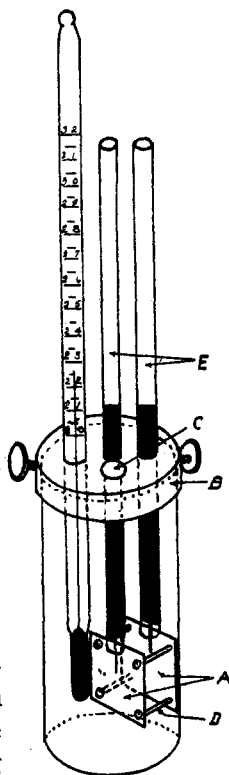


A thermometer and two glass tubes pass through the cap. The hole C allows the air to escape when the electrode is immersed into a solution. The platinum connecting wires, which are welded to the electrodes, are protected by being sealed in the tubes E, in which mercury is placed to connect the electrodes with the bridge leads.

The electrodes A are of No. 30 B & S gauge platinum foil 2 x 2 cm. squares set one cm. apart. They are firmly fastened together by means of four glass pins as shown (D). The pins have small enlargements two millimeters from each end, which serve as collars and prevent the electrodes from being crowded together. The ends of the pins pass through the electrodes and are clinched. In this way they are firmly held in place.

An ordinary 100 cc. hard glass beaker may be used to complete the cell.

The electrode has proven so convenient and trustworthy, that the writer desires to bring it to the notice of his fellow chemists and others who may perhaps find use for it, since it can well be adopted in other lines of work on conductivity. It can easily be constructed by any one having a little skill in making apparatus.



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### CORRECTION.

In the February JOURNAL, page 361, line 25 should read " $\gamma = 10 \div \text{no. of centimeters,}$ " instead of " $\gamma = 1 \div \text{no. of centimeters.}$ "

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## THE REARRANGEMENT OF ISO INTO TERTIARY BUTYL BROMIDE.

BY A. MICHAEL, E. SCHARF AND K. VOIGT.

Received January 4, 1916.

The structural rearrangement of an alkyl halide was first proven by Eltekow,<sup>1</sup> who found that isobutyl and isoamyl bromides are partially converted, by heating in a sealed tube to 230°, into the corresponding tertiary derivatives. Eltekow, and also Aronstein,<sup>2</sup> who later demon-

<sup>1</sup> *Ber.*, 6, 1258 (1873); 8, 1244 (1875).

<sup>2</sup> *Rec. trav. chim.*, 1, 1346 (1882).

strated the conversion of primary into secondary propyl bromide, were unable to reverse the reaction, although in no case could a complete isomerization be realized. It was only in 1907 that Faworsky<sup>1</sup> succeeded in proving that secondary and tertiary alkyl halides could be partially reconverted by heat into the primary products and thus explained why these reactions are limited. Michael and Leupold<sup>2</sup> found that the isomerization of isobutyl bromide begins and proceeds very slowly at 92–95°, but rapidly at 180°, and that it is much accelerated by increasing the surface of the liquid in proportion to its mass. A condition of equilibrium is reached with the formation of about 74% of tertiary from iso and about 26% of iso from tertiary butyl bromide. The change of the tertiary bromide begins, however, at a much higher temperature than its isomer and proceeds slowly even at 180°. It is evident that the relations between the velocities of isomerization do not harmonize with the usual assumption that they determine the limit of such a reaction; thus, a mixture of 74% iso and 26% tertiary butyl bromide, *i. e.*, in the proportion representing the equilibrium of the bromides in the heat, undergoes no change at 140°, although at that temperature the iso compound alone rapidly isomerizes, while the tertiary bromide alone remains practically unchanged.

The investigation was continued by Michael and Zeidler,<sup>3</sup> who showed that the isomerization of isobutyl bromide depends to a remarkable degree on the purity of the compound, very small amounts of certain substances being capable of retarding it almost completely at temperatures at which the pure product changes rapidly. Several of their preparations could be distilled only a limited number of times without undergoing some decomposition and isomerization; indeed, with two of them a small amount of tertiary bromide was formed on standing for several weeks in a brown desiccator at room temperature. The repeated fractionation of their isobutyl bromide removed some unknown impurities, whose presence greatly retarded the isomerization. In the present paper, we have endeavored to ascertain the conditions for preparing a purer isobutyl bromide; to examine the properties of such a product; and to study its rearrangement into tertiary butyl bromide quantitatively. Unfortunately, the purer substance shows such an extraordinary instability and sensitivity to the influence of positive and negative catalytes that we have not succeeded in obtaining better, *i. e.*, more constant, quantitative results than in the previous investigations. The purest isobutyl bromide was obtained by heating isobutyl alcohol with hydrobromic acid in sealed tubes to 65°; it is essential, however,

<sup>1</sup> *Ann.*, **354**, 325 (1907).

<sup>2</sup> *Ibid.*, **379**, 263 (1910).

<sup>3</sup> *Ibid.*, **393**, 81 (1912).

to use the alcohol and acid in a very pure condition. For this purpose, Merck's best alcohol was fractionated until a practically constant boiling product was obtained, which was then converted into the boric ester, the latter fractionated *in vacuo* until constant boiling, and then saponified. The hydrobromic acid was prepared catalytically, using pure bromine and electrolytic hydrogen.

To what an astonishing degree the properties of isobutyl bromide are influenced by the presence of minute, intangible impurities, is shown by the following comparison of some of the properties of our purest product with those noticed by previous observers. Isobutyl bromide has been always considered a stable substance that could be distilled an unlimited number of times without undergoing any decomposition. In the first seven preparations of the bromide we endeavored each time to increase the quality of the product by changes in the method, and added purity of the chemicals, and we noticed that the stability of the bromide decreased in direct proportion to its purity. With the eighth preparation we obtained it in a condition that any further slight changes we made did not perceptibly influence its properties. Preparation VI could be distilled twice under ordinary pressure without forming hydrobromic acid, VII only once and VIII, and the later products, not at all. Equally sensitive to the purity is the capacity of the bromide to isomerize. Michael and Leupold<sup>1</sup> heated their carefully prepared product at its boiling point for 50 hours without being able to prove the formation of tertiary bromide. Our purest products could not be distilled without some of that substance being formed; indeed, this change took place slowly when it was kept in a brown desiccator at room temperature. The same observers were able to study the rearrangement in sealed bulbs at temperatures up to 235° and only at about 260° did they notice a decided decomposition. Our best products often became brown through decomposition at 108° and at 142° they could only be heated a short time; at 260° the liquid flashed with total decomposition. Michael and Zeidler<sup>2</sup> succeeded in preparing a bromide from a comparatively inert product by repeated fractionation that practically reached the limit of rearrangement after one hour at 142°, but our purest products were equally, or more sensitive, after one distillation in a vacuum; indeed, in our last preparations the crude, undistilled products were extremely reactive.

Not alone in the liquid, but, also, in a gaseous state, is our purest isobutyl bromide much more susceptible to rearrangement than the products hitherto examined. Thus, Michael and Leupold<sup>3</sup> were unable to detect

<sup>1</sup> *Ann.*, 379, 305 (1910).

<sup>2</sup> *Ibid.*, 393, 104 (1912).

<sup>3</sup> *Ibid.*, 379, 301 (1910).

any change at  $142^{\circ}$  and, at  $184^{\circ}$ , only 2.7% of tertiary derivative was formed in  $2\frac{1}{2}$  hours; our Preparation VII showed about the same amount after 3 hours at  $100^{\circ}$  and, after  $\frac{1}{2}$  hour at  $184^{\circ}$ , it gave 53.5% tertiary butyl bromide. It seemed of interest, therefore, to determine the vapor density of this bromide. Michael and Leupold could not prove dissociation at  $184^{\circ}$ , although tertiary butyl bromide at that temperature broke down to the extent of 36%. At  $142^{\circ}$ , in a Meyer apparatus, we were unable to prove dissociation with certainty,<sup>1</sup> at  $184^{\circ}$  an amount of gas was obtained almost at once that corresponded to the normal vapor density, then for 20 minutes a further evolution of gas gradually occurred until about 50% of the bromide was dissociated. This result makes the nature of the rearrangement in gaseous condition at  $184^{\circ}$  uncertain, since, if isobutyl bromide dissociates at that temperature, evidently part of the change may proceed in this way. On the other hand, the reaction undoubtedly takes place intramolecularly in gaseous condition, as we observed the formation of tertiary bromide at  $100^{\circ}$ , while dissociation of isobutyl bromide could not be proven at  $142^{\circ}$ .

We also examined the behavior of our purest bromide in gaseous state towards asbestos, glasswool, sand and other substances that, according to Konowalow,<sup>2</sup> dissociate the vapor of such organic halides catalytically. In agreement with the results of Michael and Leupold,<sup>3</sup> we found at a temperature ( $142^{\circ}$ ) where the vapor density of the bromide is normal, that these substances are inert, as when introduced into the gas they caused no change in its volume. Even the addition of powdered "Geraeteglas," which, as we shall presently describe, increases the rearrangement of the bromide in a liquid condition very considerably, had no effect on it in a gaseous state. While we were unable to find a substance that acts as a positive catalyte on the dissociation of gaseous isobutyl bromide, it follows from our results that the phenomenon is dependent to an extraordinary degree on the purity of the compound, *i. e.*, on the removal of most minute traces of a substance or substances that show a negative catalytic influence. This result should be given full consideration in future investigations of this and similar compounds. We confirmed, too, the observations of Michael and Zeidler<sup>4</sup> on the action of negative catalytes on the liquid bromide with our purest product; such substances, as diisobutene, iso and tertiary butyl alcohol, when

<sup>1</sup> The analysis of the contents of the apparatus after heating showed indeed the presence of about 5% tertiary bromide, which according to Roozeboom's (*Ber.*, 14, 2396 (1881)) determinations would cause 0.5% dissociation, but the tertiary product may have been formed by direct isomerization.

<sup>2</sup> *Ber.*, 18, 2808 (1885).

<sup>3</sup> *Ann.*, 379, 311 (1910).

<sup>4</sup> *Ibid.*, 393, 83 (1912).

added in a small proportion, greatly decrease not only the rearrangement but the limit of the reaction.

Ground surfaces, whether of glass or of quartz, also act as negative catalytes on the rearrangement of the bromide in the liquid state. This is very noticeable when the experiments are conducted in small Hofmann bottles with ground-in stoppers and it is remarkable that the isomerization is more retarded in quartz than in glass vessels. Thus the mean value, for 1 hour at  $108^{\circ}$ , in glass bottles was 5.2%, and in those of quartz 1.9%, of tertiary bromide. In agreement with the conclusion that the ground surfaces act catalytically on the liquid bromide is the fact that in the presence of an extremely small bubble of air in the bottles the isomerization is considerably less retarded, as under the same conditions of heating, the mean values rose to 11.7% in glass and 3.8% in quartz bottles. This conclusion was further confirmed by carrying out the experiments in a quartz bottle with a long capillary neck, and with bulb only filled to one-half, and in a completely filled Hofmann bottle of the same material, when, under like conditions of heating, the mean value in the long bottle was 11.7% and in the short one 3.8% of tertiary bromide. Although the bromide in these experiments remained colorless after heating, it seems not improbable that the retardation of isomerization is due to the formation of by-products in so minute an amount that the change of coloration is not perceptible to the eye.

According to Michael and Leupold the limit of the rearrangement of iso into tertiary butyl bromide is reached when about 74% of the latter product is formed, while Michael and Zeidler, with a purer product, found it to be about 76%. With our purest isobutyl bromide the results were less concordant. Thus, with Preparation VII, we obtained 81.6% tertiary product after heating 3 hours, and 81.2% after 6 hours, at  $142^{\circ}$ , while VIII gave 75.5 and 69.1% after  $1\frac{1}{2}$  and 3 hours at the same temperature and 67.6, 73.2 and 67.0% after  $\frac{1}{4}$ ,  $\frac{1}{2}$  and 1 hour at  $184^{\circ}$ . At a lower temperature the limit was considerably less; at  $108^{\circ}$  only 16.4, 20.2 and 19.8% of tertiary product was formed after heating for  $\frac{1}{2}$ , 2 and 4 hours. These results are in accordance with the tendency of very pure isobutyl bromide to decompose readily, with the formation of unknown by-products that materially interfere with the rearrangement.

The conversion of a primary alkyl bromide into an isomer through the use of a chemical reagent was first noticed by Kekulé and Schroetter,<sup>1</sup> who found that normal propyl bromide is largely converted into the secondary product by heating with aluminium bromide. Gustavson<sup>2</sup> examined the reaction more carefully and found that it is complicated by the formation of a double compound of the salt with unsaturated

<sup>1</sup> *Ber.*, 12, 2280 (1879).

<sup>2</sup> *Ibid.*, 16, 958 (1883).

hydrocarbons formed in the process and that this double compound is also capable of converting the normal into the secondary bromide. He also noticed that the rearrangement is dependent on the temperature and on the amount of the salt. In the same manner trimethylene bromide has been converted into propylene bromide.<sup>1</sup> It seems probable that these changes are indirect, that is, the aluminium salt enters into chemical union with the bromide, and we thought it of interest to examine whether our reactive product is subject to direct, positive, catalytic influences.

It is remarkable that Jena "Geraete" glass contains such a positive catalyte, as rearrangement in it takes place almost three times as fast as in Jena hard, or ordinary soft glass. Thus, in "Geraete" glass after  $\frac{1}{2}$  hour at  $108^\circ$  about 44% of tertiary derivative was formed but only 16.9% in hard glass. We were unable to determine whether the glass itself acts directly as the catalyte, or through the formation of another compound by the chemical action of the bromide. If the latter suggestion should be correct the amount of new substance thus formed must be practically infinitesimal in quantity, for we boiled powdered "Geraete" glass a long time with isobutyl bromide and were unable to detect a solid residue in evaporation of the liquid.

The main difference between "Geraete" and the other varieties of glass used in our experiments is that it contains a considerable percentage of zinc oxide. It may be supposed, therefore, that zinc bromide formed in the action of the bromide on the glass is the active catalyte in the conversion. Indeed, this salt acts in a most minute amount as an extremely powerful positive catalyte. Thus, the presence of about 0.0001% of the salt almost doubled the rearrangement, while its presence in somewhat greater proportion (0.0004%) only increased the velocity of the reaction about 25% and caused the formation of colored by-products in small amounts and in presence of an appreciable amount the bromide after heating was dark colored and contained no tertiary product. The activity of zinc bromide in such an infinitesimal amount led us to examine whether so powerful a reagent as hydrobromic acid would extract zinc from "Geraete" glass, but we were unable to detect the presence of the metal in the acid, although the substances were digested for some hours. It is remarkable that the vessels of "Geraete" glass are less active on second use but they then show no change on further employment.

Mercuric chloride also acts as a strong positive catalyte. This salt is somewhat soluble in the bromide and solutions containing as little as 0.02% give high values of tertiary product on heating a short time at  $56^\circ$ . Another positive catalyte is hydrochloric acid; a solution of bromide with 0.3% acid contained 3% of tertiary bromide, after standing at room

<sup>1</sup> Gustavson, *J. prakt. Chem.*, [2] 36, 303 (1887).

temperature for 3 days, and the results obtained in heating such a solution showed a direct proportionality between time and percentage of tertiary bromide. On the other hand, calcium bromide and aluminium oxide are inert, and the addition of a trace of water to the bromide showed no appreciable influence at a low temperature.

The extreme susceptibility of the bromide to catalytic influences suggested that even air may play a role in the rearrangement. We found that isobutyl bromide is able to absorb a small amount of air, which may be easily shown by heating a sealed bulb with a long capillary tube and filled with bromide to within 10–15 mm. of the narrow end, when the liquid soon completely fills the vessel. An examination of the contents of the capillary tube and the bulb separately for tertiary bromide showed that the narrow part, which evidently contained a larger percentage of dissolved air, gave a somewhat greater proportion of the reaction product. The difference increased when the surface exposed to air was increased, as we were able to show by modifying the experiment; a second bulb was blown midway in the capillary of the container, which was filled with bromide until the upper bulb was half full and the experiment completed as before. These results appear to explain the fact noticed by Michael and Leupold<sup>1</sup> that the increase of surface in proportion to the mass of bromide increases the velocity of rearrangement. It seems probable that there is no influence of the surface *per se* on the rearrangement and that the larger velocity in wide than in narrow tubes in the experiments of Michael and Zeidler was due to a greater absorption of air, since the relation between surface and mass of the bromide was thereby increased. One may, therefore, refer to the influence of surface when the rearrangement is performed in the presence of air and to obtain comparable results under such conditions the mass of bromide and exposed surface should be the same in the experiments.

The above conclusion on the action of air is confirmed by the results obtained in heating the bromide in a homogeneous, liquid phase and in presence of a vacuum, although the results are less concordant among themselves, which is probably due to the experimental difficulties, than in the preceding experiments. For this purpose the bromide was first freed from dissolved air and, in one set of experiments, the bulbs with capillary ends were filled so that the expansion of the liquid on heating caused it to occupy the vacuum over it, while, in the second series, a vacuum still remained over the hot bromide. No difference in the mean values of tertiary bromide formed was found in these experiments, but in both series the amount was less than when the reaction proceeded under comparable conditions in the presence of air.

The results just described have a bearing on the question, whether

<sup>1</sup> *Ann.*, 379, 309 (1910).

the rearrangement of isobutyl bromide is subject to the influence of the free space over the liquid. Eltekow<sup>1</sup> heated the same amount of bromide in tubes of equal diameter but unequal lengths and concluded that the velocity of the reaction increases with the free space above the liquid. Michael and Leupold<sup>2</sup> repeated the experiment with iso, and also with tertiary, butyl bromide at temperatures between 140° and 235°, employing a more exact method than Eltekow. They concluded that the free space exercised little or no influence on the reaction. Later, Michael and Zeidler<sup>3</sup> made similar experiments with isoamyl bromide and found that the presence of much free space increased the rearrangement from 0.6 to 2.0%. It obviously follows from the fact that absorbed air acts as a weak, positive catalyte, that the amount of the air may under certain conditions affect the extent of the rearrangement, but not necessarily, since the air present may suffice to saturate the bromide under the conditions of the experiment, in which case the excess should not exert a further influence.

The results, too, permit, in our opinion, a definite conclusion in regard to the mechanism of the rearrangement of iso into tertiary butyl bromide. Eltekow<sup>4</sup> concluded from the increase of reactivity with free space over the liquid that the reaction occurs mainly in the gaseous bromide, *i. e.*, through dissociation into isobutene and hydrobromic acid and subsequent addition. Later<sup>5</sup> when he found that the rearrangement proceeds at a temperature lower than that of the dissociation, he concluded that the isomerization takes place directly through intramolecular shifting of the atoms. This interpretation is supported by the results of Michael and Leupold,<sup>6</sup> who gave the view a consistent theoretical basis, while Aronstein,<sup>7</sup> Faworsky<sup>8</sup> and Brunel<sup>9</sup> assume that the reaction proceeds through dissociation. The latter view represents the conservatism that has been almost invariably shown in the development of chemical theory; at first the dissociation theory was fought with a determined opposition; then, after its general adoption, an equally determined opposition is shown to other views that stand better in harmony with the observed results. Since isobutyl bromide has a greater content of free *chemical* energy than the tertiary isomer, there must exist a tendency in it to isomerize and it would be an unstable compound under ordinary conditions, if its free

<sup>1</sup> *Ber.*, 8, 1247 (1875).

<sup>2</sup> *Ann.*, 379, 265 (1910).

<sup>3</sup> *Ibid.*, 385, 292 (1912).

<sup>4</sup> *Ber.*, 8, 1244 (1875).

<sup>5</sup> Dissertation (1884); see Faworsky, *Ann.*, 354, 326, 333 (1907).

<sup>6</sup> *Ann.*, 379, 264 (1910).

<sup>7</sup> *Rec. trav. chim.*, 1, 134 (1882).

<sup>8</sup> *Ann.*, 354, 325 (1907).

<sup>9</sup> *Ibid.*, 384, 245 (1911).



*chemical* energy could overcome the chemical hindrance to the change. This chemical hindrance is represented by the affinity of bromine and the single hydrogen of the methine group to the other atoms in the molecule, primarily, however, to the carbons to which they are directly joined. With the rise of temperature this hindrance decreases while the substance is increasing in its free energy and, at a certain point, the value of the equation chemical affinity plus free *chemical* energy divided by chemical hindrance becomes positive. At this point an intramolecular rearrangement will occur, because by so doing the maximum increase of entropy with minimum expenditure of energy will be realized. In the fact that in laboratory experiments rearrangement and dissociation are sometimes concomitant lies no proof that the isomerized molecule has been formed through the latter process; indeed, it is more likely that we have unnecessarily added so much energy to the system that the isomerized product has been decomposed.

To reconcile the fact that the temperature at which the rearrangement of isobutyl bromide occurs is much lower than that at which dissociation takes place, Faworsky<sup>1</sup> refers to the researches of Menshutkin and Konowalow<sup>2</sup> and Konowalow,<sup>3</sup> who found that many substances, such as asbestos or powdered glass, may lower very considerably the temperature of dissociation of similar products in a gaseous condition; also, to those of Konowalow<sup>4</sup> and Zelinsky and Zelikow,<sup>5</sup> where, in the presence of free acid, certain esters which are otherwise stable decompose on distillation. The experiments of Menshutkin and Konowalow were repeated by V. Meyer and Pond,<sup>6</sup> who were unable to confirm their results, then Michael and Leupold<sup>7</sup> failed to notice catalytic influence of such substances on the vapor of iso and tertiary butyl bromides and, finally, we were equally unsuccessful with our purest isobutyl bromide. We found, indeed, that hydrochloric acid acts as a positive catalyte on the isomerization of liquid isobutyl bromide, but in the dissociation of that compound along with the similar hydrobromic acid an unsaturated hydrocarbon is formed and such a substance retards the reaction very considerably, indeed prevents it entirely when present in 2 or 3%. Brunel<sup>8</sup> heated isobutyl bromide to a very high temperature and concluded that catalytic influences entered into the reaction under these conditions and also in the experiments of Michael and Leupold with liquid bromide. However,

<sup>1</sup> *Ann.*, 354, 333 (1907).

<sup>2</sup> *Ber.*, 17, 1360 (1884).

<sup>3</sup> *Ibid.*, 18, 2808 (1885).

<sup>4</sup> *Z. physik Chem.*, 1, 63 (1887); 2, 6 (1888).

<sup>5</sup> *Ber.*, 37, 1374 (1904).

<sup>6</sup> *Ibid.*, 18, 1623 (1885).

<sup>7</sup> *Ann.*, 379, 300-304 (1910).

<sup>8</sup> *Ibid.*, 384, 245 (1911).

his results are not only inconclusive, but the conditions of the experiments permitted no safe inference in regard to the nature of the rearrangement even in the gaseous phase,<sup>1</sup> the more so as we now know that the temperature of dissociation depends on the purity of the bromide.

The facts revealed in this investigation stand in such a direct opposition to explanation of the isomerization proceeding by dissociation that the view is now untenable. This conclusion is inevitable when we consider that the stability of isobutyl bromide at ordinary temperature depends on the presence of an anticatalyte, and that in a pure state it slowly isomerizes, while no direct evidence of dissociation could be proven in gaseous condition at 142°; then, that the process occurs with equal facility in the liquid as it does in the liquid-gaseous phase, and, finally, that the addition of certain catalytes in infinitesimal amounts to the liquid bromide causes an enormous acceleration of the change at low temperatures, whereas no catalyte has been found that influences it in a gaseous condition.

Some of these relations are difficult to explain. Thus, it seemed probable that isomerization would take place more readily in gaseous than in liquid bromide, as the gaseous molecule appears to have the larger content of energy; also, that catalytic influence would then come readily into play. An explanation may be found that the chemical change in the liquid state takes place not in the separate molecule, but in an aggregation of them, the so-called "polymolecule,"<sup>2</sup> whose total energy may be greater than that of the gaseous molecule, and which disappears when the bromide passes into the gaseous condition. This, too, may explain the action of positive catalytes on liquid and not on gaseous bromide, the catalytes uniting with the "polymolecules" to form larger complexes with still more energy.<sup>3</sup> We have shown in this research that the purest isobutyl bromide we could prepare is not a stable body, even at ordinary temperature, and that it differs so much in many of its properties from those of a product usually considered chemically pure, that it almost seems like a different compound. To what extent do the marvelous relations between purity, properties and catalytic forces, that are so manifest in isobutyl bromide, appear in other substances? This is a new question which science can only answer by laborious investigation, but it certainly seems not improbable that it is not an isolated case and that there are other compounds, whose existence and properties under ordinary conditions depend on the play of obscure catalytic forces.

<sup>1</sup> Michael and Zeidler, *Ann.*, **393**, 89 (1912).

<sup>2</sup> Kekulé, *Ibid.*, **106**, 141 (1858); Michael, *Ber.*, **34**, 4028 (1901); **39**, 2140, 2570 (1906); *THIS JOURNAL*, **32**, 991 (1910).

<sup>3</sup> Michael, *Am. Chem. J.*, **39**, 4 (1908).

## EXPERIMENTAL PART.

## Preparation of Isobutyl Bromide.

According to Michael and Zeidler,<sup>1</sup> the best method of preparation consists in saturating at 0° a mixture of equal parts of isobutyl alcohol and constant boiling hydrobromic acid with gaseous hydrobromic acid, and heating the mixture in a sealed tube to 75–80°. The bromide obtained in this way was decidedly more sensitive to rearrangement than that prepared by any other method and a very reactive product was obtained from it by repeated fractionation. By very careful purification of all the products used in the reaction, and changes in the manipulation, we succeeded in improving the quality of isobutyl bromide made by this method to such an extent that the crude substance showed great reactivity.

The purest isobutyl alcohol obtainable was fractionated three times, using a long Hempel column; from 1 kilo about 400 g. of a product were obtained, which boiled constant within 0.15°. The isobutyl alcohol of commerce often contains traces of a basic substance, which cannot be removed by distillation and even passes over into the boric ester made from it. The alcohol purified by distillation was, therefore, extracted repeatedly with small amounts of dilute sulfuric acid, then several times with water and dried, first over fused potassium carbonate, then over lime. This was heated 6 hours at 160–175° in an autoclave with  $\frac{1}{4}$  of its weight of pure boric anhydride.<sup>2</sup> Isobutyl boric ester cannot be distilled under ordinary pressure without some decomposition and the residue left after distilling off the excess of alcohol was, therefore, fractionated two or three times *in vacuo*. In order to indicate smaller changes in the pressure during the fractionation than is possible with the usual mercury manometer, we used in connection with that instrument, one filled with nitrobenzene. The pure ester was then saponified by boiling a short time with aqueous alkali, in a flask connected with a return cooler, the alcoholic layer separated, extracted once with a little water and then dried over freshly heated lime. This product, which undoubtedly still contained a trace of water, boiled constant at 108.0° under 767 mm. We omitted drying the alcohol over calcium shavings in all our later preparations, as we were unable to procure calcium, which did not contain either carbon or nitrogen. The isobutyl alcohol prepared in this way was undoubtedly much purer than any product that had been previously made. The advantage of purifying the alcohol through the boric ester is not alone that the ester boils much higher than the alcohol, which thus permits the removal by distillation of all substances that have approximately the boiling point of the alcohol but which do not form an ester. It also permits a much sharper separation from the higher and lower

<sup>1</sup> *Ann.*, 393, 104 (1912).

<sup>2</sup> Counciler, *J. prakt. Chem.*, [2] 18, 382 (1878).

boiling alcohols, that are undoubtedly contained to an appreciable extent in all preparations of isobutyl alcohol purified solely by fractionation, as, according to Counciler's rule,<sup>1</sup> the difference between the boiling points of such alcohols is increased three times in the corresponding boric esters.<sup>2</sup> Another great advantage in this method of purification lies in the facility with which the boric esters may be saponified. Before using this method we endeavored to purify the alcohol through the benzoate; but, although we obtained a product that boiled absolutely constant, we were unable to saponify it, unless alcohol was used, without the formation of by-products.

In one of our earlier preparations of the bromide we prepared the hydrobromic acid from bromine and phosphorus, the latter substance having been purified by treatment with carbon bisulfide. In one preparation on passing the gaseous hydrobromic acid into the alcohol and acid mixture, a small amount of a white crystalline substance was formed, which showed a decided odor of garlic and was found to contain arsenic. Although no arsenic could be detected in the bromide after its purification, it showed an unusually high value of rearrangement, and there may have been, notwithstanding, traces of an arsenic compound present, which acted as a positive catalyte. In the subsequent preparations of hydrobromic acid using red phosphorus, we employed a product prepared by heating yellow phosphorus, that was freed from arsenic by two distillations with steam, and the bromide always gave smaller reaction values.

In all our later preparations of bromide, we used hydrobromic acid made catalytically from electrolytic hydrogen and bromine that had been carefully purified according to the directions of Baxter, Thorvaldson and Cobb.<sup>3</sup> The acid prepared in this way always contained a small quantity of free bromine which was removed by heating the aqueous product, saturated at 0°, after the addition of a sufficient amount of pure iron (such as is used for atomic weight work) and collecting the gas in water; after the gas ceased to come off the residue was distilled and the distillate used as the constant boiling acid.

A mixture of 40 cc. isobutyl alcohol and 40 cc. constant boiling hydrobromic acid was brought into a tube, cooled off to 0°, and saturated with gaseous hydrobromic acid, obtained by warming a saturated acid solution, to which pure iron had been added in sufficient amount to expel

<sup>1</sup> *J. prakt. Chem.*, [2] 18, 385 (1878).

<sup>2</sup> Cohn, *Pharm. Zentralhalle*, 1911, 482. We modified the method used by this chemist, using only 5% strong sulfuric acid to esterize, but the boric ester prepared in this way could not be obtained in a pure state.

<sup>3</sup> THIS JOURNAL, 33, 319 (1911). We are greatly indebted to Professor G. P. Baxter for the use of the apparatus and other facilities in his laboratory; also to Mr. F. L. Grover for his kind assistance in the preparation of the acid.

most of the air in the vessel. The operation was done in an apparatus composed entirely of glass, and, to avoid a decomposition of the acid by the ground glass surfaces, in a darkened room. After sealing the tube it was placed in an iron tube closed at both ends, and heated in a water bath for 3-4 hours at 65°. The yield of the colorless bromide was about 60 g.; a small amount was formed on further heating of the tube, but it was found inadvisable to unite it with the main product. The bromide was extracted with about 4 times its volume of water in a shaker, until the last extract ceased to give an immediate reaction with silver nitrate, then dried several days over fused calcium bromide and, finally, an hour or two before the distillation, by addition of a small amount of pure phosphorus pentoxide. The fractionation should be done in a partial vacuum, as the operation under ordinary pressure leads to the formation of some tertiary bromide. For this reason, too, a sharp boiling point of the pure bromide could not be obtained under ordinary pressure; thus, a small quantity boiled between 91.1-91.25° (755.5 mm.), while absolutely sharp and constant boiling points could be obtained with less pure products only.

All the chemicals used in the preparation of the bromide were as pure as could be made. Phosphoric anhydride was sublimed in oxygen; ordinary distilled water was distilled with addition of permanganate and then redistilled. The glass apparatus was cleaned with a mixture of nitric and sulfuric acids, then thoroughly washed out with water and finally steamed for a long time. The distillation was done in a specially constructed flask with double jacket, in which the thermometer was fastened in the inner tube by a platinum spiral and ground glass stopper. To dry this apparatus the bulb was immersed in a bath of Wood's metal and a glass tube introduced, which reached to the bottom of the bulb and to whose upper end a glass cap was sealed, which fitted on a cork on the neck of the fractionating flask: pure and dry air was then aspirated through the apparatus for a long time. The receivers were always in larger glass vessels, the necks of which were joined to the lateral tube of the fractionating flasks by means of corks.

Altogether eleven preparations of isobutyl bromide were made. In the first seven experiments the method was gradually improved and we found that the reactivity of the products varied accordingly: the last four were practically all made according to the directions given above; slight variations which we tried had no effect on the quality of the products. In the following experiments the preparations used up to VII are designated by Roman numerals; the subsequent products are grouped together under VIII. The first six products could be distilled without change under ordinary pressure in flasks of hard or soft glass, with the exception of a single flask of unknown composition, in which a decomposition, with

formation of hydrobromic acid and also a slight rearrangement to tertiary butyl bromide, was always noticed. The only difference between VII and the later preparations, was that it could be distilled once under ordinary pressure without formation of tertiary bromide or hydrobromic acid. Some of the earlier preparations gradually gave off hydrobromic acid on standing over phosphoric anhydride. Thus, a constant boiling product, after standing several days with the pentoxide, not only evolved some acid, but was colored brown; after extracting with water and drying, it boiled within  $0.4^\circ$  and contained some diisobutene. Our purest products also gave off traces of hydrobromic acid on standing a long time over the pentoxide, which should be, therefore, used with care as a drying reagent.

The most reactive preparation of bromine obtained by Michael and Zeidler<sup>1</sup> was made by heating carefully purified hydrobromic acid and isobutyl alcohol to  $75^\circ$ . This product, after 1 fractionation gave, on heating 1 hour in the vapor of xylene, 15.1% of tertiary bromide and, by repeated fractionation, a product that in some of the experiments gave about 74%, which is near the limit of rearrangement. Preparation VII before distillation yielded 53.1% tertiary bromide in  $\frac{1}{2}$  hour in xylene and 63.2% after 1 distillation and in 1 hour also gave 74%. Preparation VIII, undistilled, gave 12.9% of tertiary product after heating  $\frac{1}{4}$  hour at  $108^\circ$  and 16.3% after 1 distillation *in vacuo*, which represents the normal rate of rearrangement. We noticed with several of our earlier preparations that the velocity of isomerization could be increased up to a certain point by fractionation and that a subsequent operation led to a decrease. This was very noticeable with III, which, heated  $\frac{1}{2}$  hour in xylene, gave before fractionation 11.1% of tertiary bromide and 60.7% after two such operations, while the product obtained in the third process gave only 27.3%, although no decomposition or change could be noticed in the product.

#### Rearrangement in a Liquid Phase.

The methods used in studying the reaction were about the same as described in the previous papers.<sup>2</sup> The bromide was usually heated in a short bulb of Jena hard glass, one end of which was round and the other pulled out to a very narrow tube about 10 cm. long. The dried vessels were filled with bromide by means of a pipet, which consisted of a capillary tube, in whose upper end a small bulb was blown. The wide end of the tube was connected with a small U-tube, containing some calcium chloride and whose other side had a glass plunger working through a piece of rubber tubing. The tubes were usually filled to about one-half, so that the bromide was also present in a gaseous phase, but in some experiments the liquid completely occupied the vessel. In the earlier

<sup>1</sup> *Ann.*, 393, 104 (1912).

<sup>2</sup> *Ibid.*, 379, 304; 393, 94.

experiments the bulbs, before sealing, were connected with small drying tubes containing phosphorus pentoxide; later they were put in narrow, thin test tubes whose open ends were closed by drying tubes, and then placed in a cooling mixture of salt and ice. It was not always possible to prevent the formation of the slight white ring on sealing the containers,<sup>1</sup> but our experiments show that this has no noticeable influence on the result of the rearrangement. In other experiments, we used small Hofmann bottles, made either of soft glass or of quartz, which were enclosed in thin, narrow, sealed glass tubes. The bulbs were heated in the vapor of liquids, which were contained in Meyer vapor density mantels and whose walls were covered with asbestos paper. To determine the amount of tertiary bromide the heated product was put in a shaker for 15 minutes, with 50 cc. water and at first the filtered solution, later the whole liquid, titrated with  $N/10$ , or  $N/25$  solutions, of silver nitrate and ammonium thiocyanate, using ammonium iron alum as the indicator. With 0.1 g. bromide and  $N/25$  solutions the determinations were exact to 0.15%.

#### Normal Rearrangement in Glass and Quartz.

To determine the quality of the bromide, the product was heated for 15 minutes in the vapor of isobutyl alcohol (108°) in Jena hard glass tubes of 6 mm. internal diameter. Four of our best preparations gave the following results:

16.4, 15.7, 16.9, 16.3; mean, 16.3%.

This mean value (16.3%) may be considered as representing the normal rearrangement of isobutyl bromide under these conditions.

The mean value with a bromide of less purity is lower than that of the pure bromide. Thus, some of our earlier preparations gave under the same conditions:

14.0, 15.2, 15.1, 14.3, 15.2, 15.2, 14.0; mean, 14.7%.

After we found that a certain variety of glass shows a decided catalytic influence on the reaction, we made a series of experiments to ascertain whether Jena hard glass also exerts such an effect. For this purpose, we employed small bottles of quartz, with ground stoppers, which were filled to about one-half and enclosed in slightly wider sealed Jena glass tubes with thin walls. The 3 bottles had round bottoms and an internal diameter of 4.3 mm. and an interior height of 4 cm.

The following amounts of tertiary bromide were obtained with VIII:

At 108.4°,	for 15 min.,	11.7, 10.4, 11.4%;
At 130°,	for 5 min.,	17.7, 16.8, 15.7%;
At 142°,	for 10 min.,	41.3, 38.3, 41.8, 41.7%;
At 142°,	for 20 min.,	56.8% and for 30 minutes 63.3%.

The mean of a number of determinations in hard, as well as in ordinary

<sup>1</sup> *Ann.*, 393, 108.

soft glass tubes of the same diameter as the bottles at  $108^{\circ}$  for 15 minutes was 12.8%, at  $142^{\circ}$  for 10 minutes was 45.9%, and for 30 minutes 63%, of tertiary bromide. In the experiments of short duration the mean values are somewhat higher in glass than in quartz, but it is safe to conclude from the results that soft and Jena hard glass exercise no perceptible catalytic influence, as the actual time of heating at the temperature of the bath was evidently somewhat less with the enclosed quartz vessels. In the experiments for 30 minutes the results are practically the same.

We noticed in these experiments that the quartz vessels, even when made of the highest quality of quartz we were able to procure, with continued use gradually showed corroded surfaces. This may have come, however, from the action of the acids used in cleaning the vessels. It is remarkable, too, that the values obtained in the first determination in small Hofmann bottles, whether made of quartz or of glass, were invariably lower than those found in the subsequent experiments; indeed, in quartz vessels we found in several cases that no rearrangement took place at first at  $108^{\circ}$

#### Influence of Catalytes on the Rearrangement.

Although Jena hard glass and ordinary soft glass, notwithstanding that part of the surface of the latter sort exposed to the liquid, but not to the gaseous bromide, in some experiments was slightly corroded and therefore acted on chemically, has no perceptible influence on the reaction, we found that it is very much accelerated in Jena "Geraete" glass. Thus, in one series of experiments, which were made in tubes of the same diameter, we obtained, at  $108^{\circ}$  for  $1/2$  hour, in Jena hard glass 16.9%, while in "Geraete" glass 44% tertiary bromide was formed. The rate, therefore, was increased almost 3 times. At  $100^{\circ}$  the highest value we noticed using hard glass (6 mm.) after 30 minutes was 9.2%; in "Geraete" glass, in a narrower tube (4 mm.) after 8 minutes 11.2% and after 15 minutes 39.6% tertiary bromide was formed. The constituent of "Geraete" glass not contained in the other varieties of glass used in these experiments is ZnO and to the amount of 4.2%.<sup>1</sup> It seemed probable, therefore, that the catalytic action of this glass is due to the zinc it contains. To test this inference we made some experiments with the addition of ZnBr<sub>2</sub>. For this purpose, we introduced 1 drop of a dilute solution of ZnBr<sub>2</sub> into bulbs of hard glass, heated the tubes carefully while aspirating dry air through them until they were perfectly dry and then performed the experiments in the usual manner. Without ZnBr<sub>2</sub>, 14.7%, with it, 23.6 and 25.9% tertiary bromide was formed. According to a determination a drop of the ZnBr<sub>2</sub> solution contained 0.00002 g. of salt; and as 0.2 g. bromide was used, the addition of about 0.0001% of this catalyte, therefore, almost doubled the velocity of the reaction. A similar experiment, made

<sup>1</sup> Ost. Lehrb. d. Chem. Technol. (6 Auflage), 279.



under the same conditions but using four drops of the salt solution, gave 32.6% tertiary bromide, while with the  $ZnBr_2$  contained in 12 drops it caused the formation of dark by-products. Indeed, the addition of  $ZnBr_2$  in appreciable amount prevents the rearrangement completely, which is probably due, however, to the secondary products formed under such conditions. We thought it possible that the reagents used in cleaning the tubes of "Geraete" glass might show an influence on the rate of rearrangement, but failed to notice a difference in the results of the experiments, whether a mixture of bichromate and sulfuric acid, or concentrated hydrobromic acid, was used. Although it may be considered certain that the catalytic action of "Geraete" glass is due to the presence of zinc we were unable to ascertain whether it is owing to the action of the glass *per se*, or to the formation of a simpler zinc compound by the chemical action of isobutyl bromide in the glass. It is certain, however, that the zinc in this glass is very resistant to the action of strong chemicals, for some of the powdered material was heated for some time with concentrated hydrobromic acid and no zinc could be detected in the liquid. If a soluble zinc compound is formed during the heating of isobutyl bromide in a closed vessel of "Geraete" glass the amount is certainly infinitesimal in quantity, since we boiled the bromide in a "Geraete" glass vessel for a considerable time and could not notice a solid residue on evaporation of the liquid in a platinum dish.

That the catalytic effect of "Geraete" glass varies very considerably, will be seen from the following experiments, where, although the vessels were all made from the same piece of tubing, no relation appears between the time of heating and the extent of rearrangement, unless the latter values were quite small.

At 80.5°, in tubes of 4 mm. internal diameter:

20	40	60	80	minutes
8	11.7	15.2	8.9%	tertiary bromide

At 108°, in tubes of 8 mm. diameter:

5	10	15	25	minutes
24.0	39.7	22.3	37.5%	tertiary bromide

We also noticed that the use of the same container of "Geraete" glass a second time was followed by a decrease of its efficiency as a catalyte, which remained then unimpaired in subsequent experiments.

In acetone (56°); new tubes:

1	2	3	hours
4.4	4.5	5.3%	tertiary bromide

In methyl alcohol (66°); tubes used a second time:

10	20	30	90	135	minutes
0.6	1.0	1.4	3.7	4.0%	tertiary bromide

Although the temperature in the second series was  $10^\circ$  higher the rearrangement values are less.

In methyl alcohol ( $66^\circ$ ); tubes used a third time:

30	60	90	minutes
1.5	2.8	3.7	%

Another salt, which acts as a positive catalyte on the rearrangement of isobutyl bromide, is mercuric chloride. This salt dissolves in the bromide to the extent of about 1.5%; such a solution after standing four days in summer at room temperature did not give the test for tertiary bromide, but the reaction proceeds readily at a somewhat higher temperature. As with the use of zinc bromide, we were not only unable to find a direct connection between the time of heating and the extent of the rearrangement, but the results were sometimes quite irregular among themselves. Thus, a series, where the bromide contained 0.07% sublimate, resulted as follows:

10	20	40	60	90	minutes at $78.3^\circ$
9.5	31.5	24.1	35.4	34.8	% tertiary bromide
	22.7				

Mercuric chloride, like zinc bromide, acts catalytically only in very dilute solution; in the vapor of alcohol 0.3% sufficed to prevent the reaction. A series, heated 40 minutes at  $78.3^\circ$ , gave

0.02	0.15	0.3	% mercuric chloride
12.7	41.2	0.0	% tertiary bromide

Calcium bromide exerted no influence on the rearrangement; nor did aluminium oxide, probably because the bromide does not react on it, as the formation of aluminium bromide, even in traces, would have been undoubtedly followed by a marked reaction.<sup>1</sup>

Hydrochloric acid, however, shows a decided catalytic influence, even at ordinary temperature. Isobutyl bromide, which was saturated with the dry acid (about 0.3%) contained 3% tertiary bromide after standing two days. In the following series a quantity of such a solution was heated to  $56^\circ$ , in a carefully ground, glass-stoppered vessel and from time to time a sample was removed for analysis:

$1/2$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	$3\frac{1}{2}$	11	hours
9.5	12.3	14.9	17.0	18.3	19.7	25.1	% tertiary bromide

These results are more regular than those in the preceding experiments and further investigation is necessary to determine whether this is due to their being carried out in the same vessel, or to the nature of the catalyte.

In their experiments on the influence of negative catalytes on the rearrangement, Michael and Zeidler<sup>2</sup> used tubes filled to about one half with the solution and the substance was, therefore, in a gaseous-liquid

<sup>1</sup> Kekulé and Schroetter, *Ber.*, 12, 2279 (1879); Gustavson, *Ibid.*, 16, 958 (1883).

<sup>2</sup> *Ann.*, 393, 105 (1912).

state. In connection with the results described below on the reaction entirely in the liquid phase, we made some experiments, using negative catalytes under the same conditions. We found that the addition of diisobutene reduced the rate of the reaction very considerably. Thus, in hard glass tubes, which were entirely filled with isobutyl bromide (VIII), the rearrangement after 1 hour at  $108^{\circ}$  was 14.0% for the liquid in the narrow tube and 12.6% for the part in the bulb; with bromide containing 2.6% diisobutene the result was 6.2 and 5.2% for the narrow tube and 3.7 and 4.0% for the bulbs. A solution containing 1.3% of the hydrocarbon gave approximately the same results, *i. e.*, 7.4 and 5.5% in the contracted and 4.4 and 4.3% in the wide part of the containers. Further experiments were made with one of the earlier preparations of bromide; heated for 1 hour at  $108^{\circ}$  the mean value of a number of experiments was 13.7% for the liquid in the bulb. The addition of the following chemicals showed a marked reduction:

2.6% diisobutene	3.6 : 3.7% tertiary bromide
3.7% tertiary butyl alcohol	3.5 : 3.5% tertiary bromide
3.2% isobutyl alcohol	3.2 : 3.1% tertiary bromide

These low values are also probably near the limit of the reaction under these conditions, as heating tubes containing the same percentage of diisobutene for 2 and 4 hours gave only 4.0 and 4.1% of tertiary product.

Under the same conditions, a trace of water added to the bromide exerted scarcely any influence on the rearrangement.

#### Influence of Air on the Rearrangement.

In the preceding experiments the tubes were only partially filled with liquid bromide, so that the reaction occurred in the presence of a gaseous phase and also of air. The determination of the rearrangement of the bromide solely in a liquid phase should give, therefore, information whether air exerts an influence and, also, on the mechanism of the reaction.

In our first experiments the bromide was brought into bulbs of Jena hard glass (6 mm.) with narrow ends about 20 cm. long. These were filled until the liquid occupied about  $\frac{1}{2}$  of the narrow tubes and after sealing the bulbs alone were heated in the bath. The contents of the bulbs gave the following values:

30 minutes at $108^{\circ}$ , 11.5, 10.0, 8.5	% tertiary bromide
60 minutes at $108^{\circ}$ , 11.3, 11.9, 11.8, 12.1	% tertiary bromide
120 minutes at $108^{\circ}$ , 16.9, 13.6, 15.4	% tertiary bromide

The transpiration of the tertiary bromide during the heating was inconsiderable, as not more than 1% tertiary bromide was found in the liquid contained in the narrow ends.

As we noticed that isobutyl bromide heated under pressure has the property of absorbing a small amount of air, we made use of this property to examine the influence of air on the reaction and, at the same time,

the rearrangement in the liquid phase. The bulbs were like those used in the above experiments, only the narrow ends were somewhat shorter (about 15 cm.); they were filled with bromide to 15–20 mm. from the open end and the expansion of the liquid on heating made it occupy the entire container. In several experiments a small amount of air remained unabsorbed, but no difference in the results was noticed. After heating the entire vessels to 108° the contents of the bulbs B and of the narrow ends C were analyzed separately.

30 minutes.		60 minutes.		
B.	C.	B.	C.	
11.8	14.6	12.5	14.2	% tertiary bromide
13.8	15.7	12.8	14.0	% tertiary bromide
11.3	13.1	12.4	14.0	% tertiary bromide
11.4	11.7	12.5	13.6	% tertiary bromide

Heating for 2 and 4 hours gave 15.4 and 18.6% for B and 18.7 and 20.1% for C. These experiments show that the greater proportion of air in the bromide contained in the narrow ends causes a slight increase in the rate of rearrangement, and any relative increase of the surface of the bromide exposed to air to the amount of liquid used should, therefore, increase the velocity of the reaction, if the bromide is not saturated. This relation is plainly noticeable in the results of the following series, in which the container was modified to increase the surface of liquid exposed to air. About 10 cm. above the bulb a second bulb was blown in the narrow end and bromide introduced until the upper bulb was half full. After sealing the entire vessel was heated and the contents of the lower and that of the upper bulb, with the small amount in the capillary tube joining the two bulbs, analyzed separately. The temperature was 108° and time of heating 1 hour.

Diameter of bulbs.....	7.5	7.0	6.5	mm.
Capillary tube and upper bulb.....	19.0	17.7	16.9	% tertiary bromide
Lower bulb.....	12.3	13.1	13.5	% tertiary bromide

The mean values for the upper and lower bulbs in these experiments are 17.9 and 13.3%, while in the preceding series, where less surface was exposed to the air, they were 14.0% for the narrow tubes and 12.6% for the bulbs.

That with more surface of bromide exposed to air the velocity of the isomerization increases was proven by Michael and Leupold,<sup>1</sup> but we deemed it of interest to repeat the experiment with our purer bromide. A bulb (6 mm. diam.) and a narrow tube (about 1 mm.) were filled to one-half with bromide and heated together; the contents of the bulb contained 55.9% and that of the tube 19.3% tertiary product. Tubes of 6 and 1.2 mm. internal diameter, heated for 1/2 hour at 140°, gave the following results:

<sup>1</sup> *Ann.*, 379, 306.

1.2 mm.	6 mm.	
37.4	63.2	% tertiary bromide
43.7	55.9	% tertiary bromide

We next endeavored to modify the conditions so that isobutyl bromide free of air could be heated either entirely in a liquid phase, or in presence of a vacuum. For this purpose, some bromide was brought into a small retort-shaped glass vessel, which was held in a slanting position, and empty bulbs, with the narrow open ends facing downwards, introduced so that they remained in the limb of the vessel. The open end fitted closely for several inches into a glass tube, ending in a glass stopcock, which was bent at a right angle and was connected to it by a piece of rubber tubing. The liquid was cooled off in ice and the apparatus connected with a Geryk vacuum pump and evacuated until about  $\frac{1}{2}$  of the bromide had evaporated, when the stopcock was closed and disconnected from the pump. The apparatus was then placed upright and the open ends of the bulbs brought under the liquid. On allowing dry air to enter slowly into the apparatus, the bulbs became completely filled with bromide. The open ends of the bulbs were then connected with a vacuum pump and either sufficient bromide evaporated in a vacuum so the expansion to the liquid completely filled the tube when it was sealed and heated, or so much more that a vacuum remained in the narrow ends above the liquid. The experimental difficulties in these experiments were considerable and the results are not as concordant among themselves as those obtained in some of the previous series. At  $108^\circ$  for 15 minutes, the mean percentage of a number of experiments was in the liquid phase alone 11.6% and in presence of a vacuum it was 11.4%. It may be concluded, with considerable probability from these results, that there is little or no difference in the rearrangement of isobutyl bromide, when it is in a liquid, or in a liquid-gaseous condition, and they confirm, therefore, the conclusion from simpler and more decisive experiments. Furthermore, a comparison of these values, with the normal value in the presence of air, which is 12.8% under the same conditions, corroborates the previous conclusion that air acts as a positive catalyte on the rearrangement.

#### Influence of Ground Surfaces on the Rearrangement.

Abnormal results are obtained when the bromide is heated in small Hofmann bottles with ground glass stoppers, whether they are made of soft glass or of quartz. In the following experiments, the interior dimensions of the bottles employed were 17 mm. high and 4 mm. wide and they were heated 1 hour at  $108^\circ$ :<sup>1</sup>

Rearrangement.	In entirely liquid phase.	With air.
Glass.....	5.3, *5.9, *4.3, 5.4%	13.4, 11.3, 10.5*%
Quartz.....	1.8, 1.7, 2.2, 2.1%	4.5, 3.9,* 2.9*%

<sup>1</sup> The figures without asterisks were obtained, using the same bottle; those which have a single mark were made in different ones.

These results show that not only is there a considerable difference between the values obtained in glass and in quartz, but, also, when the bromide is present solely in a liquid state and when air is present, although there were only small bubbles in the vessels. The influence of ground surface in decreasing the rearrangement is shown very markedly in the following series of experiments, where, in the presence of air, the bromide was heated in a quartz bottle with a long narrow neck (6 cm.), whose bulb was only partially filled with liquid, and in a completely filled Hofmann bottle of quartz.

Short bottle : 4.2, 4.2, 5.0% after  $\frac{1}{2}$  hour

Long bottle : 11.7, 10.4, 11.4% after  $\frac{1}{4}$  hour

We noticed that bromide kept in bottles with ground glass stoppers gradually became somewhat colored and that the coloration was quite marked at the ground surfaces, which had, evidently, slowly decomposed the substance. Traces of such decomposition products are probably formed on heating the bromide, when it is in contact with ground surfaces, and they act as negative catalytes. In the presence of air in a small Hofmann bottle the liquid comes much less in contact with the ground surface, and still less in the long neck vessels, and there is, therefore, a corresponding decrease in the formation of by-products. Even at a higher temperature and with air space the percentage of rearrangement in a Hofmann bottle of quartz is slow; thus for 1 hour at  $184^{\circ}$  only 3.3, 4.2 and 6.9% tertiary bromide were formed, while 67% was obtained in a glass bulb, under the same conditions.

#### Rearrangement in Gaseous Condition.

A thin, sealed bulb containing isobutyl bromide was brought into a wide glass tube, which was then evacuated to 1 mm. pressure and sealed, when the bulb was broken. The tube was heated, then cooled off in a freezing mixture, the contents washed out with water and alcohol and the analysis made in the usual manner. The results are 2-3% low, as there is a mechanical loss in the manipulation.<sup>1</sup>

Heating 3 hours at  $100^{\circ}$  gave 2.3% tertiary product; 25 minutes at  $184^{\circ}$ , in a tube of Jena hard glass, gave 34.0% and in one of a soft glass 53.5%. These results are very much higher than those Michael and Leupold<sup>2</sup> obtained with their product, who noticed no change on heating to  $142^{\circ}$  for 14 hours and only 2.7% at  $184^{\circ}$  for  $2\frac{1}{2}$  hours, and they show how markedly the reaction in gaseous condition depends on the purity of the isobutyl bromide.

#### Vapor Density Determinations.

V. Meyer's method was used, but care was taken to carry out the operation in a dry atmosphere, as Konowalow<sup>3</sup> believed that moisture affects

<sup>1</sup> Michael and Leupold, *Ann.*, 379, 313.

<sup>2</sup> *Ibid.*, 379, 314 (1910).

<sup>3</sup> *Ber.*, 18, 2808 (1885).

the results. The apparatus was thoroughly cleaned after each determination, carefully dried and the evolved gas collected over 70% sulfuric acid.

In the following two determinations Hofmann bottles of quartz were used, which were introduced into the apparatus through a Mahlmann stopcock; the bottom of the Meyer tube was covered with very thin rods of Jena hard glass. The temperature of the bath was 142°.

	I.	II.
Substance.....	0.0944 g.	0.1185 g.
Volume of gas.....	18.03 cc.	22.23 cc.
Pressure.....	757.0 mm.	760.5 mm.
Temperature.....	26.4°	25.5°
Found density.....	68.7	69.1
Calculated density.....	68.5	68.5

The volume of evolved gas became constant after several minutes and then underwent no change, even though heated for 1/2 hour. After cooling, the Meyer tube was washed out with alcohol and the amount of tertiary bromide present determined in the usual manner; in I 2.4% and in II 5.0% was found, which results are probably several per cent. too low.

In other similar experiments after the volume of gas remained constant, we introduced sand and asbestos, which, according to Konowalow<sup>1</sup> act catalytically on the dissociation of tertiary amyl chloride and other analogous compounds. The addition of these substances had no effect; nor did powdered "Geraete" glass, which accelerates the rearrangement of liquid isobutyl bromide so greatly.

The following determinations were done at 184°; in I a quartz, in II a Jena hard glass, Hofmann bottle was employed, and in both experiments the bottom of the Meyer tube was uncovered; in III a hard glass bottle was used, and there were thin rods of the same material in the apparatus.

	I.	II.
Substance.....	0.1223 g.	0.0942 g.
Pressure.....	763.5 mm.	762.8 mm.
Temperature.....	21.3°	22.6°
Volume of gas.....	23.1, 33.5 cc.	18.05, 25.85 cc.
Height of acid.....	30.1, 20.6 cm.	34.8, 27.6 cm.
Found densities.....	66.8, 45.4	66.7, 45.9
Dissociation.....	Above 50%	

I and II were done with the same preparation (VIII); Experiment III, which was done with a different one, gave a final density of 48.5. After heating about one minute in all the determinations, the rapid evolution of gas ceased, and the volumes corresponded to about that of the normal density; then a slow generation of bubbles kept up for about 15 minutes.

CAMBRIDGE, MASS.

<sup>1</sup> *Ber.*, 18, 2808.