

concentrations. The diffusion current is found proportional to the nitrate concentration over a very narrow range of nitrate concentrations only. It is found that the reduction involves 6 electrons and not 8 electrons as claimed by Tokuoka and Ruzicka.

3. Small amounts of sulfate do not interfere in the uranyl procedure but they do interfere in the lanthanum procedure.

4. Uranous instead of uranyl salt can be used in the catalytic polarographic reduction of nitrate.  
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## The Catalytic Isomerization of Paraffin Hydrocarbons. II. Promoters for Catalysis by Aluminum Bromide

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Although aluminum halides, as ordinarily prepared and handled, are catalysts for the isomerization of paraffin hydrocarbons, it has been shown that the pure bromide, in the absence of moisture, has no effect on the butanes<sup>2,3</sup> or *n*-heptane,<sup>4</sup> and that anhydrous aluminum chloride does not cause any reaction of *n*-butane,<sup>2,5</sup> *n*-pentane,<sup>6</sup> *n*-hexane, *n*-heptane, and 2,2,4-trimethylpentane.<sup>5</sup> Presumably, therefore, the dry aluminum halides are inert to all paraffins at relatively low temperatures.

Addition of a hydrogen halide or water to the aluminum halide gives rise to an active isomerization catalyst. On the basis of kinetic experiments, Leighton and Heldman<sup>2</sup> postulated this substance to be  $\text{HALBr}_4$  in the case of hydrogen bromide-aluminum bromide mixtures.

It is known that other substances besides hydrogen halides may function as "promoters" for aluminum halide catalysis.<sup>7</sup> To determine the role of the promoter and hence to gain an insight into the mechanism of halide-catalyzed isomerization, *n*-butane has been subjected to the action of carefully purified, anhydrous aluminum bromide with various promoters added. The results of these experiments are here reported.

### Experimental

Aluminum bromide was prepared and handled as in previous work<sup>2,3</sup> except in a few cases, in which it was finally distilled *in vacuo* into thin capsules and sealed. The capsules could be broken open in a reaction tube when desired by action of a glass-enclosed iron core activated either by a solenoid or shaking.

Two *n*-butane preparations were employed, part of both having been used in earlier work.<sup>2,3</sup> These were stored over phosphorus pentoxide at 0°.

The sodium chloride and sodium bromide were Merck reagent grade. Hydrogen bromide was prepared as previously described,<sup>2</sup> and hydrogen chloride was made by heating potassium acid sulfate with sodium chloride and puri-

fied by dry ice to liquid air distillations. Boron trifluoride was taken from an Ohio Company cylinder.

Eastman Kodak "practical" methyl bromide was subjected to fractionation on the column described below, and the heart cut was stored at 0° over Drierite in the dark. The product was colorless. The methylene dibromide was a Kahlbaum sample, and the *n*-butyl bromide was Eastman Kodak Co. "white label."

All volatile materials were introduced into the reaction tubes containing aluminum bromide essentially in the manner previously described.<sup>2</sup> In the cases of sodium chloride and sodium bromide, the salts were weighed in the tubes before these were sealed to the manifolds (or before a capsule was introduced).

No manifold was used after *n*-butyl bromide or boron trifluoride had been distilled into a reaction tube on it.

Since exclusion of moisture and hydrogen bromide was of the utmost importance in this work, and since activity of the "anhydrous" aluminum bromide as a catalyst is a test for very small traces of these promoters, blanks were run on all manifolds of tubes used, and also on a capsule from the same batch as those used here. Two of these blanks have been previously reported,<sup>8</sup> while others were run under different conditions and for much longer times. In one blank experiment, which was run at 25.0° for 3.0 days with shaking, the charge of aluminum bromide far exceeded its solubility in *n*-butane.<sup>3</sup>

In none of these blanks was there any reaction, recovery of the original *n*-butane being practically quantitative. This result cannot be stressed too strongly, since the validity of the results and the conclusions to be drawn therefrom would be vitiated if the aluminum bromide itself were not completely inactive.

After reaction and freezing of the sealed tube in liquid air, residual pressure was estimated from the Tesla coil glow, except in one experiment with air. No tubes tested showed appreciable amounts of permanent gas formation.

The aluminum bromide content in the tubes was determined after reaction either by direct weighing after removal of all volatile material or by analysis as aluminum oxide. In experiments where capsules of the halide were used, the weight had been determined previously from the known length density of the glass tubing leading to the capsule and the weight of the capsule plus a measured length of tubing before and after distilling in the aluminum bromide.

Before analysis, the volatile material from an experiment was passed through potassium hydroxide pellets and phosphorus pentoxide. With the organic bromides, the charge was first treated with ethanalamine.

Four methods of analysis were employed: low temperature fractional distillation using a manually operated 3 mm. i. d. Podbielniak micro-precision type R column,<sup>9</sup> dew pressure,<sup>3,10</sup> "float point,"<sup>2</sup> and aniline point.<sup>11</sup>

(1) National Research Fellow in Chemistry, 1942-1943.

(2) Leighton and Heldman, *THIS JOURNAL*, **65**, 2276 (1943).

(3) Heldman and Thurmond, *ibid.*, **66**, 427 (1944).

(4) Sensel, Dissertation, Western Reserve University, Cleveland, Ohio, 1938.

(5) Ipatieff and Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

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

(7) 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.

(8) Ref. 2, Experiments 41 and 42.

(9) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931); **5**, 119 (1933).

(10) Savelli, Seyfried and Filbert, *ibid.*, **13**, 868 (1941).

(11) Ludemann, *ibid.*, **12**, 446 (1940).

### Results

The results of the experiments are given in Table I, along with a rather detailed summary of the visual observations, as these are of importance in the following discussion.

Although there are possible objections as to the quantitative character of all analyses except the fractionations, the results are sufficiently clear-cut and show enough internal agreement to justify their use, especially in view of the clean character

of the reaction and the exploratory nature of the work. It must be emphasized that the small percentage conversions in some experiments are real, since the concomitant blanks used showed no reaction.

The correction for the original *i*-butane content of the hydrocarbon was negligible except in the case of a few experiments with sodium bromide and chloride, where the distillations were performed with extreme care. In other experiments, the analyses are reported to the nearest per cent. of the total butanes.

TABLE I

SUMMARY OF PROMOTER EXPERIMENTS

Substance	Promoter Moles $\times 10^4$	$Al_2Br_6$ , moles $\times 10^4$	$n-C_4H_{10}$ , moles $\times 10^4$	Temp., °C.	Time, hr.	Analyses, % <i>i</i> - $C_4H_{10}$
"Air"	? <sup>f</sup>	2.63	250	25.0	72.0	4 <sup>a</sup>
"Air"	? <sup>f</sup>	6.10	500	25 = 3	334	18 <sup>b</sup>
HBr	33.8	13.0	250	25.0	96.0	14 <sup>a</sup>
HBr	19	31.9	250 <sup>h</sup>	25.0	72.0 <sup>i</sup>	17 <sup>a</sup>
HBr	19.8	8.47	500	25 = 3	149	38 <sup>b</sup>
HBr	1.66	3.66	250	84 = 2	12.0	8 <sup>b</sup>
HBr	4.14	2.95	250	84 = 2	12.0	15 <sup>b</sup> , 13 <sup>c</sup> , 15 <sup>d</sup>
HBr	21.1					
Gelacol <sup>i</sup>	0.377 g.	10.6	500 <sup>k</sup>	25 = 3	283 <sup>l</sup>	75 <sup>b</sup>
HCl	1.5	15.7	107	84 = 2	58.7	59 <sup>b</sup> , 61 <sup>d</sup>
HCl	5.6	3.49	107	84 = 2	44.4	>69 <sup>m</sup>
NaBr	51.8	21.4	250 <sup>n</sup>	25.0	96.0 <sup>i</sup>	0.4 <sup>a</sup>
NaBr	30.6	15.2	500 <sup>o</sup>	25 = 3	286	10 <sup>b</sup>
NaBr	29.1	10.1	500 <sup>o</sup>	50 = 1	47.8 <sup>i</sup>	1.3 <sup>a</sup>
NaBr	3.76	0.87	107 <sup>o</sup>	84 = 2	58.7	5 <sup>b</sup> , 5 <sup>c</sup> , 5 <sup>d</sup>
NaBr	10.9	1.60	107 <sup>o</sup>	84 = 2	44.4	12 <sup>a</sup> , 12 <sup>d</sup>
NaCl	47.0	43.4	250 <sup>n</sup>	25.0	96.0 <sup>i</sup>	0.5 <sup>a</sup>
NaCl	6.22	1.75	107 <sup>o</sup>	84 = 2	44.4	38 <sup>a</sup> , 40 <sup>d</sup>
NaCl	8.71	1.48	107 <sup>o</sup>	84 = 2	34.9	31 <sup>a</sup> , 36 <sup>d</sup>
CH <sub>2</sub> Br	40	13.2	250 <sup>p</sup>	25.0	96.0	11 <sup>a,q</sup>
CH <sub>2</sub> Br <sub>2</sub>	300	19.1	500	25 = 3	405	75 <sup>a,r</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	? <sup>s</sup>	2.42	107 <sup>t</sup>	84 = 2	58.7	62 <sup>c</sup> , 62 <sup>d</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	6.5	9.35	107 <sup>u</sup>	84 = 2	12.0	36 <sup>d</sup>
BF <sub>3</sub>	4.4	19.6	250 <sup>v,w</sup>	25.0	96.0 <sup>i</sup>	>45 <sup>a,s</sup>
BF <sub>3</sub>	5.4	0.69	107 <sup>v</sup>	84 = 2	58.7	20 <sup>d</sup>
BF <sub>3</sub>	11	1.52	107 <sup>v</sup>	84 = 2	44.4	42 <sup>d</sup>

<sup>a</sup> Distillation analysis. <sup>b</sup> From dew pressure. <sup>c</sup> From float point. <sup>d</sup> From aniline point. <sup>e</sup> Charge frozen out, opened to air for ca. 15 sec., sealed. <sup>f</sup> Traces of white pasty solid noted. <sup>g</sup> Capsule of  $Al_2Br_6$  exposed to air one min., then thoroughly pumped. <sup>h</sup> Not all  $Al_2Br_6$  dissolved. <sup>i</sup> Shaken continuously. <sup>j</sup> Dehydrated aluminum hydrate, Hammill and Gillespie, Inc., New York. <sup>k</sup> Solid turns dark orange red when  $Al_2Br_6$  capsule broken in presence of Gelacol. <sup>l</sup> Occasional shaking. <sup>m</sup> Aniline point being approached at 100°, when tube burst. <sup>n</sup> Crystalline solid at bottom, and apparently a solid plug of  $Al_2Br_6$  above it. <sup>o</sup> Granular solid at bottom. <sup>p</sup> Homogeneous, colorless solution. <sup>q</sup> No traces of low boiling material; nothing boiled higher than *n*-butane up to hold-up of column. <sup>r</sup> Of the butane fraction. Traces of low-boiling material observed; also some high-boiling fraction, too complex to identify. <sup>s</sup>  $13 \times 10^{-4}$  mole of *n*-C<sub>4</sub>H<sub>9</sub>Br distilled into  $Al_2Br_6$ , which was then subjected to high-vacuum pumping for seven hours. Yellowish viscous liquid remained in addition to some solid  $Al_2Br_6$ . <sup>t</sup> Small amount of yellowish lower layer; after reaction, traces of red-brown oil. <sup>u</sup> Red-brown viscous lower layer formed. <sup>v</sup> Liquid phase cloudy; white powdery solid formed. <sup>w</sup> The atom ratio of Al to Br in the residue was 1 to 2.80. <sup>x</sup> Some analyzate lost. If part lost was of same composition as analyzed fraction, then sample contained ca. 75% *i*-butane.

### Discussion

The experiments with "air" show how effective moisture is in activating aluminum bromide with respect to butane isomerization, in agreement with earlier observation.<sup>2</sup>

Alumina increases the rate of isomerization considerably. With approximately the same amount of aluminum bromide and hydrogen bromide, less conversion was achieved in over two months at room temperature<sup>12</sup> than that encountered here in less than twelve days. The *n*-*i*-butane equilibrium was undoubtedly reached<sup>13,14</sup> in the alumina experiment, so that the rate of isomerization is probably even faster than that indicated by the result.

That some chemical interaction between the catalyst and alumina occurs is likely in view of the striking color change when they are brought into contact, although the heterogeneity of the system may be sufficient to account for the increased rate.

Hydrogen chloride is apparently a more efficient promoter than hydrogen bromide. This agrees with the findings of Glasebrook, Phillips, and Lovell on the isomerization of *n*-pentane catalyzed by aluminum bromide.<sup>6</sup>

The experiments with sodium chloride and bromide yield very important results. Both may act as promoters for aluminum bromide. Sodium chloride is better than sodium bromide. While neither is as good as hydrogen bromide at room temperature, both rapidly approach it in activity with rising temperature.

Since butyl bromide reacts rapidly with aluminum bromide to form a typical red-brown viscous lower layer with evolution of hydrogen bromide, it is not possible to say whether the complex material resulting from dehydrobromination and subsequent condensations or the hydrogen bromide itself is the true promoter, or even perhaps unreacted butyl bromide. The experiment in which a small amount of *n*-butyl bromide was introduced into the aluminum bromide and then

(12) Compare ref. 2, experiment 4.

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

(14) Rossini, Prosen and Pitzer, *J. Res. Natl. Bur. Stds.*, **27**, 529 (1941).

thoroughly pumped points toward the conclusion that the complex products of dehydrohalogenation may act as promoters, although these may react to produce more hydrogen bromide upon solution in *n*-butane.

Methyl bromide and methylene bromide also act as promoters. Methyl bromide and aluminum bromide form colorless solutions which do not change in properties with time, so that formation of hydrogen bromide is ruled out. Indeed, it is difficult to see how hydrogen bromide could be split out by any simple process. No lower layer formed in the methylene dibromide experiment; again it is hard to visualize a reaction evolving hydrogen bromide.

Perhaps the most surprising results are those with boron fluoride, which is seen to be an excellent promoter for the reaction, with apparently a small temperature coefficient. The fluoride reacts with aluminum bromide in butane to give mixed aluminum bromide-fluoride and (presumably) boron tribromide. This reaction has been observed previously in the absence of solvent.<sup>16</sup>

All these facts can be correlated by the hypothesis that the necessary condition for paraffin isomerization engendered by aluminum bromide is the presence of aluminum at least partially coordinated with bromine or chlorine. It is not necessary for the  $\text{AlBr}_4^-$  group to be an anion *per se*, nor is it stringently imposed that only bromines be bound to the aluminum.

The compounds  $\text{NaAlBr}_4$  and  $\text{NaAlBr}_3\text{Cl}$  are known;<sup>16,17</sup> here the binding is certainly ionic in character. The experimental indications are that the unsymmetrical anion is the better catalyst. It may be that the low solubility of these compounds in butane at room temperature accounts for their small catalytic activity; the high temperature coefficient observed could then be related to large heats of fusion of the salts.

Leighton and Heldman advanced evidence to show that  $\text{HAlBr}_4$  was the true catalytic agent in their experiments.<sup>2</sup> In the non-polar, low dielectric butane solvent, the bond between the hydrogen and bromine would probably not be ionic in character.  $\text{HAlBr}_3\text{Cl}$ , which is apparently a better catalyst, might well be more ionic, but more information is needed before the interesting point that the unsymmetrical aluminum tetrahalides are the better catalysts can be interpreted.

(15) Gamble, Gilmont and Stiff, *THIS JOURNAL*, **62**, 1257 (1940).

(16) Kendall, Crittenden and Miller, *ibid.*, **48**, 963 (1923).

(17) Plotnikow and Yakubson, *Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R.*, **4**, 120 (in German) (1938).

Compounds of the type  $\text{RAlBr}_3\text{X}$  have been shown to exist in solution.<sup>18</sup> The experiments with methyl bromide and methylene bromide indicate that these compounds are true catalysts for butane isomerization. With butyl bromide the conclusion is less certain, due to the previously mentioned reaction producing hydrogen bromide. Although aluminum bromide forms a complex with (and polymerizes) the resulting olefins, this complex may not be catalytically active. Montgomery, McAteer and Franke<sup>13b</sup> presented evidence which can be interpreted by assuming an aromatic-aluminum bromide complex which is stabler than  $\text{HAlBr}_4$  and is not catalytically active.

It is not certain that all the water was removed from the alumina preparation used, and hence it is not possible to say that the increased rate of isomerization in the presence of alumina is due only to its surface properties. The color noticed indicates the possibility of an irreversible change, such as the formation of  $\text{HAlOBr}_2$  and like compounds from  $\text{HBr}$ ,  $\text{Al}_2\text{Br}_6$ , and  $\text{Al}_2\text{O}_3$ .

The explanation of the catalytic activity of boron fluoride-aluminum bromide mixtures is in all probability connected with the reaction to form a mixed aluminum halide. A possible explanation for both phenomena can be given by proposing reactions of the type  $\text{BF}_3 + \text{Al}_2\text{Br}_6 = (\text{Al}_2\text{Br}_5)^+ (\text{BF}_3\text{Br})^-$  producing transitory cations of aluminum with an open orbital on one end of the ion. Although such ions are not formally similar to the  $\text{AlX}_4^-$  groups of the preceding instances, reasons for believing them to be powerful catalysts for paraffin isomerization are advanced in the following paper.

### Summary

Under conditions which obviate the possibility of the presence of extraneous moisture or hydrogen bromide, sodium bromide, sodium chloride, hydrogen chloride, methyl bromide, methylene bromide, *n*-butyl bromide, and boron trifluoride all promote the aluminum bromide-catalyzed isomerization of *n*-butane. Alumina increases the rate in the presence of hydrogen bromide.

These results can be correlated by the hypothesis that tetrahedrally coordinated aluminum groups such as  $\text{AlX}_4^-$  and  $\text{HAlX}_4$  are the true catalysts for paraffin isomerization.

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(18) See ref. 3, footnotes 18, 19, 20.