrogen bromide at dry-ice temperature (at which the hydrogen bromide was stored as a liquid), and transferred to a reaction vessel by distillation into liquid air. The size of the doses could be calculated from the known volume of the dosers and the perfect gas equation, and was checked by actual titration. The amount of hydrogen bromide used could be varied by expansion of the smaller volume into the larger, taking the latter, etc.

Runs were made as in the qualitative experiments. As a precaution against explosion, all tubes were wrapped in cheesecloth and copper gauze; but even though the pressure in some cases was calculated to be over 15 atmospheres in a tube, no bursting ever resulted.

After a run, following distillation of the butane into the analytical apparatus, the weight of the aluminum bromide was obtained by difference after severing the tube from the distillation train. The aluminum bromide always remained as a fine white powder. Its melting point, as taken in two experiments, was the same as that of the pure starting catalyst; after melting, it recrystallized in lustrous rhombohedra as before.

Tubes were usually tested with the Tesla coil after reaction and freezing out in liquid air. In a few instances, the pressure in the vessel was too low to give a glow until it was warmed slightly. The estimated residual pressure was never greater than 10^{-1} to 10^{-2} mm.

Analysis.—Most of the analyses were made on a dew pressure apparatus essentially like that of Savelli, Seyfried and Filbert.[6] The accuracy was always 1% or better of the total sample, and for low percentage conversions was about 0.5%. However, in some of the analyses reported in Table II, an extra significant figure has been kept, merely for use in calculating derived quantities. The vapor pressures at 0° of the pure *n*- and *i*-butane used were found to be 768 and 1193 mm., respectively.

In some of the runs, a differential density float of the type described by Randall and Longtin[7] but blown with a bulb at the top to lessen sticking of the bobble to the container wall, was used for analysis. The method consists in measuring the temperature at which an unknown sample has the density of the float, which was calibrated with pure *n*-butane, using the density data of Coffin and Maass.[8] In the temperature range employed it was found by analyzing known samples that the composition and float point of butane mixtures were linearly related.

Both the dew pressure and float point analyses were sensitive to traces of hydrogen bromide remaining in the butanes. In suspect cases, analyses were repeated until consistent results were obtained.

In a few cases, the equilibrium vapor pressure of the product at 0° was taken. The composition of the liquid could be calculated using Raoult's law, which the butanes obey accurately at 0°.[6,9] Analyses by all three methods on the same sample agreed within experimental error.

It was always assumed that only butanes were present

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(5) Melting points recorded range from 90 to 97.5°; see Winter and Cramer (*Ind. Eng. Chem.*, **32**, 856 (1940)) for a review of the literature. Richards and Krepelka (THIS JOURNAL, **42**, 2221 (1920)) used a similar procedure for purifying aluminum bromide in determining the atomic weight of aluminum, but they did not report any physical constants for the pure halide.

(6) Savelli, Seyfried and Filbert, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 868 (1941).

(7) Randall and Longtin, *ibid.*, **11**, 44 (1939).

(8) Coffin and Maass, THIS JOURNAL, **50**, 1427 (1928).

(9) Hachsmuth, *Ind. Eng. Chem.*, **24**, 82 (1932).

in a product mixture. If reactions to produce lighter or heavier hydrocarbons or unsaturates occurred, agreement in analyses by three different methods would be exremely unlikely. Furthermore, production of hydrogen and methane would be expected. From the glow given by the Tesla coil and the vapor volume of the reaction vessels, it was calculated that the amount of permanent gas formation was always <0.01%. Montgomery, McAteer and Franke[4] detected a small amount of methane and ethane, but this did not increase with time. In the present work not even traces of these hydrocarbons were indicated.

The slightest traces of unsaturated hydrocarbons will give rise to a yellow color and usually a lower layer in the presence of aluminum bromide. The sensitivity of this test precludes all possibility of the presence of unsaturates either in the original butane samples or in the reaction products.

The only other side reaction possible, that of the disporportionation of two butane molecules to give propane and a pentane (or ethane and a hexane) appears extremely unlikely in view of the internal agreement among various analyses based on the assumption of the two-component system. Also, other investigators[4,10] have found no propane below 80° and only negligible amounts up to 100°.[11]

Results

In Table I are included the results of experiments performed with aluminum bromide transferred in air into reaction tubes. Rate experiments are summarized in Table II. The volume used was derived from the moles of butane added, using the specific volume data of Sage, Webster, and Lacey[12] for *n*-butane and Sage and Lacey[13] for the *iso* compound. Three assumptions have been made, namely: (1) that the amount of butane in the vapor phase was negligible compared with that in the liquid, (2) that there was no volume change on addition of aluminum bromide and hydrogen bromide, and (3) that the volume did not change appreciably during a run. None of these assumptions introduces a serious approximation, the effect of (3) being minimized by taking initial rates in almost every case.

The columns headed $d(i)/dt$, (moles) (cc. × sec.)$^{-1}$ and $d(n\text{-})/dt$, etc., give the average rate of the forward and reverse reactions, respectively, represented by the equation

$$n\text{-}C_4H_{10}(\text{liq.}) = i\text{-}C_4H_{10}(\text{liq.}) \qquad (1)$$

in usual units of kinetic work.

The last column gives the average rate divided by the concentration of $HAlBr_4$ and butane, both expressed in moles/cc. The significance of this column is discussed below. The concentration of $HAlBr_4$ was calculated from the stoichiometry corresponding to the equation

$$Al_2Br_6 + 2HBr = 2HAlBr_4 \qquad (2)$$

assuming that the reaction has an equilibrium constant so large that the reactant added in limiting quantity exists essentially completely as $HAlBr_4$ at equilibrium. Reasons for this hypothesis are given in the discussion.

TABLE I

Experiments with Exposed Aluminum Bromide

Initial hydrocarbon charge, 2.51 × 10^{-2} moles *n*-butane

Expt. no. (arbitrary)	Time, days	Temp., °C.	Al_2Br_6, moles × 10^4	HBr, moles × 10^4	Analyses, % i-C_4H_{10} (from dew pressure)
1	99	0–4	14.3	23	67.7
2	99	0–4	7.96	15	65.3
3	66	25 ± 3	8.25	0	41.8^{a} 43.5^{b} 45^{c}
4	61	25 ± 3	10.01	16	53.8 54.6^{a} 56.2^{b} 54^{c}
5	67	25 ± 3	9.48	0	54.8^{b}
6	110	25.00	3.43	21	60.3
7	110	25.00	2.61	0	54.9 55.0^{d}
8	110	25.00	8.53	0^{e}	67.2
9	9	50.0	1.56	21	41.2
10	9	50.0	1.52	10	47.2
11	7	50.0	2.85	10	60.8
12	80 min.	56.0	0.81	10	5.5
13	3	65.0	1.91	16	47.4 46.8^{d}
14	3	65.0	2.53	21	58.7
15	3	65.0	2.03	0	42.4
16	9	65.0	1.43	14	62.2
17	93	25 ± 3	3.19^{f}	0	0
18	93	25 ± 3	5.39^{f}	29	24.0
19	93	25 ± 3	1.46^{f}	30^{g}	0

[a] Analysis from float point measurement. [b] From vapor pressure at 0°. [c] On basis of vapor pressure at CO_2 snow temperature. [d] Low temperature micro fractionation. [e] Tube frozen in liquid air after transfer of aluminum bromide and before evacuation. [f] Al_2Cl_6. [g] Moles of H_2O added directly to reaction tube and frozen while pumping.

Discussion

A survey of Table I reveals that anhydrous aluminum bromide, without conscious addition of a promoter, is an effective catalyst for the isomerization of *n*-butane if it is exposed to the atmosphere. Qualitatively, addition of hydrogen bromide does increase the rate of isomerization somewhat, the magnitude of the promoter effect being obscured by the long duration of the experiments.

In many cases, notably experiments 8, 11 and 16 (and possibly 1 and 2), equilibrium has been approached, but until more results are obtained with various starting mixtures of *n*- and *i*-butane, no further comments are justified. Such equilibrium experiments are now in progress.

Aluminum chloride, which is only very slightly soluble in *n*-butane, was employed as catalyst in the last three experiments reported in Table I. The chloride alone, even after exposure to the atmosphere, has no effect on butane (experiment 17). Addition of hydrogen bromide results in reaction, but the rate of isomerization with aluminum chloride is slower than that with the bromide, as shown by experiment 18. The same conclusion was reached by Glasebrook, Phillips and Lovell[14] with *n*-pentane. The slower rate may be due to the low solubility of aluminum chloride in paraffin hydrocarbons.

That the catalytic effect in these experiments

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(10) Schuit, Hoog and Verheus, *Rec. trav. chim.*, **59**, 793 (1940).

(11) After the original manuscript was submitted, the products of two long-duration experiments, one at 25 and one at 65°, were analyzed by distillation through a micro fractionating column. Nothing boiling below *i*-butane could be detected in either case, and the analyses were in excellent agreement with previous dew pressure determinations on the same samples (see Table I).

(12) Sage, Webster and Lacey, *ibid.*, **29**, 1188 (1937).

(13) Sage and Lacey, *ibid.*, **30**, 673 (1938).

(14) Glasebrook, Phillips and Lovell, THIS JOURNAL, **58**, 1944 (1936).

TABLE II

RATE EXPERIMENTS

Expt.	Time, sec. × 10^{-3}	Temp., °C.	n-C_4H_{10}, moles × 10^4	Al_2Br_6, moles × 10^4	HBr, moles × 10^4	Analyses, % i-C_4H_{10}	$d(i\text{-})/dt$, (moles)(cc. × sec.)$^{-1}$ × 10^7	$\frac{d(i\text{-})/dt}{(HAlBr_4)(n\text{-}C_4H_{10})}$ (moles/cc.)$^{-1}$ sec.$^{-1}$
					A. n-Butane			
20	<0.90	Room	107	7.38	1.93	0		
21	71 da.	Room	251	0	15.5	0		
22	3 da.	65.0	251	0	36.1	0		
23	4.80	65.0	224	0.17	0	0		
24	4.80	65.0	224	1.74	0	0		
25	4.80	65.0	224	4.53	0	0		
26	14.4	53±0.4	251	3.0	1.93	16.9[a]	1.10	0.148
27	7.50	53±0.4	251	3.0	1.93	13.2	1.65	.2222
28	14.4	53.0	251	1.05	1.93	19.4	1.26	.170
29	4.80	65.0	251	4.05	0.241	1.2	0.23	.29
30	4.80	65.0	251	1.93	.504	2.5	.47	.28
31	4.80	65.0	251	4.78	.682	3.4_4	.65	.29
32	4.80	65.0	251	6.85	1.36	8.48	1.60	.357
33	4.80	65.0	251	1.40	1.93	9.19	1.74	.273
34	4.80	65.0	251	2.06	1.93	7.45	1.41	.222
35	4.80	65.0	251	1.67	1.93	9.69	1.83	.288
36[b]	4.80	65.0	251	1.80	1.93	9.19	1.74	.273
37	4.80	65.0	107	5.65	3.86	28.0	(5.28)	(.222)
38	4.80	65.0	251	0.191	1.93	1.8	0.34	.27
39	4.80	65.0	251	.493	1.93	5.0_2	0.95_7	.30
40	3.40	78.5	251	2.12	1.93	9.45	2.44	.410
41[c]	12 hr.	85	251	1.22	0	0[d]		
42[c]	12 hr.	85	251	4.39	0	0[e]		
					B. i-Butane			
			i-C_4H_{10}			% n-C_4H_{10}	$d(n\text{-})/dt$	$\frac{d(n\text{-})/dt}{(HAlBr_4)(i\text{-}C_4H_{10})}$
43	<0.90	Room	247	0.920	1.93	0		
44	4.80	65.0	220	3.92	0	0		
45	4.80	65.0	220	4.53	0	0		
46	4.80	65.0	247	2.44	.504	1.5	0.27	0.18
47	4.80	65.0	247	2.38	.682	2.2	.39	.19
48	4.80	65.0	106	1.93	.682	3.6	.64	.14
49	4.80	65.0	247	5.30	1.93	4.5[a]	.77	.15
50	12.6	65.0	247	0.276	1.93	3.2	.22	.13

[a] Analysis by float point measurement. [b] Glass beads added to give surface–volume ratio approximately twenty times that in other tubes. [c] Experiments performed by one of us (JDH), to be published in THIS JOURNAL. [d] By float point and aniline point measurements. [e] From dew pressure and float point.

was not due to the presence of alumina or a hydrated form alone is shown by experiment 19, in which water in great excess over that required to give aluminum oxide or aluminum hydroxide completely was added to aluminum chloride. There was no isomerization, whereas aluminum chloride plus hydrogen bromide produced reaction.

Experiments 23, 24, 25, 44 and 45, and (under more severe conditions) 41 and 42 demonstrate that completely anhydrous aluminum bromide does not act as a catalyst for the isomerization of butanes whereas addition of hydrogen bromide, as shown by other experiments in Table II, gives rise to a conveniently measurable rate of isomerization. Hydrogen bromide alone has no action on n-butane, as would be expected (Experiments 21 and 22).

Using 5 mole per cent. of aluminum bromide (calculated as the monomer) as catalyst, Montgomery, McAteer and Franke[4] observed a slow isomerization of the butanes at room temperature. Our results in Table I are qualitatively in agreement with theirs, although the equilibrium data they reported, 78–82%[4a] and 75–80%[4b] of the *iso* form in the liquid phase at 27° after two months, correspond to a greater conversion than we have been able to achieve with n-butane.

Montgomery, McAteer and Franke also carried out initial rate determinations on n-butane isomerization at 30° in Pyrex bomb tubes,[4b] obtaining a rate constant varying from 0.030 to 0.043 mole per cent. of i-butane per hour per mole per cent. aluminum bromide. No hydrogen bromide or water was added. Traces of these substances were found to increase the rate considerably, and the reaction tubes and catalyst were evacuated before introduction of butane. We have pumped for hours aluminum bromide that has been in contact with the air for less than a minute, and it is still an active catalyst; but rigid exclusion of moisture does give rise to an inactive substance with respect to butane isomerization. The phenomenon is probably due to the formation of a basic aluminum bromide with an extremely low dissociation pressure, which, upon being dissolved, can react further to produce hydrogen bromide. This hypothesis is in line with the observation of small amounts of a white, pasty solid in all qualitative experiments. The apparent reproducibility of the rates reported by Montgomery, McAteer and Franke may be due to the constancy of their method of transfer of aluminum bromide.

For the experiments at 65°, the last column in Table II, $\mathrm{d}(i \text{ or } n\text{-})/\mathrm{d}t/(\mathrm{HAlBr_4})(n\text{- or } i\text{-}\mathrm{C_4H_{10}})$, is a constant within the limits of error for each isomer. The $\mathrm{HAlBr_4}$ concentration is calculated assuming a large equilibrium constant for reaction (2). Since the butane concentration is a constant at any given temperature for mole fractions approaching unity (its inclusion in the denominator is discussed later), the initial rate of isomerization of either *n*- or *i*-butane must be first order with respect to the postulated $\mathrm{HAlBr_4}$.

If the equilibrium constant for reaction (2) were small or intermediate in magnitude, the rate would involve a term $(\mathrm{HBr})(\mathrm{Al_2Br_6})^{1/2}$. The rate "constant" shows pronounced drifts when the rates are plotted against the above function.[15]

Since only initial rates were taken (the experimental errors being such that the average rate for 10% conversion is indistinguishable from an initial rate for 1% conversion), the order of reaction with respect to butane is an open question. Only in one experiment, 37, did reaction proceed far enough to attempt to obtain the order with respect to *n*-butane, but no conclusion can be drawn from it. We can therefore write only

$$\mathrm{d}(i\text{-})/\mathrm{d}t = k_1(\mathrm{HAlBr_4})f[(n\text{-}\mathrm{C_4H_{10}})] \quad (3)$$

and

$$\mathrm{d}(n\text{-})/\mathrm{d}t = k_2(\mathrm{HAlBr_4})f[(i\text{-}\mathrm{C_4H_{10}})] \quad (4)$$

However, the simplest mechanism to fit expressions (3) and (4) gives a first order dependence of rate on butane concentration, and involves only a collision between $\mathrm{HAlBr_4}$ and the hydrocarbon. The present work gives no insight into the mechanism of the rearrangement of the butanes upon collision with the catalyst. Furthermore, it should be borne in mind that hydrogen bromide is only one of many substances that are effective promoters for halide-catalyzed isomerizations,[16] and that the mechanism may vary with different catalysts.

If we assume for the moment that the rate-determining step in the isomerization is the collision of $\mathrm{HAlBr_4}$ and a butane molecule, we may write that $f[(\mathrm{C_4H_{10}})] = (\mathrm{C_4H_{10}})$, and

$$\mathrm{d}(i\text{-})/\mathrm{d}t = k_1(\mathrm{HAlBr_4})(n\text{-}\mathrm{C_4H_{10}}) \quad (5)$$

$$\mathrm{d}(n\text{-})/\mathrm{d}t = k_2(\mathrm{HAlBr_4})(i\text{-}\mathrm{C_4H_{10}}) \quad (6)$$

From Table II, the average results at 65° are $k_1 = 0.28_2$ and $k_2 = 0.15_8$. Keeping in mind the assumption involved, we have $K_{(1)} = k_1/k_2$, at 65°, $K_{(1)} = 1.7_8$. The results in the literature are too widely divergent for a critical comparison.[17] We have performed an experiment starting with 69.8% *i*-butane. After eighteen days at 50 and one at 65°, the product analyzed 63.7% *i*-butane. This result, coupled with that of experiment 16, serves to narrow the value of the equilibrium constant down to within the approximate limits of 1.65 and 1.75, which is in good agreement with the ratio of the rate constants calculated from the assumed rate law.

The Arrhenius activation energy, ΔE, for the forward reaction is 9.2 kcal. per mole, the probable error being of the order of 0.5–1.0 kcal. From the relation

$$k_1 = A\mathrm{e}^{-\Delta E/RT} \quad (7)$$

and the value of k_1 at 65°, we find $A = 10^{5.4}$ $(\mathrm{mole/cc.})^{-1}$ $\mathrm{sec.}^{-1}$, which is to be compared with the frequency factor of 10^{13}–10^{14} usually obtained in second order reactions. The abnormally low value is probably to be attributed to a steric effect encountered in the catalyst–hydrocarbon collision.

Summary

The homogeneous liquid phase isomerization of *n*-butane was studied, using special precautions to insure control of conditions. Aluminum bromide and hydrogen bromide mixtures were employed as catalyst. The reaction is chemically clean-cut.

Completely anhydrous aluminum bromide has no action on *n*- or *i*-butane, but traces of moisture are sufficient to engender isomerization in the presence of the halide. From the rate studies it is concluded that $\mathrm{HAlBr_4}$ is the true catalytic agent in this case.

The apparent activation energy for the isomerization of *n*-butane is 9.2 kcal./mole. From the rate constant and activation energy, a temperature-independent rate factor of $10^{5.4}$ is calculated. This is very much smaller than that predicted from collision rate considerations.

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[15] It is conceivable that the first step in the reaction is formation of a complex between butane and aluminum bromide, followed by collision with HBr. Rate expressions derived from such mechanisms involve the above term, which is not proportional to the observed rate.

[16] Other promoters used are hydrogen chloride, alkyl halides, Gustavson's compounds, etc.; see ref. 2. Preliminary experiments have revealed that *n*-butyl bromide is at least as effective a promoter as hydrogen bromide.

[17] Schuit, Hoog and Verheus[10] obtained an average $K = 2.03$ at 60°, which is good agreement considering the effect on K of small errors in analysis. Moldavskiĭ and Nizovkina (*Compt. rend. acad. sci. U. R. S. S.*, **23**, 919 (1939); *C. A.*, **34**, 931 (1940)) obtained either 2.8 or 3.8 at 70°; see Reference 2, pp. 30, 227.