[Contribution from the Department of Chemistry of Bryn Mawr College.]

DISSOCIATION AND REARRANGEMENT OF ISO- AND TERTIARY-BUTYL BROMIDES IN THE GASEOUS STATE AT HIGH TEMPERATURES AND THEIR FORMATION FROM HYDROGEN BROMIDE AND ISOBUTENE.

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Received June 13, 1917.

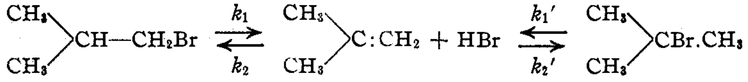
The investigation of the equilibrium reached, in the gaseous state, in the intramolecular rearrangement of iso- and tertiarybutyl bromides, was taken up by the author several years ago, as a starting point in the study of the relation between the constitution of the alkyl radicals and their affinity for various negative atoms or radicals. Results have at times been obtained which were inexplicable and apparently inconsistent with each other, but, in the end, it has been possible to propose an explanation of all of the conflicting results, as far as the rearrangement in the gaseous state is concerned, and to calculate the desired equilibrium.

The work conveniently falls under three heads:

I. The dissociation of these bromides at high temperatures.
II. The union of hydrogen bromide with isobutene.
III. The equilibrium between the bromides at 275°.

The discussion of these points must be preceded by a consideration of some of the peculiarities in the behavior of these substances.

When either iso- or tertiarybutyl bromide is heated much above 100° for any length of time a mixture of the two is likely to be obtained, although the velocity of this isomerization varies greatly. If the bromides are heated in the liquid state, the resulting mixture contains, according to Michael and Zeidler,[1] 76% of tertiary bromide; according to Michael, Scharf and Voigt,[2] in experiments with very pure bromide, a variable amount. The mixture formed by heating these bromides in the gaseous state are of variable composition depending upon the conditions of the experiment. During the heating in the gaseous state at higher temperatures, both bromides dissociate into hydrogen bromide and isobutene, as represented in the following scheme:



As the following experimental results show, when these bromides are heated to sufficiently high temperatures and sufficiently long, a normal condition of equilibrium is reached between the two bromides and their dissociation products. The variation in the composition of the products obtained from these experiments is due to the variable behavior of the

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[1] *Ann.*, 393, 92 (1912).

[2] This Journal, 38, 656 (1916).

dissociation products upon cooling. Here, as well as in the process of dissociation, curious catalytic influences come into play, and these have not been subject to exact control. All of the facts observed can, however, be consistently explained. It has become gradually more evident that the behavior of these substances in the liquid and the gaseous states presents two separate problems, and there is no assumption in what follows that the conclusions reached with regard to experiments of the latter sort are applicable to the former.

The author has already published experiments[1] with these bromides in which their susceptibility to catalytic action was established. Michael and Zeidler[2] criticized the conclusion reached on the ground that the influences designated as catalytic might rather have been "anticatalytic." This would not have affected the main point at issue, but, in any case, the term catalytic was used there, as it is here, to designate either accelerating or retarding influences.

We shall assume that in the case of two reactions related as a reaction and its reverse, any catalytic agent will affect both to the same extent; but that in the case of reactions not so related, even though they may be very similar reactions, catalysts may not affect them equally. Thus any influence affecting k_1 will affect k_2 equally, and the same with regard to k_1' and k_2'; but any given catalyst may not affect these two pairs of reactions to the same extent. As was formerly pointed out,[3] the dissociation may go on rapidly while the complete equilibrium is attained only slowly. The ratio of the undissociated bromides is plainly not a function of k_1 and k_1' alone, but of the ratios k_1/k_2 and k_1'/k_2'. If it can be shown that catalytic actions of the above sorts exist, all apparent anomalies in the behavior of these bromides in the gaseous state can be readily explained.

The catalytic action in the gaseous state can be observed in the varying rate of dissociation of the bromides, which can be followed accurately; and in the experiments on the formation of the bromides from hydrogen bromide and isobutene. The extent of the rearrangement during any given time depends upon several factors so that its significance is less obvious, but in many of the author's earlier experiments,[4] where the heating was short, the extent of the change iso ⟶ tertiary bromide runs roughly parallel to the degree of dissociation. The reason why the two are not exactly proportional and why the same parallelism does not appear in the reverse change will appear in what follows.

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[1] *Ann.*, 384, 245 (1911).

[2] *Ibid.*, 393, 92 (1912). Other objections raised by these investigators will be discussed below.

[3] Brunel, *Ibid.*, 384, 250 (1911).

[4] *Loc. cit.*

The existence of catalytic influences in connection with the dissociation of isobutyl bromide is sufficiently evident from an examination of its recorded behavior. Eltekoff[1] found no dissociation below 213°; Michael and Leupold[2] found none below 184°, and this conclusion was confirmed by Michael, Scharf, and Voigt.[3] In the author's experiments such dissociation was in several cases observed in the neighborhood of 150°, and both there and at higher temperatures the rate of dissociation varied greatly in different experiments. Dissociation of the tertiary bromide has more frequently been observed, but comparison of the results of Michael and his collaborators with those of the author is sufficient to show that there are decided variations in the behavior of this isomer also. In general, the author has found isobutyl bromide to undergo dissociation much more rapidly than other observers, the tertiary isomer somewhat less rapidly.

The variation in the results obtained with isobutyl bromide in Michael's laboratory, has been shown to be due to the greater purity of the later specimens used, and it, therefore, appears possible that the ease of dissociation at temperatures near 150° in the author's former experiments was due to a comparatively high degree of purity of the bromide used, although it was not prepared with the precautions exercised by Michael, Scharf, and Voigt. These investigators showed that this bromide is surprisingly susceptible to the effect of slight traces of impurities, and their results indicate that the variation in the behavior of this isomer is due to the presence or absence of retarding rather than accelerating catalysts.

Menschutkin and Konowaloff,[4] and Konowaloff,[5] claimed that the dissociation of certain tertiary alkyl esters was accelerated by the walls of the containing vessel or by catalytic substances introduced, but these results could not be confirmed by the work of Meyer and Pond[6] or by extensive experiments in Michael's laboratory.[7] Yet in such a case negative results are not entirely convincing in the face of positive results of other investigators. The author's former experiments offered some evidence for this sort of catalysis,[8] in that a coating of decomposition products on the wall of the vapor density bulb appeared to retard both the process of dissociation and the re-union of the dissociation products. But the course of the reactions was not always consistent with this explanation,

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[1] *Ber.*, **81**, 1244 (1875).

[2] *Ann.*, **379**, 263 (1911).

[3] THIS JOURNAL, **38**, 656 (1916).

[4] *Ber.*, **17**, 1361 (1884).

[5] *Ibid.*, **18**, 2808 (1885).

[6] *Ibid.*, **18**, 1623 (1885).

[7] Michael and Leupold, *Ann.*, **379**, 302 (1911); Michael, Scharf and Voigt, *Loc. cit.*, p. 673.

[8] *Ann.*, **383**, 452 (1911).

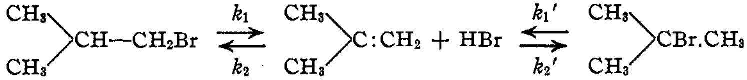
and, as Michael and Zeidler[1] stated, a negative catalytic effect of decomposition products might have rather come into play. No further evidence for this sort of catalysis has been obtained, and some of the experiments in Part II below offer evidence against it.

In any case, the possibility of marked alteration of the velocity of dissociation of these bromides by catalytic action is unquestionable.

As regards the unequal effect of catalysts on the behavior of the two isomers, the great variation in the relative rates of dissociation of the two in the hands of different investigators points in this direction. This is also the only assumption which will explain the results obtained in the following vapor-density determination with isobutyl bromide at 220°. Further confirmation of this conclusion has now been found in examining the reaction of hydrogen bromide with isobutene to form butyl bromide. If we admit the existence of catalytic influences affecting unequally the *rates of dissociation* of these two bromides, we must also expect that the relative *rates of formation* of the two (k_2 and k_2') will be susceptible to similar variation, so that the union of hydrogen bromide with isobutene, a reaction previously supposed to give rise, always, to formation of tertiary bromide only, must, under properly varied conditions, lead to formation of varying relative amounts of the two. It will be shown below that this is the case, the results being, in fact, strikingly in support of the theory.

I. Dissociation Constants of the Bromides.

Recalling the scheme adopted above to represent the conditions when these bromides are heated



$$\begin{array}{l}CH_3\\CH_3\end{array}\!\!>CH{-}CH_2Br \underset{k_2}{\overset{k_1}{\rightleftarrows}} \begin{array}{l}CH_3\\CH_3\end{array}\!\!>C{:}CH_2 + HBr \underset{k_2'}{\overset{k_1'}{\leftrightarrows}} \begin{array}{l}CH_3\\CH_3\end{array}\!\!>CBr.CH_3$$

let $K_i = k_1/k_2$, and $K_t = k_1'/k_2'$, be the dissociation constants, respectively, of iso- and tertiarybutyl bromides.

Then, if K_m represents the ratio of the undissociated bromides present,

$$K_m = \frac{\text{tert. bromide}}{\text{iso-bromide}} = \frac{k_1}{k_2}\Big/\frac{k_1'}{k_2'} = \frac{K_i}{K_t}.$$

The molar concentration of isobutene per liter will equal that of the hydrogen bromide. Let C_d be the concentration of one (either) dissociation product, and C_i and C_t, those, respectively, of the iso- and tertiarybutyl bromides.

Since the ratio of the undissociated molecules of the two bromides is always the same at equilibrium, we can calculate a dissociation constant for this mixture of bromides which will eventually be present, which ever bromide is used for this experiment. That is, the quotient

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[1] *Ann.*, **393**, 92 (1912).

$$\frac{C_d^2}{(C_i + C_t)v} = K,$$

will be constant, v being the total volume occupied by the gases; for, since $C_t = K_m C_i$,

$$K = \frac{C_d^2}{(C_i + C_t)v} = \frac{C_d^2}{(C_i + K_m C_i)v} = \frac{1}{1 + K_m} \cdot \frac{C_d^2}{C_i v},$$

that is, K is equal to the dissociation constant of one of the bromides, $C_d^2/C_i v$, multiplied by a constant. When the ratio of the bromides present at equilibrium, K_m, is known, we can calculate the constants for the individual bromides, since

$$(1)\quad K_i = \frac{C_d^2}{C_i v} = (1 + K_m)K \quad \text{and} \quad (2)\quad K_t = \frac{C_d^2}{C_t v} = \frac{1 + K_m}{K_m} K.$$

The experiments for the determination of the dissociation constant of the mixture of bromides, K, at 225° and 275°, are reproduced in the following tables. The apparatus used was that already described elsewhere.[1] It possessed the advantage of permitting the use of sufficient material so that it could be purified and analyzed accurately after the experiment. Its volume was 1.138 liters at 275°, and 1.136 at 225°. The other necessary data are the amount of bromide taken, and the temperature and pressure readings, which are given in the tables. The fourth column gives the pressure that would have been found if no dissociation had occurred. The excess of the last column over 100.0 gives the percentage of the bromide dissociated.

The dissociation constant, referred to concentrations in mols per liter, is calculated from the following equation:

$$K = \frac{\%\ \text{dissociated}^2 \times \text{weight bromide}}{\%\ \text{undissociated} \times 136.69 \times 1.138},$$

136.69 being the molecular weight of butyl bromide, and 1.138 the volume of the vapor density bulb.

In general, all of the pressure readings taken have not been given. The temperature was kept as constant as possible and frequent readings were taken, but only those necessary to show the course of the reaction until a permanent condition was reached are here reproduced. Tables V and VI are taken from the former paper by the author, these being the only ones of the earlier experiments which were carried to equilibrium. At the beginning of a determination, a reading was frequently taken in the neighborhood of 100°, in order to be certain that no error had been made in weighing the bromide introduced, as indicated by the corespondence between the calculated and observed values of the pressure. The readings in some cases recorded at the close of the experiments in the

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[1] *Ann.*, 384, 260 (1911).

neighborhood of 100°, furnish examples of the behavior emphasized in our former paper, namely, that the dissociation products in these experiments were very slow in recombining above temperatures at which the bromides in the bulb condensed (about 60–70°).

The products from the experiments were treated for a few minutes with fused potassium carbonate to remove a small amount of free hydrogen bromide which was present, boiled for a few seconds in a small long-necked flask to expel isobutene, if present, then treated with phosphorus pentoxide. Weighed amounts were then shaken up with water in sealed glass tubes for an hour or more, by which only the tertiary bromide is decomposed, and the hydrobromic acid was titrated. In a few cases these products were analyzed, in the manner formerly described[1] for their total bromine content. The results of such analyses are given in per cent. C_4H_9Br, and indicate that no appreciable amounts of decomposition products were present.

The times in the tables are given in minutes, the pressures in millimeters of mercury.

DISSOCIATION CONSTANT AT 275°.

I.

2.954 g. Isobutyl Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
15 m.	93°	431	434.4	99.2
90	278	1150	651.1	176.6
175	278	1159	651.1	178.0
230	275	1141	647.6	176.2
290	275	1143	647.6	176.5
322	92	....	...	...
345	95	770	436.6	176.3

.% dissoc., 76.4. K = 0.0469.
% tert. bromide, 92.74, 92.54.

II.

2.806 g. Isobutyl Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
10 m.	92°	411	411.5	99.9
30	290	....	...	...
40	275	721	615.1	117.2
155	276	1087	616.3	176.4
220	275	1091	615.1	177.4
245	275	1093	615.1	177.7

% dissoc., 77.6. K = 0.0484.
% tert. bromide, 91.76, 91.61.

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[1] *Ber.*, **44**, 1006 (1911).

III.

2.973 g. Isobutyl Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
17 m.	102°	451.5	448	100.8
30	265	....	...	...
50	278	1162	665.3	177.2
75	278	1149	655.3	175.3
105	275	1122	651.7	172.1

% dissoc., 77.2. K = 0.0500.

No analysis.

The decrease in pressure here is probably to be attributed to decomposition, as the specimen of bromide was at least a year old. The experiment was necessarily stopped before a permanent value was attained. Inasmuch as there was not usually any decrease in pressure in the experiments at this temperature, the maximum is used for the calculation. If the value 72.1% dissociation is used, K = 0.0355 is obtained.

IV.

2.411 g. Tertiary Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
15 m.	101°	366	362.2	101.1
38	275	670	528.3	137.8
105	275	948	528.3	179.5
204	276	945	529.3	178.5
215	276	949	529.3	180.0

% dissoc., 79.3. K = 0.0470.

% tertiary bromide, 94.00.

V.

3.453 g. Tertiary Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
14 m.	100°	....	...	...
18	100	518	517.5	100.1
113	275	1270	757.0	167.8
135	275	1326	757.0	175.2
145	275	1329	757.0	175.6
166	100	901	517.5	174.5

% dissoc., 75.4. K = 0.0512.

% tertiary bromide, 94.50. % C_4H_9Br, 100.26.

VI.

2.497 g. Tertiary Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
26 m.	101°	377	375.2	100.5
38	260	....	...	...
73	273	898	545.4	164.7
118	278	987	550.4	179.3
148	276	984	548.4	179.4
173	100	661	374.2	176.6

% dissoc., 79.4. K = 0.0490.

% tertiary bromide, 93.72. % C_4H_9Br, 100.20.

VII.

2.104 g. Tertiary Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
13 m.	94°	310.5	310.3	100.1
30	271	644	457.9	140.7
90	280	837	465.5	179.8
185	275	841	461.2	182.3
250	275	838	461.2	181.7
252	275	842	461.2	182.3

% dissoc., 82.0. K = 0.0504.

% tertiary bromide, 93.63.

DISSOCIATION CONSTANT AT 221°.

VIII.

3.468 g. Isobutyl Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
22 m.	105°	521	526.7	98.9
35	205	....	...	...
75	223	1162	689.3	168.6
82	223	1166	689.3	169.1
180	222	1060	687.9	154.1
330	222	1018	687.9	148.0
355	221	1015	686.6	147.8

% dissoc., 47.9. K = 0.00981.

% tertiary bromide, 72.44, 72.70.

IX.

3.606 g. Isobutyl Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
21 m.	219°	919	711.0	129.3
34	227	1208	722.5	167.2
42	227	1193	722.5	165.1
300	223	1054	716.8	147.0
370	220	1047	712.4	147.0

% dissoc., 47.0. K = 0.00966.

% tertiary bromide, 71.96, 72.27.

X.

2.323 g. Isobutyl Bromide.

Time.	Temp.	$P_{obs.}$	$P_{calc.}$	$100\frac{P_{obs.}}{P_{calc.}}$
26 m.	225°	468	463.6	101.0
50	230	480	468.3	102.5
113	219	778	458.0	169.9
125	221	787	459.9	171.1
140	220	782	458.9	170.4
310	220	725	458.9	158.0
420	222	712	460.8	154.5
470	222	713	460.8	154.7

% dissoc., 54.6. K = 0.00980.

% tertiary bromide, 70.12.

For the two following experiments a roughly weighed mixture of the two bromides was used, of approximately the composition given:

XI.

3.075 g. Mixture, 84% Iso-, 16% Tertiary Bromide.

Time.	Temp.	$p_{obs.}$	$p_{calc.}$	$100\,\frac{p_{obs.}}{p_{calc.}}$
30 m.	218°	876	605.5	144.8
65	219	946	606.3	156.0
275	224	926	612.4	151.2
495	222	924	610.0	151.5
545	221	919	608.8	151.0
580	221	917	608.8	150.6

% dissoc., 51.0. K = 0.01049.

% tertiary bromide, 75.65, 75.40. % C_4H_9Br, 99.77.

XII.

2.07 g. Mixture, 73% Iso-, 27% Tertiary Bromide.

Time.	Temp.	$p_{obs.}$	$p_{calc.}$	$100\,\frac{p_{obs.}}{p_{calc.}}$
10 m.	230°	547	417.3	131.1
110	223	640	411.4	155.5
145	221	650	409.8	158.6
360	217	638	406.5	157.0
410	220	639	409.0	156.2
426	220	641	409.0	156.7

% dissoc., 56.6. K = 0.00982.

% tertiary bromide, 77.07.

The above data are now summarized in Tables XIII and XIV. In the second and third columns are given the amount of bromide used and the degree of dissociation reached. The fourth column gives the time during which the degree of dissociation remained constant before the experiment was considered ended. The numerals in the first column refer to the preceding tables.

Expts. I–III and VIII–X are with isobutyl bromide; IV–VII with the tertiary; and XI and XII with the mixtures indicated above in connection with the experiments concerned.

Dissociation Constant at 275°.

XIII.

Expt.	G. bromide.	% dissocn.	Time const.	K.
I	2.954	76.4	60 m.	0.0469
II	2.806	77.6	25	0.0484
III	2.973	77.2	...	(0.0500)
IV	2.411	79.3	110	0.0474
V	3.453	75.4	10	0.0512
VI	2.497	79.4	30	0.0490
VII	2.104	82.0	142	0.0504

Mean value, K = 0.0490.

Dissociation Constant at 221°.

Expt.	G. bromide.	% dissocn.	Time const.	K.
VIII	3.468	47.9	25 m.	0.00981
IX	3.606	47.0	70	0.00966
X	2.323	54.6	50	0.00980
XI	3.075	51.0	370	0.01049
XII	2.070	56.6	16	0.00982

Mean value, K = 0.00992.[1]

In the vapor-density determinations in the neighborhood of 220° it is to be observed that the pressure passes through a maximum value, well marked in the experiments where pure isobutyl bromide was used, less decided in the last two determinations with mixtures of the bromides, then falls to a permanent value. The explanation of this behavior was formerly suggested by the author,[2] but the evidence was not sufficient to establish with certainty. It appears that the two sets of reaction velocities, k_1 and k_2, and k_1' and k_2', are not accelerated or retarded by the same influence. If, when isobutyl bromide is heated, the conditions are such that this isomer is dissociated (and formed) readily, that is, k_1 and k_2 are large, while, at the same time, the tertiary bromide is formed (and dissociated) only slowly, that is, k_1' and k_2' are small, then the isobutyl bromide may be expected to dissociate at first much as if it alone were present. Very little tertiary bromide will be formed for a time. *The pressure so produced will be greater than it would be if the bromide present were a mixture of the two isomers.* In the course of time the second bromide is formed and the pressure, after reaching a maximum, falls to a permanent value. In the extreme case, we could calculate the dissociation constant of the isobutyl bromide used from the maximum pressure reached, assuming none of the other isomer to have been formed at this point in the experiment.

This conclusion involves the assumption that the dissociation of isobutyl bromide into isobutene and hydrogen bromide is a step preliminary to the formation of the isomeric tertiary bromide, and there is no reason to doubt that this is the mechanism of the reaction in these experiments. Michael and Leupold[3] hold the view that when dissociation of isobutyl bromide is observed at lower temperatures it is because tertiary bromide has been formed by direct intramolecular isomerization and has subsequently undergone dissociation. Michael, Scharf, and Voigt[4] also appear to consider this true for temperatures below 184°. Nearly all of the author's earlier experiments[5] indicated, however, that even at lower tempera-

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[1] The average of the temperatures at which the equilibrium constant has been determined is 221°.

[2] *Ann.*, 384, 250, 264 (1911).

[3] *Ibid.*, 379, 269 (1911).

[4] This Journal, 38, 656 (1916).

[5] *Ann.*, 384, 263 (1911).

tures the dissociation was the intermediate step in the reaction, in that the amount of dissociation observed was too great to be accounted for by dissociation of the amount of tertiary bromide found in the product. This is particularly obvious in Expt. V at 185°, and undeniable also in Expt. VII at 150°. In the latter case 34.6% dissociation was observed at 150° after 115 minutes' heating, while the product contained 43.91% tertiary bromide. The view of Michael and Leupold would demand that this tertiary bromide should here be over 75% dissociated, which could not occur at this temperature.

The author is of the opinion that this explanation of the mechanism of the isomerization through dissociation, which is undoubtedly true for higher temperatures, is equally true whenever the rearrangement occurs in the gaseous state. Michael and Leupold[1] held it to be incorrect because they observed isomerization at temperatures where they could not observe dissociation. But it is to be noted that their vapor-density determinations in which they could discover no dissociation of the bromides did not extend over as great a length of time as the rearrangement experiments, and dissociation may eventually have occurred in the latter. In the experiments of Michael, Scharf, and Voigt, rearrangement in the gaseous state is observed at temperatures as low as 100°, but their method of examining the products of the experiments leaves room for questioning the results. The entire contents of their sealed tubes or of the vapor-density apparatus were washed out with water, shaken sufficiently long to decompose the tertiary bromide, and the hydrobromic acid titrated. In view of their statement on p. 655 that their best products "often became brown through decomposition at 108° and at 142° they could only be heated a short time," it appears possible that either bromine or hydrogen bromide may have been present in tubes heated three hours at 100° or in the products of the vapor-density determinations at 142°, and such products would have been included in the titration as evidence of tertiary bromide. The evidence therefore does not appear conclusive as to the occurrence of rearrangement in the gaseous state without dissociation.

Michael and Zeidler[2] criticized the author's former vapor-density determinations[3] on account of the irregular course of the temperature and pressure readings. It is evident, however, from the above experiments at 220° that the regular course of the dissociation of isobutyl bromide at this temperature, and, doubtless, at lower temperature also (at least, in this apparatus) is the attainment of a maximum with subsequent fall to a permanent value. It is sufficiently obvious that at various points on the rising or falling arm of this curve the temperature could be lowered

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[1] *Ann.*, 379, 276 (1911).

[2] *Ibid.*, 393, 90 (1912).

[3] *Ibid.*, 384, 263 (1911).

or raised, respectively, without at once producing a parallel change in the degree of dissociation. This was, therefore, the origin of the irregularities criticized by Michael and Zeidler, as was supposed at the time, and Expts. I, II and VI of this earlier paper can, therefore, now be regarded as furnishing confirmation of this peculiar behavior of isobutyl bromide seen in the experiments described above.

Free Energy of Dissociation.—In Part III, the value K_m, the ratio of tertiary to isobutyl bromide at equilibrium, is found to be 4.01 at 275°. The dissociation constants for iso- and tertiarybutyl bromides, K_i and K_t, can, therefore, be calculated for this temperature, according to (1) and (2) above.

$$K_i = (1 + K_m)K = 0.246,$$

and

$$K_t = 1 + K_m/K_m\, K = 0.0612.$$

These are the dissociation constants when the concentrations are expressed in mols per liter. From these the free energies of dissociation can be calculated from the equation $A = RT \ln K$. Taking $R = 1.985$, and the temperature as 548° absolute, we find

$$RT \ln K_i = -1526 \text{ cals., and } RT \ln K_t = -3039 \text{ cals.}$$

These values with the opposite sign are the free energies of formation of the bromides from isobutene and hydrogen bromide. The relation between these values and the constitution of the bromides is discussed in Part III, below.

Heat of Addition of HBr to Isobutene.—Having, now, the dissociation constants for two temperatures, we can calculate the heat of addition of hydrogen bromide to isobutene—that is to say, the heat of addition for the case where the two bromides are formed in the ratio in which they are present at equilibrium. The heat of formation of the individual isomers cannot be calculated, since we have not determined the variation of K_m with the temperature.

According to van't Hoff's equation,

$$\frac{d \ln K}{dT} = -\frac{Q}{RT^2}, \text{ or } (\ln K_2 - \ln K_1) = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

$T_2 = 548$, and for T_1 the mean value from the experiments at approximately 220°, or $T_1 = 494$ (A), is used. K_1 and K_2 have the values given above. We find for the heat of dissociation

$$Q = -15886 \text{ cals.}$$

The heat of addition is, of course, +15886 cals.

The heat change in this reaction has not been determined calorimetrically. Louginine[1] has, however, determined the heat of addition of hy-

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[1] *Compt. rend.*, 150, 1346 (1910).

drogen bromide to certain hydrocarbons of this series in toluene solution, and a comparison of the results is not without interest. Louginine's results were corrected for the heat of solution of the hydrobromic acid, but not for that of the other substances. Caprylene, $C_5H_{11}CH : CHCH_{3\,diss.} + HBr_{gas} = C_8H_{17}Br_{diss.} + 16481$ cals. Amylene, $(CH_3)_2C : CHCH_{3\,diss.} + HBr_{gas} = C_5H_{11}Br_{diss.} + 17614$ cals. Methyl-2-pentene-2, $(CH_3)_2C :\text{-} CHC_2H_{5\,diss.} + HBr_{gas} = C_6H_{13}Br + 19008$ cals.

The heat of the reaction between isobutene and HBr, calculated above, can be made roughly comparable to these values if we estimate the heat of reaction of HBr to liquid isobutene, assuming the heats of vaporization to be proportional to their absolute boiling points (Trouton's rule). That of isobutene should be approximately 6000 cals. (to be subtracted); that of mixtures of bromides about 9000 cals. (to be added), *i. e.*, 3000 cals. to be added to the value above (15886 cals.). This gives nearly 19000 cals. for the heat of addition of gaseous hydrogen bromide to liquid isobutenes.

II. The Reaction between Hydrogen Bromide and Isobutene.

Since it is clear that the rates of dissociation of iso- and tertiarybutyl bromides are susceptible to catalytic influences, and that catalysts do not affect the two equally, it is to be expected that the reverse reaction, the formation of these two bromides from hydrogen bromide and isobutene, will be similarly subject to catalytic action. If the effect of any such catalyst on the formation of the two isomers is not the same, we should expect to obtain by this reaction varying relative amounts of the two isomers.

This is contrary to past experience, for this reaction of hydrogen bromide and isobutene has been one of the few that have been supposed to give rise exclusively to one of the isomers possible in such an additive reaction. Roozeboom,[1] in fact, recommended this as a method for the preparation of tertiarybutyl bromide, and Michael and Zeidler[2] prepared one of their purest specimen of this bromide in this way. Only once has the formation of isobutyl bromide by this reaction been observed, namely, by Ipatiev,[3] who carried the reaction out in acetic acid solution, and obtained, in two experiments 5% and 16%, respectively, of this isomer.[4]

Since, however, we have observed that isobutyl bromide may dissociate at least as rapidly as the tertiary bromide, if, not, in fact, somewhat more rapidly, we should expect that the reaction between hydrogen bromide and isobutene would give rise, under proper conditions, to as much as

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[1] *Ber.*, 14, 2396 (1881).

[2] *Ann.*, **393**, 109 (1912).

[3] *Ber.*, 36, 1988 (1903).

[4] Michael and Zeidler, *Ann.*, **385**, 267 (1911), as well as Ipatiev and Dechanow, *Jahresb.*, 1904, 832, found that the addition of halogen acids to several amylenes proceeds abnormally when carried out in acetic acid solution.

50% of the former isomer. Experiments were, therefore, undertaken in this direction. In general, it was found that isobutyl bromide can be obtained by this process in varying amounts, and under conditions which it has not been possible to reproduce exactly. We finally obtained a product containing more than the expected 50% of this isomer.

The cause of the wide variation must plainly lie in catalytic action; but, although several possible causes were tested, consistent results were not obtained. The ratio of the velocities of formation of these two isomers appears to be subject to greater variation than that of their velocities of dissociation, and the conditions can be only partially defined. The following statements can, however, be made:

First. The union of hydrogen bromide and isobutene at temperatures high enough so that the bromides formed remain in the gaseous state, occurs slowly. In every case where the union has undoubtedly occurred under these conditions, considerable isobutyl bromide has been obtained, and it appears altogether probable that this will always be the case.

Second. The union of hydrogen bromide with isobutene in the presence of liquid bromide—a condition which soon exists if the temperature is below the boiling points of the bromides—takes place *much more readily than in the absence of the liquid phase.* Furthermore, in all cases where liquid bromide has undoubtedly been present pure tertiary bromide has been formed. The conclusion that in the presence of liquid bromide only tertiary bromide is *ever* formed, in its absence considerable isobutyl derivative is *always* formed, provided any reaction at all occurs in the latter case, is in accord with all of our results; yet one can hardly venture, after having worked with these compounds, to state categorically that such a rule will hold without exception. Nevertheless, the formation of isobutyl bromide is a slow process under the most favorable conditions yet observed, so that the nearly instantaneous formation of the tertiary isomer in the presence of the liquid phase leaves little opportunity for the formation of the former.

In view of the recent observations of Michael, Scharf, and Voigt,[1] showing the extreme susceptibility of isobutyl bromide to the presence of slight amounts of foreign substances, it appears possible that more careful purification of the materials used would have yielded results of interest. Yet the purity of the hydrogen bromide used varied considerably without producing a corresponding effect upon the products obtained.

Reaction in the Gaseous State.

The procedure, which finally yielded products containing considerable amounts of isobutyl bromide, consisted in allowing the reaction to take place in the vapor density bulb used for the above experiments on the dissociation of the bromides, or in large round flasks. The bulb or flask

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[1] *Loc. cit.*

was evacuated, heated to the temperature of the experiment, and the gases were then introduced. The gases were measured only roughly on account of the haste necessary in handling the hydrogen bromide in a gas buret over mercury. The pressure in the apparatus was also measured only approximately, by the height of the mercury in the burets. These estimates of the pressures are, however, here given, since they show that the union of the gases occurred only gradually. The two gases were at first introduced until there was a small excess pressure, then further amounts were added in the course of an hour or more, as the pressure in the apparatus decreased.

The isobutene was prepared according to Butlerow[1] from isobutyl bromide and potassium hydroxide. The hydrogen bromide was prepared by passing hydrogen and bromine over a glowing spiral of platinum wire. Bromine from a well-known firm was used, and hydrogen from the purest zinc for analytical purposes, and C. P. hydrochloric acid. The presence of free hydrogen could be avoided by heating the bromine flask until an excess of bromine passed along in the mixture. The hydrogen bromide was then passed over fused ferrous bromide to remove bromine, and over calcium bromide to dry it.

The products were purified as in Part I, the tertiary bromide decomposed and determined as usual, and the remainder assumed to be isobutyl bromide. In a few cases the latter also was analyzed. In the following description of the experiments, the pressure is indicated by the height of mercury by which it was more (+) or less (—) than atmospheric pressure. The volume of the gases was measured at room temperature.

1. Vapor-density bulb at 100°. Isobutene and hydrogen bromide introduced in sufficient amounts to bring the pressure to approximately 760 mm. The bulb was then heated for four hours at 105–130°, cooled, allowed to stand for a while, and the product purified and analyzed.

Found: 48.1% isobutyl bromide.

2. The bulb was then cleaned with alcohol and ether only. At 140°, 375 cc. hydrogen bromide and 425 cc. isobutene were introduced (calculated to fill the bulb 802 cc.). Additional amounts of the gases were then introduced at intervals for four hours, as the union went on so that this could be done with $p = +4$ to 10 cm. In all, 505 cc. of each were introduced. Before introduction of the last 60 cc. of gas, at the end of four hours, $p = +1+2$ cm. At the end of 6 hours, at 115° (p = about 0), the experiment was stopped. From the excess of gas introduced, about 40% appeared to have reacted at this time.

Found: 22.3% isobutyl bromide.

At the end of this series of experiments analyses are given which show

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[1] *Z. Chem.*, 13, 238, 544 (1870); *Ber.*, 3, 622 (1871).

that the insoluble portion of the products of Expts. 1–3 was nearly, if not quite, pure butyl bromide.

3. The bulb was now cleaned with sulfuric acid-dichromate mixture. At 120°, 600 cc. hydrogen bromide, and 300 cc. isobutene were introduced (p positive). Calculated for this temperature, 845 cc. After 11 minutes (p = —1 cm.) the amount of isobutene was increased to 400 cc. (p = +3 cm.). After 24 minutes (p negative), more isobutene was introduced. At the end of 50 minutes 650 cc. isobutene had been added (total volume of gas 400 cc. in excess of that calculated to fill the bulb), and p = +15 cm. The bulb was kept for seven hours longer at 105–115°.

Found: 55.8% isobutyl bromide.

4. A 3300 cc. round flask was next fitted with rubber stopper and glass tube with stopcock, and the gases were all introduced at the beginning of the experiment. After 6 hours of heating the flask stood 24 hours cold. The product was completely soluble in water and, since it was very impure from contact with the rubber stopper, no analysis was made.

5. This same flask was cleaned with bichromate mixture, the neck drawn out, and a stopcock sealed on. At 100°, 1900 cc. isobutene were first introduced. Hydrogen bromide was then liquefied in carbon dioxide and ether, and gas from the vaporization of this was introduced until the pressure was considerably in excess of that of the atmosphere. At the end of three hours of heating at 100–120° the pressure was still considerably above that of the atmosphere, but after 6 hours about equal to it. After 7$^1/_2$ hours the flask was cooled and the product analyzed.

Found: 23.1% isobutyl bromide.

6. A 2-liter flask, very old, but unused, was then employed. The inner surface of this flask, after vigorous heating with dichromate mixture, appeared slightly crystallized. This was closed with rubber stopper and stopcock. 1200 cc. isobutene were then introduced, then hydrogen bromide from the liquefied acid, to some excess pressure. After 30 minutes (p negative) more HBr was added. After 55 minutes, 100 cc. more isobutene were added. After 3$^1/_2$ hours the heating was discontinued, the temperature having varied from a little less than 100° to 1220°. During the last hour there was little decrease of the pressure in the flask. The product was rather impure.

Found: 18.4% isobutyl bromide.

As evidence that the insoluble substance obtained in the above experiments was isobutyl bromide, the products insoluble in water from Expts. 1–3 were united and shaken with a large amount of water to remove the last traces of tertiary bromide. The clear, somewhat yellowish oil was treated with fused potassium carbonate to remove acid, if present, and dry it. Weighed amounts were then sealed in hard glass tubes, as in all of the analyses for total bromine, and heated to 150° with water for several hours. The hydrobromic acid was titrated with silver nitrate.

I. 0.4051 g. required 11.57 cc. $AgNO_3$, 0.249 N.
II. 0.3609 g. required 10.74 cc. $AgNO_3$.
% butyl bromide found: I, 97.89%; II, 100.99%.

In the above experiments the union of hydrogen bromide and isobutene undoubtedly occurs partly in the absence of liquid bromide. In all cases where the course of the reaction was followed, it progressed slowly. In all but Expt. 4 considerable isobutyl bromide was formed, and in this case impurities from the rubber stopper may have prevented any reaction in the gaseous state. In this experiment, unfortunately, no observations of the pressure were made which could show whether or not any reaction occurred while the substances were in the gaseous state.

Reaction in the Presence of Liquid Bromide.

Numerous experiments were carried out in which isobutene and hydrogen bromide were passed through tubes of various sorts at various temperatures. The products were condensed in a short glass or platinum condenser. After varying results had been obtained, in many cases only pure tertiary bromide, it appeared that the gases might not be uniting in the tubes used, but, rather, in the condenser and receiver, where liquid bromides were present. The possibility of this was tested as follows:

7. The gases were passed merely through a short, water-cooled condenser. Bromide was readily formed and was completely soluble in water, being, therefore, tertiary bromide.

This result appears to be due merely to the presence of a liquid phase. The above condenser was moistened with isobutyl bromide and the gases were passed through it. The product was formed readily as before. The first twelve drops were thrown out in order to avoid the pressure of the bromide introduced. The product then collected was, as before, completely soluble in water. The action of liquid bromide is not, therefore, specific in causing the formation of the same isomer. Rather it appears to be only the formation of tertiary bromide that is so accelerated.

8. A test tube was then fitted with a two-holed stopper, with exit-tube and Y-shaped entrance tube, and the two gases were passed through it. The gases were introduced at approximately the rate of 100 bubbles (less than 100) per minute, the hydrogen bromide being passed through saturated aqueous solution and the isobutene through water. For the first few minutes considerable hydrogen bromide passed through the tube, but at the end of 15 minutes liquid was visible in the test tube. The tube became warm, and was immersed in water at 25°. At the same time the rate of passage of the gases was then increased to at least 600–800 bubbles a minute (too rapid to count), but even at this greatly increased rate

the odor of hydrogen bromide was now only slightly noticeable at the exit tube, indicating that nearly complete union was occurring. The exact instant when the liquid appeared or when the union of the gases became more rapid could, of course, not be determined but the difference between the earlier and later parts of the experiment was unmistakable. The product was completely soluble in water.

The use of a smaller test tube and the lowering of the temperature to —18° had no effect upon the result from such experiments.

The moistening of this bulb with isobutyl bromide was also without effect upon the product.

9. Isobutene was then liquefied (b. p. —4°), and at a temperature of —78 to —71° hydrogen bromide was passed in. A crystalline product, easily melted by the warmth of the hand on the tube, soon appeared. This was doubtless the tertiary bromide which solidifies above this temperature. When the volume was somewhat more than double that of the original isobutene, the tube was allowed to stand for 75 minutes in the freezing mixture, then allowed to come to room temperature. Considerable hydrogen bromide boiled off, perhaps, also, some isobutene. The product was completely soluble in water. It is to be noted that in these experiments the presence of 1–2% isobutyl bromide can always be recognized without titration by the presence of visible insoluble drops.

10. The following experiment, carried out in the vapor-density bulb, shows that even in this apparatus in which isobutyl bromide appears to be either dissociated or formed with unusual ease, the formation of this isomer can be observed only in the absence of liquid bromide. The bulb was cleaned with bichromate mixture and in the course of 45 minutes, at a temperature of 50–80°, about 800 cc. each of the gases were introduced (calculated to fill the bulb, 1000 cc.). Liquid bromide soon appeared. At the end of an hour the bulb was cooled and the product tested. It contained no insoluble bromide. This single experiment would hardly be conclusive by itself, but it is entirely in agreement with the results of the preceding experiments.

The above experiments, 7–10, lead to the conclusion that when hydrogen bromide and isobutene unite in the presence of liquid bromide, the reaction occurs readily and the product consists entirely of the tertiary bromide. There is nothing to indicate whether this reaction occurs at the liquid surface or between the gases dissolved in the liquid phase. In either case it is to be expected that the presence of the liquid phase at higher temperatures will facilitate the reverse reaction, the dissociation of tertiarybutyl bromide; and it is also to be expected that the small amount of dissociation occurring in the liquid phase itself upon heating will be more quickly attained with this isomer than with the other. This fact may have some bearing upon experiments, such as many of those of

Michael and his collaborators, in which the isomerization is brought about by heating the bromides in the liquid state, but there are no data available which would justify any conclusion regarding this.

Experiments in Heated Tubes.

A brief description will suffice of numerous experiments in which isobutene and hydrogen bromide were passed through glass tubes heated to various temperatures. Varying amounts of isobutyl bromide were obtained, frequently none at all, and never more than 18.5%. The cause of the variation we have not found, but the following statements can be made:

First. No relation was found between cleanliness of the tubes (cleanliness attainable by treatment with bichromate mixture followed by standing with water) and formation of isobutyl bromide, this isomer having at times been formed in tubes in which a whitish coating, which always appeared after one or two experiments, was plainly visible.

Second. Temperatures from 85° to 275° were employed without any evidence of relation between temperature and composition of the product.

Third. Isobutyl bromide has not been obtained with tubes of one kind of glass in preference to another.

Fourth. No photochemical effect has been observed.

Nothing has been observed which contradicts the conclusion that the formation of isobutyl bromide, when it occurs, is the result of union of the gases in absence of liquid bromide, such reaction, however, taking place slowly. In these experiments it must, therefore, have occurred in the heated tubes themselves. The formation of tertiary bromide may also have occurred to some extent in the tubes, but may well have occurred largely in the condenser or receiver. The length of time during which the gases were in the heated tubes in passing through them was, at most, only about 1.5 minutes, which, in view of the slowness of the reaction between them, should not permit very extensive union. If the above described experiments had been carried out first, many experiments similar to the following could have been dispensed with.

For the following experiments, 14–16, a glass tube 12 mm. in diameter and 35 cm. long was sealed at one end to a capillary to serve as exit; at the other end, it branched into two narrow tubes, through which the gases entered, being thus heated before they came together. This apparatus was heated in an oil bath. The air in the tube was usually displaced by a current of nitrogen just before each experiment, yet the occasional omission of this precaution seemed to have no effect upon the results.

The hydrogen bromide was usually obtained by heating the aqueous solution saturated at 0°. This acid was derived from various sources and varied a good deal in purity, but no relation between the purity of the acid and the result of the experiment could be observed.

11. These experiments were carried out several years ago by my student, Mr. D. B. Lake. The hydrobromic acid solution was prepared by generating hydrogen bromide with bromine and red phosphorus, the excess of bromine being removed by passing the gas over red phosphorus. The rate of passage of the isobutene and hydrogen bromide was watched by bubbling them through water and saturated hydrobromic acid solutions, respectively. The rate of the latter was not absolutely constant, but the two were kept as nearly the same as possible and were approximately as stated. The separate experiments were carried out at different times, but the tube was not cleaned at all between them.

Temp.	Bubbles per min.	% isobutyl bromide.
150°	100	8.5%
150	60	10.6
150	120	16.0
185	60	18.6
150	125	6.3
150	245	7.3
150	60	12.4
150	145	11.4

12. A few months later the tube was cleaned and the following experiment was carried out. Without interruption, the temperature was changed and the products were collected separately.

Temp.	Bubbles per min.	% isobutyl bromine.
180°	220–250	12.8%
185	220–250	4.3
100	220–250	0.0

13. The tube was cleaned again.

At 175–190°, 175 bubbles per minute, 8.1% isobutyl bromide was formed; on continuation of the same experiment under the same conditions, 5.3% isobutyl bromide.

14. The experiment was repeated some time later with the same tube, but with hydrogen bromide from hydrogen and bromine, as in Expts. 1–6. This was probably purer than the hydrogen bromide used for 15 and 16. At 105°, 120°, 140° and 250° only tertiary bromide was obtained.

A new apparatus was now constructed out of 7 mm. tubing, bent back and forth upon itself, so that a considerable length could be gotten into a small space, and the apparatus was heated in an air bath. The gases entered separately and passed through 100 cm. of tubing each before mixing, after which they passed through a length of 200 cm.

With this apparatus the results were no more satisfactory. At temperatures from 100° to 275° the product contained from 92 to 100% tertiary bromide, usually nearly 100°. The following experiments are typical:

15. 98°: No insoluble bromide in product. 100°: **Product** continued to be entirely soluble.

16. On the following day, without any cleaning of the tube: 275°. Only a half dozen drops of liquid were obtained in the course of 20 minutes. The tube was cooled to 150° and the gases were driven out with air. On passing the gases through again, bromide collected readily, and contained 14% of insoluble bromide. This was the largest percentage of isobutyl bromide ever obtained with this apparatus, and the hydrogen bromide for this experiment was obtained by heating a solution reddish in color, and, from its odor, evidently one of the least pure sources of hydrogen bromide which we used.

It is unfortunate that in this experiment an analysis for total bromine present was not made; but throughout the course of this work such analyses were frequently made, and since the bromine present was never far from that demanded for butyl bromide, these analyses were neglected in many cases.

After we had begun to use hydrogen bromide from hydrogen and bromine for all of the experiments, other tubes were tried: a Jena combustion tube, a new soft glass tube, a short platinum tube (140-160°). In all cases pure tertiary bromide resulted.

The gases were passed through a short, transparent quartz-glass tube at 130° and 150°, illuminated by an iron arc giving wave lengths down to about $225\mu\mu$. Tertiary bromide was formed. Illumination of the glass tubes with tungsten lamps had already proved to be without effect upon the product.

Although we can offer no explanation of the irregularity of the above experiments, 11-16, the formation of such a large amount of tertiary bromide in most cases is not difficult to explain. From Expts. 1-10 it is evident that the gases unite slowly as long as no liquid bromide is present, but that in the presence of the latter the union is rapid and only the tertiary isomer is formed. It is, thus, probable, that in the above experiments the reaction occurred largely in the condenser or receiver, as suggested above. There only tertiary bromide should be formed.[1]

Isobutene was also passed through aqueous hydrobromic acid solutions saturated at 0°, 50° and 100°. Only tertiary bromide was obtained. In acetic acid and isobutyric acid the result was the same. In the case of

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[1] It was thought that it might be possible to pass the gases from these tubes over some substance which would absorb the free hydrogen bromide, before the product was condensed, in order to obtain the bromide unquestionably formed in the heated tube. Potassium carbonate failed to absorb the hydrogen bromide. Potassium hydroxide would be too likely to decompose tertiary bromide. A high-melting amine or amide appeared a possibility. Benzamide was tried, but it was found that the large amount of such a substance required to absorb the necessary amount of hydrogen bromide made the method altogether impracticable.

the latter, the solubility was so small that the two gases were passed through it several times alternately. The result with acetic acid conflicts with that of Ipatiev, mentioned above; but we are not prepared to say that some slight, and apparently non-essential, alteration in the conditions of the experiment would not cause the formation of the isobutyl bromide observed by him.

As regards the catalytic effect of liquid bromide on the union of these gases, we must refer again to the evidence offered in support of this conclusion in the author's former paper,[1] in order to answer the criticisms of Michael and Zeidler.[2] After the dissociation of one of the bromides had been measured (at 150–275°), the apparatus was, in a number of cases, cooled to 100°, kept there until constant, and a pressure reading taken. Little combination of the dissociation products had occurred, except in one case. In a number of these experiments, the bath was then opened and the heat turned off, until the temperature had dropped sufficiently so that condensed liquid was visible in the vapor-density bulb. The bath was then closed and heated as quickly as possible to a temperature in the neighborhood of 100°. It was then found in every case so tested that the reunion of the gases had gone on, while the liquid was present, more rapidly than before it was present. In one of the most striking cases (Expt. 15), no reunion of the dissociation products had occurred in 18 minutes at 90°, yet it proceeded to the extent of over 30% in an interval of 36 minutes, during which the liquid was visible for *only three minutes*.

Michael and Zeidler[3] have raised several objections to these experiments. In the first place, they note that the rate of reunion of the dissociation products in the presence of liquid bromide in one experiment is not as great as in the absence of liquid *in a different experiment*. The variability of the velocity of these reactions in different experiments was however, one of the features emphasized by the author, as evidence of the susceptibility to catalytic action. The only comparison which appears valid is that of the rate of reunion of the gases in the presence of liquid with the rate in the immediately preceding period of the same experiment.

Michael and Zeidler next note that in one experiment where the rate of reunion was slow just preceding the appearance of the liquid, it was more rapid at a temperature a hundred degrees higher. But this is not surprising. Two factors are concerned in such a comparison: first, the distance of the reaction from its end point, which was, of course, greater at the lower temperature; and, secondly, the effect of the temperature difference. In view of the usual temperature coefficient of chemical reaction velocity—a decrease of one-half or more for every ten degrees' drop in temperature—this comparison in not unfavorable to the point at issue.

[1] *Ann.*, 384, 265ff. (1911).

[2] *Ibid.*, 393, 90 (1912).

[3] *Ibid.*, 393, 90 (1912).

Michael and Zeidler also note that there is great difficulty in determining the exact instant when a liquid appears in such a vessel. The possibility of a too favorable interpretation of the data in this respect was realized, and, in consequence, in stating the comparative velocities before and after appearance of the liquid, it was assumed that it was present from the time of the last pressure reading at a temperature well above the condensation temperature, to the time of the first measurement, following the evaporation of the liquid, when a constant temperature in the neighborhood of 100° had again been attained. Attention was, in fact, called to this method of estimating the time during which the liquid was present.[1] If the time during which the liquid was visible had been taken for comparison, the evidence for the conclusion reached would have been much stronger. At the partial pressure of the vapor of the bromides in the bulb, their boiling point could not have been far different from that at which the liquid was actually observed—usually about 60–70°.

Their further objection to the irregular course of the dissociation in these experiments has been sufficiently discussed above.

III. The Equilibrium between Iso- and Tertiarybutyl Bromides in the Gas State.

It is now possible to calculate the equilibrium between these bromides. The basis for this calculation is furnished by the first experiments carried out in this direction, the results of which could not be interpreted at the time.

In these experiments the bromides were sealed in small, thin-walled bulbs. These were placed in tubes of about 275 cc. capacity, which were in turn sealed, after which the small bulbs were easily broken. In some cases the air was first displaced by nitrogen, but this precaution appeared to be of little, if any, consequence. These tubes were then heated in the bomb furnace, with temperature regulation. It was thought that the composition of the product obtained after the heating would represent the ratio of the bromides at equilibrium. The results were, however, variable, and it was eventually concluded that the method was worthless. The experiments described above now make the course of the reaction under these conditions clear, and make possible the calculation of the desired equilibrium between the undissociated bromides.

During the heating, which was usually continued for a longer time than later experiments showed to be necessary, equilibrium was established between the two bromides and their dissociation products, hydrogen bromide and isobutene. The tubes always cooled off in the furnace. During this time, as shown in Part II, little re-union of these dissociation

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[1] *Ann.*, 384, 266 (1911).

products would occur, while only gaseous substances were present. Nevertheless, it might occur to some extent, and in as far as it did take place, some isobutyl bromide would doubtless be formed. We attribute the variation in the composition of the resulting products to the varying extent to which this reunion took place, while the tubes were cooling and before liquid bromide was formed. Most of the reunion must, however, have occurred after liquid bromide appeared, and under these conditions only tertiary bromide should be formed.

The length of the heating varied greatly in these experiments, yet there is no relation between this factor and the relative amounts of the bromides in the product recovered. None of the results can be attributed to insufficient heating, since it appears that three or four hours is more than sufficient for the attainment of equilibrium at this temperature.

These experiments are summarized in the following table. At the time they were carried out, it was not realized that the amount of bromide taken or the volume of the tubes was of any interest, so that these were not always measured. Fortunately, however, they were recorded in most cases.

The purification of the products, and the analyses, were carried out as usual. The analysis for total bromine present is given in terms of per cent. butyl bromide whenever it was made. The analytical results are the average of duplicates in practically all cases. We may add that in all of this work the duplicate determinations of the tertiarybutyl bromide present usually agreed within 0.2 or 0.3%. A number of experiments giving products with 85–90% tertiary bromide have been omitted from the table for the reason given below.

I.

Experiments with Isobutyl Bromide. Temp. 275°.

	Wt. bromide.	Vol. tube.	Length of heating.	% tert. bromide.	% C_4H_9Br
1	2.437	300	7 hrs.	78.25	98.57
2	2.522	262	2.5	82.58	100.75
3	3.905	278	4.5	83.07	....
4	3.301	190	3.5	84.36	98.08
5	3.91	...	3.5	85.28	99.53
6	2.359	278	12	86.03	....
7	2.745	312	11	86.59	99.32
8	2.212	265	8	87.79	100.77
9	...	...	4	88.08	100.41
10	3.002	274	8	89.89	....
11	...	...	5.5	90.60	....
12	...	...	6.5	90.81	....
13	...	...	5.5	90.99	....
14	...	...	5.5	91.23	....

II.

Experiments with Tertiarybutyl Bromide. Temp. 275°.

	Wt. bromide.	Vol. tube.	Length of heating.	% tert. bromide.	% C_4H_9Br.
15	2.910	235	8 hrs.	85.39	98.89
16	2.607	290	11	88.78	100.00
17	2.687	312	8	89.99	98.79
18	...	...	3.5	90.48	....
19	...	...	4.75	90.71	99.76
20	2.779	275	8	91.12	....
21	2.428	247	9.75	91.22	99.15
22	2.491	285	9	91.40	....
23	...	...	3.5	91.41	100.60
24	...	294	9.25	91.38	....

Although the per cent. of tertiary bromide found in the products of these experiments is subject to wide variation, it is obvious that there is maximum value, more clearly marked in Table II than in Table I, which is not surpassed. This appears to give the clue to the course of the reaction.

From the results described in Part II, it is to be expected, as just stated, that the reunion of the hydrogen bromide will occur very slowly in these tubes, as they cool, and it could be predicted that in many cases no such reunion would probably occur until the liquid bromide is present. Since, in such a case, these dissociation products will unite to give only tertiary bromide, there will be a maximum amount of this isomer possible in the products and we consider that this is just what occurs in the cases in the above tables, where the maximum amount of tertiary bromide is recorded. *In such cases the amount of isobutyl bromide present in the product is just what was present at 275°*, where a state of equilibrium existed. The amount of tertiary bromide present at 275° will be the amount found at the end of the experiment, less the amount formed during the cooling. Accepting this assumption, and knowing the dissociation constant for the mixture of bromides, the calculation of the desired equilibrium is possible.

An average value may be calculated as follows: For the volume of the tubes, 285 cc. are taken. A small change in this value does not effect the result greatly. For the amount of bromide, 2.546 g. are taken, this being the average of the amounts in those experiments giving more than 90% tertiary bromide, in as far as this was recorded. The dissociation constant at 275°, for concentrations in terms of mols per liter, is 0.049. For concentrations in grams per liter this becomes $136.69 \times 0.049 = 6.70$.

If x = the number of grams of bromide dissociated, we have

$$\frac{x^2}{(2.546 - x) \times 0.285} = 6.70,$$

from which $x = 1.448$ g. bromide dissociated.

The per cent. dissociation 1.448/2.546 = 56.9%.

The amount of bromide undissociated at 275° is, therefore, 43.1% of the whole.

The maximum amount of tertiary bromide in the products, we may take as 91.4%, leaving 8.6% isobutyl bromide. This amount of the latter isomer is assumed to have been present at 275°. The 43.1% of the bromide undissociated at 275° was, therefore, made up of 8.6% isobutyl and 34.5% tertiarybutyl bromide.

The ratio K_m = 34.5/8.6 = 4.01.

Or, of the undissociated bromide, 34.5/43.1 = 80.05% was tertiary bromide.

Instead of using the average values of the various factors involved, we may calculate the ratio of the bromides from those individual experiments in which all of the data are recorded.

We obtain thus, from Expt. 20, 80.37% tertiary bromide; from Expt. 21, 80.37%; from Expt. 22, 79.91%. The average of these is 80.22%. We take the value above, of 80.05%, giving K_m = 4.01, as the most probable value.

It would appear that we should be able to base similar calculations upon the experiments for the determination of the vapor density in Part I. This would be the case, provided we could be certain that any of the results represent cases where all of the dissociation products gave tertiary bromide on cooling—that is, maximum values for the tertiary bromide in the product. Since the concentration of the gases in the vapor density apparatus was smaller than in the sealed tubes, and the dissociation product was greater, the possible amount of tertiary bromide in the product was greater. The product of Expt. V contained 94.5% tertiary bromide, therefore 5.5% isobutyl derivative. At 275°, 24.6% of the bromide present was undissociated. If we assume that here no isobutyl bromide was formed upon cooling, 5.5% out of this 24.6% was isobutyl derivative, the remainder tertiary, giving a value for K_m, of 2.78, instead of 4.01 found above. This discrepancy may be due to the fact that the number of experiments of this sort was too small to make it certain that 94.5% tertiary bromide represented the maximum for this experiment. But we may also note that the part of the product taken as isobutyl bromide is small—5.5%—and includes all decomposition products present, at least, all that do not give hydrogen bromide with water. If the amount of this isomer were 4.9% instead of 5.5% the value of K_m would have been 4.02, approximately the value found above. Evidently calculations of the equilibrium constant based on these vapor-density experiments cannot be given much weight.

Michael and Leupold[1] obtained variable results on heating the bro-

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[1] *Ann.*, **379**, 212ff., 220 (1911).

mides in the gas state, in some cases finding only 73% of tertiary bromide when the end point had apparently been reached. This can be accounted for by the formation of considerable isobutyl bromide during the cooling, although it is not clear why this should have occurred to such an extent in this particular case.

The equilibrium between the bromides in the liquid phase appears to lie between 74 and 76%,[1] but it is to be expected that this value would differ from that for the gas phase, and that it would differ in this direction since equilibrium must exist in the two phases simultaneously when both are present. The vapor pressure of the tertiary bromide is higher than that of the isobutyl bromide at lower temperatures, so that we may expect the ratio of its concentration in the gas phase to that in the liquid phase to be, for all temperatures, higher than for the isobutyl derivative. This would obviously lead to a higher per cent. of tertiary bromide at equilibrium in the gas phase, as found. It appears possible that the later, divergent values found for this equilibrium by Michael, Scharf, and Voigt[2] may have been due to decomposition of their unstable specimens of isobutyl bromide.

Discussion of Results.

The above results can only be interpreted as indicating that the radical $(CH_3)_3C$— has a greater affinity for the bromine atom than has the radical $(CH_3)_2CH.CH_2$—. The decrease in free energy when tertiary changes to isobutyl bromide can be calculated from the relation $A = RT \ln K_m$. With $K_m = 4.01$, $R = 1.985$, and $T = 548$, we find $A = 1511$ cals.

We consider this to mean that the tertiarybutyl radical exerts a *stronger attractive force* upon the bromine atom than the isobutyl radical does. In view of the position of carbon in the middle of the periodic system and of hydrogen among the metallic elements, and in view of the corresponding affinity of hydrogen for bromine, we consider that the difference in the attraction exerted upon the bromine atom by these two radicals is largely a function of the location of the hydrogen atoms in the two radicals.

With regard to the relative effectiveness of hydrogen atoms in different positions in the molecule, the best guide appears to be Michael's scale of influence. According to Michael,[3] the following scale represents the order in which the atoms fall as regards the decrease in their influence

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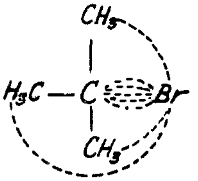
[1] Michael and Zeidler, *Ann.*, **393**, 88 (1912).

[2] This Journal, **38**, 657 (1916).

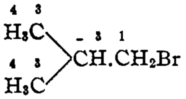
[3] *Ber.*, **39**, 2139 (1906). This scale has been supported by many investigations, mostly dealing with reaction velocities of the compounds concerned. Although other factors than chemical affinity are concerned in determining reaction velocities, the successful application of this scale in so many cases justifies the conclusion that it gives indications of the affinities concerned.

upon any carbon atom, numbered 1, with their degree of removal from it: 2–3–5–6–4......

The author pictures the conditions within such a molecule somewhat as follows: Between the atoms joined together in the molecule there are fields and lines of force, probably electrical force. In addition to this, however, between atoms not joined by any indicated valence such lines of force are not altogether absent, being present in greater or less degree depending upon the character of the atoms. The conceptions of "partial," "residual," "Neben" valence, etc., are based upon such a conception in some form or other. This can be represented by formulas such as those of Kaufmann:[1]



If we examine the formulas for these two butyl bromides, numbering the atoms according to Michael's system:



$$\left.\begin{array}{l}\overset{4}{H}_3\overset{3}{C}\\ \overset{4}{H}_3\overset{3}{C}\end{array}\right\rangle \overset{3}{C}H.\overset{1}{C}H_2Br \qquad (\overset{3}{H_3C})_{\overset{2}{3}}.\overset{1}{C}Br$$

we find nine hydrogen atoms in position 3 in the tertiarybutyl radical, six of which are transferred to position 4, a much less effective position, in the isobutyl radical. The above scale, which indicates the relation between the position of the hydrogen atoms in such a radical and the affinity the radical for negative atoms or groups, may then be interpreted as indicating that atoms in position 3 with respect to the carbon atom joined to the bromine in these molecules, are favorably located for the existence of many more lines of force between them and the bromine than are H-atoms in position 4. For this reason the tertiarybutyl radical exerts the stronger attractive force upon the bromine atom.

Summary.

The equilibrium between iso- and tertiarybutyl bromides and their dissociation products, hydrogen bromide and isobutene, at 221° and 275°, has been studied. A dissociation constant has been determined for the mixtures of bromide present at equilibrium, and the heat of formation of this mixture of these isomers has been calculated.

It has been shown that catalytic influences come into play in the formation as well as in the dissociation of these bromides. It is concluded that the reaction between hydrogen bromide and isobutene occurs slowly when liquid bromide is absent, and that under these conditions isobutyl bromide is usually, if not always, formed. In the presence of liquid bromide the reaction proceeds much more rapidly and only tertiary bromide is obtained.

Taking the above facts into account, it has been possible to calculate the ratio between the undissociated bromides at 275°.

BRYN MAWR, PA.

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[1] "Die Valenzlehre," Stuttgart (1911).