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).

to isobutane and hexanes. These results are given in Table I.

TABLE I

EFFECT OF OXYGEN UPON THE ISOMERIZATION OF n-PENTANE USING ALUMINUM CHLORIDE AS A CATALYST AT 25°

Experiment	1	2	3	4
Reaction time				
Dark, hours	257	96	0	0
Sunlight, hours	0	0	9^b	12^b
Agitation	Yes	Yes	No	No
Reagents used: moles per 100 moles of n-pentane				
$AlCl_3$	23.0^a	23.0^a	24.3^a	22.5
O_2 (as air)	0	0.013	0.007	0.016
Analyses, mole %				
Isobutane	....	48.3	11.5	40.9
n-Butane		0.5	0	1.7
Isopentane	1.0	27.5	25.3	32.3
n-Pentane	98.5	7.3	59.5	11.8
Hexanes	....	16.4	3.7	13.3

[a] The reaction tubes contained 123 parts by weight of activated coconut charcoal, 10–12 mesh, per 100 parts of aluminum chloride. [b] Temperature, 25° (±2°).

Similar results were observed when n-butane, which is more resistant than n-pentane is toward isomerization, was treated with aluminum chloride–charcoal catalyst in the presence of air containing approximately 0.01 to 0.02 mole of oxygen based on 100 moles of butane introduced. It is interesting to note that after 141 hours of agitation at 25° in the dark, about 39% of isobutane was formed. The experimental results are given in Table II.

TABLE II

EFFECT OF OXYGEN UPON THE ISOMERIZATION OF n-BUTANE USING ALUMINUM CHLORIDE AS A CATALYST AT 25°

Experiment	5	6	7
Reaction time			
Dark, hours	121	141	0
Sunlight, hours	0	0	16^b
Agitation	Yes	Yes	No
Reagents used: moles per 100 moles of n-butane			
$AlCl_3$[a]	16.07	17.40	17.05
O_2 (as air)	0.0168	0.0196	0.0112
Analyses, mole %			
Isobutane	29.9	38.6	7.2
n-Butane	70.1	59.0	91.3
Pentanes and higher	0	2.1	2.1

[a] The reaction tubes contained 123 parts by weight of activated coconut charcoal, 10-12 mesh, per 100 parts of aluminum chloride. [b] Temperature, 25° (±2°).

Since aluminum chloride is only sparingly soluble in hydrocarbons, it was decided to investigate the effect of oxygen upon the isomerization of n-butane using aluminum bromide as a catalyst. At the concentration adopted this catalyst was completely soluble in n-butane at 25°. The results of these experiments with aluminum bromide can be compared with more reliability than can those obtained with aluminum chloride, since the surface and particle size of the catalyst had no effect upon the rate of the reaction. These results are given in Table III. As in the case of aluminum chloride, the reaction was carried out in sealed glass tubes at 25°. It was found that in the absence of air, aluminum bromide did not cause the isomerization of n-butane even when the solution was exposed to sunlight for eight hours and then allowed to stand in the dark for an additional five hundred hours. The isomerization proceeded, however, when 0.06 mole of air per 100 moles of n-butane was added and the mixture was kept in the dark for 192 hours; the yield of isobutane produced was 7.5%. Nitrogen alone will not cause the isomerization of n-butane to isobutane under similar conditions.

The degree of isomerization is a function of the amount of oxygen added (Expts. 11 and 12) and of the length of time the material is exposed to sunlight (Expts. 12, 13, and 14). After thirty-one hours of exposure and in the presence of 5 moles of oxygen, as air, per 10,000 moles of butane, 63.6% of isobutane was formed. This represents 80% of the equilibrium value at 25°.[2]

In the presence of sunlight the rate of isomerization increases. The sunlight probably exercises a photochemical action upon the halogenation of alkanes by the halogen liberated from the oxidation of aluminum halides.

It is believed that the addition of oxygen results in the formation of a new catalyst composition,[3] presumably an oxyaluminum halide–hydrocarbon complex as will be described in detail under the section, "Mechanism of Isomerization." The added oxygen, although in small amounts, must be introduced extraneously since the paraffinic fractions normally subjected to isomerization do not contain oxygen. Although the catalyst has good activity, it will be necessary to introduce, either continuously or intermittently, controlled amounts of oxygen in order to maintain the desired activity of the catalyst.

Effect of Aluminum Bromide Admixed with Lower Layer Complex upon Isomerization.—It was noticed that a solution of aluminum bromide in n-butane became immediately cloudy when exposed to sunlight in the presence of a small amount of air; after a while the solution became clear and a lower layer deposited. After six hours of exposure to sunlight, 14% of the n-butane charged was converted to isobutane. A similar type of a lower layer is formed also when the reactants are not exposed to sunlight; but the rate of its formation is much slower. In order to investigate the isomerizing properties of the lower layer in the absence of any freshly added air, two sets of experiments were made in which n-butane

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[2] H. Pines, B. Kvetinskas, L. S. Kassel and V. N. Ipatieff, THIS JOURNAL, **67**, 631 (1945).

[3] H. Pines and R. C. Wackher (to Universal Oil Products Company) U. S. Patent 2,341,286 (February 8, 1944).

Table III

Effect of Oxygen upon the Isomerization of *n*-Butane in the Presence of Aluminum Bromide at 25°

Experiment no.	8	9	10	11	12	13	14
Reaction time							
Dark, hours	500	215	192	22	17	139	102
Sunlight, hours	8[a]	...	...	2[a]	4[a]	8[a]	31[a]
Charge							
$AlBr_3$, mole/100 mole n-C_4H_{10}	10.0	12.7	11.0	11.8	11.0	11.1	9.44
Gases added	0	$N_2:O_2$-1	Air	$N_2:O_2$-1	Air	Air	Air
O_2, mole/100 mole of n-C_4H_{10}	0	0.226	0.06	0.157	0.06	0.044	0.055
Analyses, mole %							
i-Butane	0	8.7	7.5	15.7	9.5	39.7	63.6
n-Butane	99.5	90.7	91.8	84.3	90.1	59.0	35.0
Pentanes and higher	0.5	0.6	0.7	0	0.4	1.3	1.4

[a] Temperature, 25° (±2°).

was subjected to treatment with: (a) aluminum bromide–lower layer complex, (b) aluminum bromide, substantially freed from lower layer.

The experimental technique consisted in converting part of the aluminum bromide into a lower layer complex as described above (experimental data are given in Expt. 15, Table IV). After removal of the non-condensable gases and butanes, the reaction vessel was recharged with fresh *n*-butane and sealed. After allowing the reactants to come to room temperature, a portion of the clear *n*-butane–aluminum bromide solution was poured into the side tube, cooled and sealed off. The original reaction vessel contained most of the lower layer and part of the aluminum bromide. It was found that *n*-butane treated with the lower layer and aluminum bromide isomerized to the extent of 64.5 mole per cent. (Expt. 17) while the homogeneous solution which contained aluminum bromide and perhaps some of the lower layer, isomerized only to the extent of 14.8% (Expt. 16). It can be seen that the lower layer complex has a promoting effect upon the isomerization *n*-butane even in the absence of added oxygen (Table IV).

Table IV

Combined Effect of Aluminum Bromide–Lower Layer Complex upon Isomerization of *n*-Butane at 25°

Experiment no.	15	16	17
Reaction time, hours			
Dark	0	153	153
Sunlight	6[c]	8[c]	8[c]
Charge:			
$AlBr_3$, g.	7.4	(2.5)[a]	(4.9)[b]
n-Butane, g.	10.6	6.3	5.7
Air, cc.	80	0	0
$AlBr_3$, mole/100 mole C_4H_{10}	15.1	8.7	19
Oxygen, mole/100 mole C_4H_{10}	0.4	0	0
Partial pressure of O_2	0.16	0	0
Analyses, mole %			
Ethane	0	0	2.8
Propane	0	0	5.6
i-Butane	14.3	14.8	64.5
n-Butane	85.5	84.5	26.0
Pentanes and higher	0.2	0.7	1.1

[a] Free from lower layer complex. [b] Contains lower layer complex. [c] Temperature, 25° (±2°).

Effect of Lower Layer Complex Upon Isomerization.—The isomerizing effect of lower layer complex, freed from unreacted aluminum bromide, was investigated. The complex was prepared by the action of air on a solution of aluminum bromide in *n*-butane (Expt. 18, Table V). The hydrocarbon and the non-condensable gases were removed by evacuating the reaction vessel to about 10^{-3} mm. of mercury. The vessel contained lower layer complex and aluminum bromide, the latter, being relatively soluble in hydrocarbons, was leached out. The complex, freed from aluminum bromide, and containing 0.7 g. of combined "aluminum bromide," was used as a catalyst for isomerization of *n*-butane. It was found that even in the presence of such small amounts of catalyst and in the absence of any air, 17.5% of the *n*-butane charged was converted into isobutane (Table V).

Table V

Effect of Lower Layer Complex Free from Non-combined Aluminum Bromide upon Isomerization of *n*-Butane[a]

Experiment no.	18	19
Charge		
$AlBr_3$, g.	5.54	0.7[b]
n-Butane, g.	13.84	11.90
Air, cc.	120	0
$AlBr_3$, mole/100 mole C_4H_{10}	8.67	1.28
Oxygen, mole/100 mole C_4H_{10}	0.42	0
Analyses, mole %		
Isobutane	55.8	17.5
n-Butane	44.2	82.5

[a] The experiments were carried out at 20–25° and the reaction tube was exposed to sunlight for fifteen hours. [b] The lower layer is composed of a complex containing 0.7 g. of aluminum bromide in a combined form.

Analysis of the Lower Layer Complex.—A quantitative study was made of the products resulting from the reaction of air with aluminum bromide dissolved in *n*-butane in molar proportions: $C_4H_{10}:AlBr_3:O_2$–100:9.5:0.30. The experimental data are given in Table VI. It was found that all of the oxygen entered reaction; the gases which were pumped off, to 10^{-3} mm. of mercury, from the reaction tube held at liquid nitrogen temperature, consisted of 95% nitrogen and 5% paraffinic hydrocarbons. Analysis of the latter indicated that it was composed of 80% of methane and 20% of ethane. The condensable gases consisted of 63.6% of isobutane and 1.4% of pentanes, the remainder being *n*-butane. Hydrogen bromide was recovered from the reaction, equivalent to 1.25 moles per 1 mole of oxygen reacted. The lower layer complex formed, freed of uncombined aluminum bromide, on hydrolysis yielded unsaturated hydrocarbons. The atomic ratio of bromine to aluminum in the complex was equal to 2.5.

Mechanism of Isomerization.—In order to explain the effect of oxygen upon the isomerization of *n*-butane or *n*-pentane in the presence of either aluminum chloride or aluminum bromide, two hypotheses are presented, both involving the formation of hydrogen halide and alkyl halides.

TABLE VI

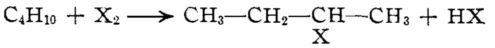
ANALYTICAL DATA PERTAINING TO THE PREPARATION OF THE "LOWER LAYER COMPLEX"

Experiment no.	14
Duration, hours	
Dark	102
Sunlight	31
Temperature, °C.	25–35
Charge, g.	
$AlBr_3$	6.05
n-Butane	13.90
Air 160 cc. at s. t. p. oxygen	0.048
nitrogen	0.158
Recovery, g.	
Nitrogen (129 cc. at s. t. p.)	0.16
Hydrocarbons	13.76
Hydrogen bromide (in decanted soln.)	0.13
Aluminum bromide (in decanted soln.)	4.49
Aluminum (in lower layer)	0.16
Bromine (in lower layer)	1.17
Hydrocarbons (in lower layer)	0.2
Analysis of gases non-condensable at −78°, mole %	
Oxygen	0.0
Nitrogen	95.0
Paraffins	5.0
Index of paraffins	1.2
Analysis of gases condensable at −78°, mole %	
Isobutane	63.6
n-Butane	35.0
Pentanes and higher	1.4

Alkyl halide, as a source of carbonium ion, acts as a chain starter for isomerization as was described in the previous paper.[4]

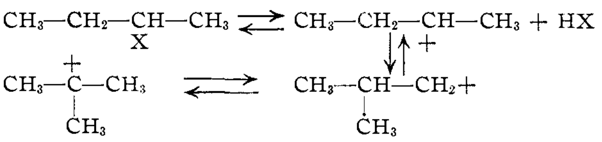
Hypothesis A.—Aluminum halide reacts with oxygen to yield aluminum oxyhalide and halogen. The latter reacts with the alkanes to form alkyl halides and hydrogen halide.

$$\mathrm{AlX_3 + {}^1/_2O_2 \rightleftarrows AlOX + X_2} \qquad (1)$$

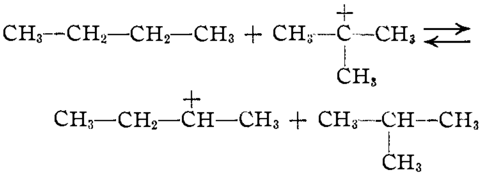


$$\mathrm{C_4H_{10} + X_2 \longrightarrow CH_3{-}CH_2{-}\underset{X}{CH}{-}CH_3 + HX} \qquad (2)$$

The reaction represented in Eq. 2. proceeds much faster in the presence of sunlight; the consumption of halogen causes the shift of the equilibrium toward the right in Eq. 1. The alkyl halide formed (Eq. 2) acts, in the presence of catalysts, as a chain starter for the isomerization of alkanes.[4]



$$\begin{array}{ccc} \mathrm{CH_3{-}CH_2{-}\underset{X}{CH}{-}CH_3} & \rightleftarrows & \mathrm{CH_3{-}CH_2{-}\overset{}{CH}{-}CH_3 + HX} \\ & & \downarrow\uparrow + \\ \mathrm{CH_3{-}\overset{+}{\underset{CH_3}{C}}{-}CH_3} & \rightleftarrows & \mathrm{CH_3{-}\underset{CH_3}{CH}{-}CH_2^{+}} \end{array} \qquad (3)$$



$$\begin{array}{l} \mathrm{CH_3{-}CH_2{-}CH_2{-}CH_3 + CH_3{-}\overset{+}{\underset{CH_3}{C}}{-}CH_3 \rightleftarrows} \\ \mathrm{CH_3{-}CH_2{-}\overset{+}{CH}{-}CH_3 + CH_3{-}\underset{CH_3}{CH}{-}CH_3} \end{array} \qquad (4)$$

Hypothesis B.—Alkanes are oxidized in the presence of aluminum halide to form

$$\mathrm{C_4H_{10} + O_2 \xrightarrow{AlX_3} 2C_4H_9OH} \qquad (5)$$

The use of aluminum chloride as an oxidation catalyst was noted by Friedel and Crafts[5] who found that upon passing moist air through a mixture of benzene and aluminum chloride, some oxygen is fixed, resulting in the formation of phenol and other oxygenated hydrocarbons.

The butanol formed (Eq. 5) may react with aluminum halide to form butoxyaluminum dihalide.[6]

$$\mathrm{C_4H_9OH + AlX_3 \longrightarrow C_4H_9OAlX_2 + HX} \qquad (6)$$

Part of the butanol may also react with the hydrogen halide formed

$$\mathrm{C_4H_9OH + HX \rightleftarrows C_4H_9X + H_2O} \qquad (7)$$

The alkyl halide produced may act then as a chain starter for the isomerization of butane as given in Eqs. 3 and 4.

In order to throw some light upon the validity of the hypothesis (A), the effect of oxygen upon aluminum bromide was investigated. It was found that by treating aluminum bromide with pure oxygen at room temperature a slight but definite reaction occurred, as evidenced by the coloration owing to liberated bromine; the product resulting from such oxidation, after the removal of unreacted oxygen, showed slight catalytic properties toward the isomerization of *n*-butane, yielding 6.6–13.8% of isobutane. The treatment of aluminum bromide at 100° with an

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[4] H. S. Bloch, H. Pines and L. Schmerling, THIS JOURNAL, **68**, 153 (1946).

[5] C. Friedel and J. M. Crafts, *Compt. rend.*, **86**, 884 (1878).

[6] P. Tsukervanik and K. Tokareva, *J. Gen. Chem., U. S. S. R.*, **5**, 764 (1935).

approximately equal molal mixture of oxygen and nitrogen did not seem to increase the degree of oxidation. The experimental results are given in Table VII. The fact that the oxidation of aluminum bromide by means of pure oxygen or oxygen–nitrogen mixture is slow does not exclude the possibility that in hydrocarbon solution it may proceed much faster, especially since the liberated bromine reacts with the hydrocarbons and therefore is removed from the reaction zone.

TABLE VII

EFFECT OF PRETREATMENT OF ALUMINUM BROMIDE WITH OXYGEN UPON THE ISOMERIZATION OF *n*-BUTANE

Experiment no.	20	21	22	23
Reaction time, hours	138	117	141	119
Temperature, °C.	25	25	25	25
Charged:				
Aluminum bromide, g.	3.04[a]	3.18[b]	2.24[c]	2.28[d]
n-Butane, g.	7.07	7.45	5.20	6.34
$AlBr_3$ mole/100 mole C_4H_{10}	9.32	.....	9.36	7.38
Hydrocarbons recov., g.	6.90	7.22	5.25	6.23
Analyses, mole %				
i-Butane	9.2	6.2	6.6	13.8
n-Butane	89.5	93.5	92.3	86.0
Pentanes and higher	1.3	0.3	1.1	0.2

[a] The aluminum bromide was treated with 170 cc. (at s. t. p.) of oxygen at 20–25° for 476 hours, after which the reaction vessel was kept in liquid nitrogen and the oxygen was pumped off to 10^{-2} mm. of mercury pressure. [b] Treated with 170 cc. of oxygen at 20–25° for 693 hours; the reaction vessel was kept at 0° while being pumped out. [c] The aluminum bromide was treated with 150 cc. of oxygen–nitrogen mixture (46.3% O_2 and 53.7% N_2) at 100° for one hour. The vessel had a reddish tint because of the liberated bromine. The gases were pumped out at room temperature; 140 cc. of gas was recovered. [d] Treated with 135 cc. of nitrogen–oxygen mixture (48.2 O_2 and 51.8% N_2) at 100° for thirteen hours; 120 cc. of gas consisting of 46.9% O_2 and 53.1% N_2 was pumped out at room temperature and at 10^{-3} mm. of pressure. From the analysis obtained it was calculated that only 9 mole per cent. of aluminum bromide underwent oxidation to form assumedly AlOBr.

Attempts to Isomerize *n*-Butane with Ethylaluminum Bromides and Ethoxyaluminum Bromides.—One of the possible explanations of the action of oxygen upon aluminum bromide solution in *n*-butane and the catalytic properties of the "lower layer complex" produced, involves the formation of an alkoxyaluminum bromide (Hypothesis B). It was of interest therefore to determine whether organoaluminum compounds, and especially oxygenated organoaluminum compounds, act as a catalyst for the isomerization of *n*-butane. For this purpose ethylaluminum dibromide ($C_2H_5AlBr_2$) and diethylaluminum bromide $(C_2H_5)_2AlBr$ prepared by Dr. J. M. Mavity of our laboratories, were selected for this study.[7a]

It was found that neither ethylaluminum dibromide nor diethylaluminum bromide, both of which were completely soluble in *n*-butane, was an isomerizing catalyst.

The ethoxyaluminum bromides were prepared by treating the ethylaluminum bromide in *n*-butane solution with oxygen according to the equations

$$C_2H_5AlBr_2 + {}^1/_2O_2 \longrightarrow C_2H_5OAlBr_2$$
$$(C_2H_5)_2AlBr + O_2 \longrightarrow (C_2H_5O)_2AlBr$$

In each case a white and slightly gelatinous precipitate was at first formed, which after approximately twelve hours was dissolved completely. At the end of the reaction time, there was only a slight trace of crystalline material in the vessel containing the diethylaluminum bromide while a small but definite quantity of lower layer was present in the sample containing the ethylaluminum dibromide; in the latter case 3.1% isomerization had occurred. No hydrogen bromide was detected in either case. It is possible that greater stability of the ethylaluminum bromides results in a much slower reaction rate. The experimental data are given in Table VIII.

TABLE VIII

EFFECT OF ETHYLALUMINUM DIBROMIDE AND DIETHYLALUMINUM BROMIDE UPON THE ISOMERIZATION OF *n*-BUTANE AT 25°

Experiment no.	24	25	26	27
Reaction time, hours	283	192	138	138
Charged				
n-Butane, g.	6.64	6.65[d]	6.28	5.94[e]
Ethylaluminum dibromide, g.	1.24	1.24[b]	0	0
Diethylaluminum bromide, g.	0	0	2.40	2.40[c]
Air, cc. at s. t. p.	0	270	0	195
Recovery, g.				
Hydrocarbons	6.55	6.62	6.13	5.89
Residue	....	1.30	....	2.58
Gases, uncond. in liquid N_2, cc. at s. t. p.	....	217[a]	....	155[a]
Analyses of hydrocarbons				
Isobutane	....	3.1	....	.....
n-Butane	100	96.0	100	100
Pentanes and higher	....	0.9	....	.....

[a] Consists of 100% nitrogen. [b] Ethylaluminum dibromide from Expt. 24 was used. [c] Diethylaluminum bromide from Expt. 26 was used. [d] Molal ratio of $C_4H_{10}:C_2H_5AlBr_2:O_2 = 100:4.9:0.63$. [e] Molal ratio of $C_4H_{10}:(C_2H_5)_2AlBr:O_2 = 100:14.5:0.052$.

Experimental

Apparatus.—A general description of the high-vacuum apparatus will be found in a previous publication of this series.[1] A drawing of the reaction tube used in the present work is shown in Fig. 1 and described more fully below. The Toepler pump was of the automatic type fully described by A. Stock.[7b]

Materials.—The source and purification of the aluminum chloride and aluminum bromide has been previously described.[1]

Phillips C. P. *n*-butane and *n*-pentane was purified in the high-vacuum apparatus by the usual degassing and low-temperature distillation as described for *n*-butane.[1]

Burrell 10–12 mesh charcoal as received was weighed and inserted into the side tubes A of the reaction tube assembly shown in Fig. 1 through a small opening B. After sealing the opening and inserting the aluminum chloride sample in side tube C and cooling, the apparatus was evacuated and heated to drive off moisture and absorbed gases. The aluminum chloride was then sublimed to tube D and tube C was sealed off. Liberated gases

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[7a] Butylaluminum bromide which would be more appropriate for this investigation was not available and its preparation has not been reported in the literature.

[7b] A. Stock, *Z. Elektrochem.*, **23**, 35 (1917).

were pumped off; the charcoal again flamed while the gases were being pumped. Further sublimations of the aluminum chloride to the main tube E and side tube of charcoal were then carried out in a closed system as previously described.[1]

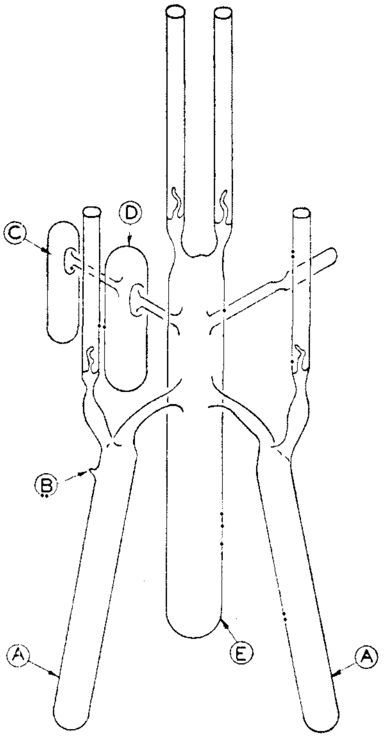

Fig. 1.—Reaction tube assembly.

Air was taken from the laboratory and contained 20.9% oxygen. It was dried upon entering the high-vacuum apparatus, at a rate of approximately 50 cc. per minute, by passing through phosphorus pentoxide and then through a Dry Ice trap and liquid nitrogen trap located on the distillation line of the high-vacuum apparatus. Air was admitted to 600–650 mm. pressure. The cooling was then removed from the liquid nitrogen trap to assure no condensation of air and the reaction tube, which was cooled with Dry Ice, was sealed off.

The oxygen–nitrogen mixtures were made from Linde c. p. oxygen and nitrogen. These were mixed in a gas bottle from which they were admitted to the reaction tube upon drying as described above for air.

Procedures.—In general the procedure for these experiments consists essentially of adding the aluminum halide to the reaction tubes as previously described[1] or as in the case of aluminum chloride on charcoal as described above. The *n*-butane or *n*-pentane was then added and while kept in Dry Ice the air was added and dried as above-described simply by opening a stopcock to the atmosphere. After the reaction tube was sealed off it was either kept in a dark, constant temperature bath or exposed to the sunlight by suspending it on a ring stand. The outdoor temperature varied from 20 to 30°. The tube was not agitated in the latter case. Analysis of the hydrocarbon contents was made by low-temperature distillation.[1]

The experiment showing the effect of aluminum bromide–lower layer complex upon isomerization was performed as follows: Lower layer was produced by treating *n*-butane with air, and aluminum bromide in excess of its solubility in the *n*-butane at room temperature.

The reaction tube was then resealed to the vacuum apparatus and the liquid was distilled off and all material was pumped off to 10^{-3} mm. of mercury pressure with the tube at room temperature. *n*-Butane was again added and the vessel was sealed off. After warming to room temperature to allow the liquid to dissolve some of the aluminum bromide and lower layer, a portion of the clear liquid was carefully poured into tube A and both tube A and E were cooled simultaneously in Dry Ice. Tube A was then sealed off and both samples were allowed to react.

For the experiment showing the effect of lower layer complex upon isomerization the procedure was identical to that described directly above, up to the point at which the tubes were simultaneously cooled. Only tube E was cooled (slowly) and *n*-butane was recondensed in the main tube leaving a solid deposit in the side tube. This process of leaching out the soluble aluminum bromide by alternately warming the butane to room temperature, pouring to the side tube, and distilling back into the main tube was performed four times; the fourth time the material was poured into a second side tube A (Fig. 1) and upon evaporation, no visible sign of aluminum bromide was noticed. After the side tubes were sealed off *n*-butane was again added to the main tube and allowed to react as described above.

The experiment showing a quantitative analysis of the products resulting from the reaction of air with aluminum bromide dissolved in *n*-butane was performed as follows: After reaction of the charged materials the reaction vessel was immersed in liquid nitrogen and resealed to the vacuum line. The apparatus was then evacuated, the tip of the reaction tube was broken, and the gases were pumped off to 0.01 mm. of mercury by means of the Toepler pump, and collected over mercury. Analysis of the gas was made by Goeckel absorption methods.[8] The reaction vessel was then sealed off and after being warmed to room temperature to dissolve the aluminum bromide, the clear solution was poured into the side tube. The side tube was then immersed in liquid nitrogen and sealed off. The tip of this side tube was then broken and the volatile components were distilled off at atmospheric pressure and condensed for analysis, first being passed through standard potassium hydroxide solution. The standard potassium hydroxide solution was titrated with standard sulfuric acid for hydrogen bromide. The main portion of the lower layer or complex remaining in the main reaction tube was decomposed with water, in the vacuum apparatus, and the products were quantitatively analyzed for aluminum and bromine.

In the experiments with ethylaluminum, dibromide, and diethylaluminum bromide the materials were added similarly to the method of adding aluminum halides except that the former were handled under an atmosphere of dry nitrogen.

Acknowledgment.—The authors wish to thank Professor V. N. Ipatieff for the interest shown in the progress of this work.

Summary

The effect of oxygen upon the isomerization of *n*-butane and *n*-pentane in the presence of aluminum chloride or aluminum bromide has been studied.

It was found that the addition of 0.007 mole per cent. oxygen, in the form of air, to *n*-pentane is sufficient to convert 40% of the *n*-pentane to butanes and isopentane using aluminum chloride catalyst; in the absence of oxygen the reaction does not proceed.

The catalytic effect of an aluminum bromide–oxygen–hydrocarbon complex formed by the action of air upon the solution of aluminum bromide in *n*-butane was studied.

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(8) UOP Laboratory Test Methods for Petroleum and its Products, UOP Method No. G-84-40.

The action of oxygen upon aluminum bromide was investigated.

The effect of ethylaluminum dibromide and of diethylaluminum bromide in the presence and in the absence of air upon the isomerization of *n*-butane was investigated.

The mechanism of isomerization was discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BUFFALO]

The Defect in the Magnetic Susceptibility of Manganese Dioxide and Other Compounds of Manganese[1]

BY J. T. GREY, JR.[2]

The magnetic susceptibility of manganese dioxide has been measured in several previous investigations, but the values recorded are widely divergent, for $\chi_{\text{obs.}}$ varied from 26.03×10^{-6} at 37° to 66.2×10^{-6} at 20°. Moreover, when the atomic moment of the quadrivalent manganese ion was calculated from the accepted value of the mass susceptibility it was found that the value did not check that calculated theoretically for an atom with three unpaired electrons, assuming only the spin moments to be effective. A survey of the literature revealed that this defect in the magnetic susceptibility was not peculiar to manganese dioxide, but that it existed in the oxides and certain salts of all the transition elements.

These deviations have been attributed in the past to the interatomic field effects within the crystal lattice, but no clearly defined explanation had been advanced. Therefore, it was the purpose of this investigation to measure accurately the mass magnetic susceptibility of manganese dioxide and certain other compounds of manganese and to attempt to derive therefrom an explanation for the observed defect in the magnetic susceptibility.

Experimental

Method of Measurement.—The method of measurement and the apparatus used in this research were the same in principle as that used previously in this Laboratory.[3]

A refined apparatus was built to ensure greater accuracy and efficiency. The specific changes were as follows: (a) A glass capsule was employed to hold the sample and a glass compensator was attached to the suspension system so that the magnetic contribution of the capsule was cancelled. (b) Possible residual magnetism in the field source was eliminated by using an air core magnet instead of an iron core magnet. (c) The gas-filled photo tube was replaced by a high vacuum type tube which had more constant characteristics. (d) The mechanical interrupting contacts in the magnet circuit were replaced by an arrangement of Thyratrons which freed the circuit of variable contact resistances. (e) The current output of the generator was stabilized by floating a battery across the output terminals. (f) The current in the magnet circuit was measured directly. (g) The temperature was thermostatically maintained at 30.0 ± 0.1°.

Each of the experimental runs was made in accord with a routine procedure. A glass-stoppered Pyrex capsule was packed full of the sample, stoppered, weighed and laid on the glass suspension hooks in a definite position. The magnets and their supports were affixed and the thermostatically controlled temperature-housing was sealed. The apparatus was started and after the entire setup had had time to reach thermal equilibrium, the resistance in the magnet circuit was varied until the observed deflection of the capsule, and its contents, reached the predetermined standard value which had been decided upon during the calibration. When this deflection had been maintained constant for a period of ten minutes—approximately forty magnetization cycles—the system was considered to be at equilibrium and the voltage drop across the standard resistance in the magnet circuit was recorded.

The magnetic susceptibility of the material was then calculated by substituting in the equation, $m\chi = C/E^2$, which was readily deduced by considering the variables in a given experimental run. Thus, since the effect of the magnetic field on the capsule is nullified by the compensator and the capsule and its contents are always raised to the same total deflection, the only variables are the mass, the susceptibility and the magnetic field strength. Further, it was shown that the field strengths in the range employed in this investigation were directly proportional to the current in the magnet circuit, or inversely proportional to the voltage drop across the standard resistance, see Fig. 1.

The apparatus was calibrated with several purified compounds of accurately known susceptibility. The susceptibilities were corrected to 30°. The results are shown in Table I; the individual values of C are the average of at least two determinations in every case.

TABLE I

CALIBRATION CONSTANTS

Compound	χ at 30°	C
$(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$	31.23×10^{-6}	4.14×10^{-8}
$NH_4Fe(SO_4)_2\cdot 12H_2O$	29.10×10^{-6}	4.13×10^{-8}
$K_4Fe(CN)_6$	6.87×10^{-6}	4.11×10^{-8}
$CuSO_4\cdot 5H_2O$	5.90×10^{-6}	4.10×10^{-8}
Average value of C		4.12×10^{-8}

Preparation and Analysis of Compounds.—It is general knowledge that manganese dioxide is extremely difficult to purify and it is doubtful that the compound has ever been prepared pure enough to conform to the formula MnO_2. In an unpublished work, Frazer and Weld have recorded measurements of the partial pressure of oxygen in equilibrium with manganese dioxide at various temperatures, and it was shown, in general, that the manganese-to-oxygen ratio depended strongly on the past history of the sample and its mode of preparation. Empirical formulas such as $MnO_{1.88}$ have been typical.

Manganese dioxide was, therefore, extremely difficult

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[1] An investigation under the direction of Dr. J. H. Frazer, presently Major, U. S. Army.

[2] Abstracted from a thesis by the author, submitted to the Faculty of the Graduate School of the University of Buffalo, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1940.

[3] J. H. Frazer and Long, *J. Chem. Phys.*, **6**, 462 (1938).