THE REARRANGEMENT
of
1-BROMOBUTANE

Thesis

by

Archibald Y. Jameson

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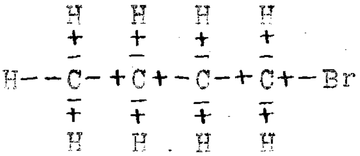
Introduction

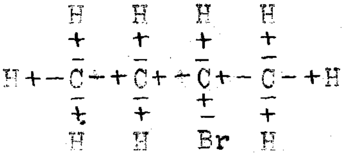
This research was undertaken for the purpose of determining whether, at elevated temperatures, 1-bromobutane, $CH_3CH_2CH_2CH_2Br$, could not be caused to rearrange to 2-bromobutane, $CH_3CH_2CHBrCH_3$, a problem which is of importance in the bearing it has on two opposing theories recently advanced to explain the structure of organic molecules.

One of these theories, supported by Cuy[1] and others,[2] holds that carbon atoms are polar in the same way as, but to a less degree than, inorganic compounds, and that the carbon atoms of a chain tend to become alternately positive and negative, the stability of the chain depending on how closely this condition is fulfilled. Should we write, now, the polarity formulae, after Cuy, of 1- and 2-bromobutane,



$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & + & & + & & + & & + & \\ & - & & - & & - & & - & \\ H-- & C & -+ & C & +- & C & -+ & C & +-Br \\ & - & & - & & - & & - & \\ & + & & + & & + & & + & \\ & H & & H & & H & & H & \end{array}$$

1-bromobutane



$$\begin{array}{ccccccccc} & H & & H & & H & & H & \\ & + & & + & & + & & + & \\ & - & & - & & - & & - & \\ H+- & C & -+ & C & +- & C & +- & C & -+H \\ & - & & - & & + & & - & \\ & + & & + & & - & & + & \\ & H & & H & & Br & & H & \end{array}$$

2-bromobutane

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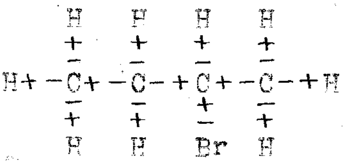
[1] Cuy, J. Am. Chem. Soc. 42, 503 (1920)

[2] Stieglitz, ibid. 44, 1301 (1922); Lapworth, J. Chem. Soc. 121, 416 (1920); and Kermack and Robinson, ibid. 121, 427 (1920)

we would see that the alternation in the case of 1-bromobutane is much more regular than in the case of 2-bromobutane, and we would expect, therefore, that if an equilibrium mixture of the two could be established, the primary form would greatly predominate, if indeed any secondary were present at all. Cuy, however, seems to have overlooked the possibility of representing the polarity formula of 2-bromobutane by



$$\begin{array}{cccccccccccccc}
 & & H & & & H & & & H & & & H & & \\
 & & + & & & + & & & + & & & + & & \\
 & & - & & & - & & & - & & & - & & \\
H+ & - & C & + & - & C & - & + & C & + & - & C & - & +H \\
 & & - & & & - & & & + & & & - & & \\
 & & + & & & + & & & - & & & + & & \\
 & & H & & & H & & & Br & & & H & &
\end{array}$$

in which the alternation is better. The possibility of writing a number of formulae for one substance is a weakness of the theory.

The other concept of the polar conditions within an organic molecule is that of electron displacement induced by the atoms or groups joined to carbon. This theory, explained by Lewis[3] in detail, when applied to the bromobutanes requires that the primary form should completely disappear in an equilibrium mixture. Since any transformation of one bromobutane into the other must be a dissociation into butene and hydrogen bromide followed by recombination, and since the dissociation products

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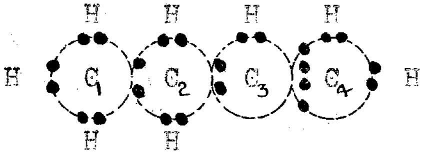
[3] Lewis, "Valence and Structure of Atoms and Molecules" Chem. Cat. Co. New York, 1923.

of both 1- and 2-bromobutane are identical, it is evident that the factors which control the addition of hydrogen bromide to the double bond of butene will determine the character of the equilibrium mixture. In the electronic formula for butene,



in which the circles represent surfaces of spheres where electrostatic conditions are zero, C_3 differs from C_4 in that one substituent of the former is the ethyl group while the corresponding substituent of the latter is hydrogen. The general recognition that alkyl groups are more positive than hydrogen means that the four electrons of the "double bond" must lie closer to C_4 than to C_3. This displacement of electrons away from the surface of the sphere on which they lie in such non-polar compounds as methane gives in effect a relative polarity to the two <u>sides</u> of each carbon atom, as shown below.

$$-C_1+\ -C_2+\ -C_3+\ -C_4+$$

This theory, then, requires that when hydrogen bromide adds to butene the bromine atom go to C_3, and the hydrogen atom to C_4.

1-bromopropane has been found[4] to rearrange to 2-bromopropane, and though several workers[5,6] have studied the transformation of iso- to tertiary butyl bromide, only Meyer and Müller[7]

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[4] Kekulé and Schrotter, Ber. 12, 2279 (1879)

seem to have investigated the equilibrium conditions existing between the primary and secondary forms. These investigators heated 1-bromobutane under a reflux in the presence of iron wire which had been corroded by bromine, but subsequent fractionation showed that no change had taken place. They then repeated the experiment leading in a strong current of hydrobromic acid, but found again that there had been no rearrangement. Finally, a portion of 1-bromobutane with a length of corroded iron wire was sealed into a glass tube and heated on a water bath for seven hours, but, save for a little charring, the contents of the tube were unaltered.

Analytical Method

The 1-bromobutane used in this research was prepared by treating 1-butanol, Eastman, b.p. 116 - 117°, with sodium bromide and sulfuric acid.[8] It was washed with concentrated sulfuric acid

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Aronstein, *ibid*. 14, 607 (1881) and 16, 391 (1883)

5. Eltekoff, *ibid*. 8, 1244 (1875) finds that isobutyl bromide is completely transformed into tertiary butyl bromide.

6. Michael and Leupold, Ann. 379, 263 (1911); Michael and Ziedler, *ibid*. 393, 92 (1912); Brunel, Ber. 44, 1000; Scharf and Voight, J. Am. Chem. Soc. 38, 653 (1916) find that an equilibrium (70 - 80% tertiary) is established between the two isomers.

7. Meyer and Müller, J. Prakt. Chem. 46, 182 (1892)

to remove any butanol, then with water until neutral, dried over anhydrous copper sulfate, and distilled; the portion boiling at 99.0°, uncorrected, was collected. The 2-bromobutane, obtained directly from Eastman, was likewise washed with concentrated sulfuric acid, and with water, was dried over calcium chloride, and distilled. Of this material, the portion coming over at 90 - 91°, uncorrected, was used.

The first step in this research was the development of a suitable method of analysis for mixtures of 1- and 2-bromobutane. W. P. Baxter, who did some preliminary work with these substances, finding that the reaction rates of propyl and isopropyl bromides with silver nitrate solution were considerably different[9], discovered a similar inequality in the reaction rates of the butyl bromides with the same reagent, an inequality which was taken advantage of in investigating unknown mixtures of the two substances. After some introductory experiments with various concentrations of silver nitrate solution, with various temperatures, and times of agitation, the following procedure was adopted: A sample of liquid, closely approximating 0.1 gram, was weighed from a Lunge acid pipette into a small test tube, about 90 mm. long by 25 mm. wide, and the tube tightly stoppered to preclude loss of sample

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[8] University of Ill. Bulletin, <u>6</u>, 18 (1920)

[9] Michael and Leupold, Ann. <u>379</u>, 288 (1911)

by evaporation. 10.00 cc. of approximately 0.20 n silver nitrate solution were next added to the tube from a calibrated pipette, and the mixture agitated by means of a small paddle whirling at a constant rate for exactly three hours at a temperature of 22° (maintained by a water bath around the tube.) After this period of agitation, the contents of the tube were quantitatively transfered to a beaker, where the excess of silver nitrate was titrated with standard potassium thiocyanate solution in the presence of ferric aluminum sulfate as an indicator. Pure 2-bromobutane, when subjected to this treatment, reacts to the extent of 82 percent, 1-bromobutane to 3.8 percent, while mixtures of the two liquids give intermediate values. From Table I, which is a compilation of the results of twenty-three analyses of mixtures of various and known compositions, Curve I is plotted, percent total bromide by analysis as ordinates against percent composition by weight as abscissae. Strictly, a sufficient number of points was not determined to indicate beyond question the character of Curve I, but a straight line approximates the true curve well within the error of the experimental methods. One can, then, by the aid of this curve, read off the percentage composition of any unknown mixture of the two bromides, once having determined the percentage of total bromide reacting.

Rearrangement of 1-Bromobutane

1-bromobutane was caused to rearrange to 2-bromobutane by heating two to seven grams in sealed glass tubes, 12 mm. in diameter, and varying in length from 60 to 110 mm. These tubes were suspended in the vapors of boiling benzoic acid, at 248°; a preliminary experiment (by W. P. Baxter) had shown that less than one percent of 2-bromobutane was formed after 20 hours' heating at 180°, so it was felt that to secure a reasonable reaction rate a temperature well above 200° should be used. All the work was done at this temperature.

A sealed tube, after having been heated the desired length of time in the vapor bath, was cooled, broken, and the contents washed with water until neutral (for a certain pressure of hydrobromic acid had almost always been built up.) The liquid was next dried by shaking with a small quantity of anhydrous copper sulfate, after which the clear liquid was drawn into the Lunge pipette, and was analysed. Duplicate analyses were made of the contents of all tubes, and reasonable checks were invariably obtained. Table II gives the results of the various runs.

Discussion and Conclusions

From an average of the velocity constants for each experiment, Curve II, percentage of 2-bromobutane against time of heating, is plotted. The agreement among the individual constants, though not very good, yet indicates that the reaction is monomolecular; a very close agreement would not, of course, be expected, for errors inherent in the method of analysis are numerous. The velocity constants of Experiments 6 and 9 were not included in the average, for the product of the first was badly charred, while the time of heating of the second was not accurately known. The mean value is 0.029 from which the greatest deviation is about 31 percent.

Curve II indicates that 1-bromobutane rearranges completely to 2-bromobutane at 248°, a behavior which is in marked contrast to that of isobutyl bromide.[6] To confirm this conclusion, 6 grams of 2-bromobutane were heated in a sealed tube of Pyrex glass for 29 hours at the standard temperature of the research. When the tube was broken under water it was found that no pressure had been built up, and titration of the water with which the material was washed with a standard base showed 1.1 percent dissociation into hydrobromic acid, assuming that any hydrogen ions must have come from the breaking down of butyl bromide into butene and hydrobromic acid. A portion of the washed and dried product of this tube was subjected to the silver nitrate analysis, the results of which follow:

	Wt. of Sample	Percent total bromide	Percent Secondary
a)	0.106 g.	83	100
b)	0.105 g.	85	100

Yet these values do not indicate that the secondary bromide has undergone no change during the heating, for it appeared a deeper brown than the material of any other experiment. The remainder of the 6 grams was fractionated under a very small and efficient column:

Fraction	Temperature Range	Quantity (roughly estimated)
1	below 89.5° (uncor.)	20%
2	89.5 - 90.2°	24%
3	90.2 - 92.0°	40%
4	92.0 - 95°	8%
5	dark residue	8%

The distillation, as with other fractionations during this research, could not be continued because of violent bumping in the brown residue.

A similar fractional distillation was carried out with the product of number 8 (Table II), 1-bromobutane which had been heated for 50 hours, and two of the fractions were analysed by the silver nitrate method:

Fraction	Temperature Range (uncorrected)	Approximate Quantity	Percent 2-bromobutane by analysis
1	below 89.6°	25%	97
2	89.6 - 90.1°	40%	96
3	90.1 - 91.2°	17%	
4	91.2 - 93.5°	8%	
5	brown residue	10%	

In the case of Experiments 8 and 9, the dissociation into hydrogen bromide was determined by titrating the wash water with 0.54 N sodium hydroxide solution; dissociations of 3.1 and 4.2 percent were calculated.

One particularly interesting experiment (number 2) was performed for the purpose of determining if the rate of rearrangement was influenced by the free volume in the reaction tube, or by the dimensions of the liquid surface. Three tubes, a, b, and c, were heated for 3 hours and 40 minutes at 248°. Tubes a and c were identical in all respects, but in the vapor bath the former was suspended in a vertical position, while the latter was hung horizontally. Tube b, while of the same diameter as the other two, was about twice as long so that its free volume was three times that of a or c. Tube b was hung vertically. Exactly the same quantity of liquid was placed in each tube. Arranged as described, b has three times the free volume of a and c, c has three times the liquid surface of a and b, while a has the same free volume as c and the same liquid surface as b. Considering that the tangent to Curve II at the three hour point is very steep indeed (about 6 percent per hour), and that the silver nitrate method of analysis grows more and more inaccurate as lower percentages of the secondary form are determined, depending as it does on a difference in two burette readings that is smallest at low concentrations of the secondary form, it is seen that the analyses of the three tubes are in very close agreement. Further, the liquid in the tube that had the largest free volume (tube b) was evidently more dissociated than that in the other tubes, for it was a dark brown where the other products were quite colorless; and this liquid showed by analysis a slightly lower value of 2-bromobutane. One concludes, then, that the rate of rearrangement does not depend on the dimensions of the liquid surface, nor on those of the free volume, but that a large free volume favors dissociation.

Summary

i) A method of determining 2-bromobutane in the presence of 1-bromobutane has been developed.

ii) 1- and 2-bromobutane were heated separately in sealed tubes at 248°.

iii) 1-bromobutane rearranges completely to 2-bromobutane at 248°, while 2-bromobutane, save for a little charring, remains unaltered.

iv) The rearrangement of 1-bromobutane to 2-bromobutane is better explained by the electron displacement theory than by the alternate polarity theory

TABLE I

Analysis of Known Mixtures of Butyl Bromides at 22°

No.	Weight of 1-bromobutane	Weight of 2-bromobutane	Percent 2-bromobutane by Wt.	Cu. cm. of 0.2032 N $AgNO_3$	Cu. cm. of 0.1171 N KSCN	Percent total bromide by analysis
1	0.147 g	0.000 g	0.0	9.97	16.97	3.6
2	0.151 g	0.000 g	0.0	10.04	17.04	4.0
3	0.120 g	0.000 g	0.0	10.01	17.07	3.9
4	0.158 g	0.000 g	0.0	9.99	16.98	3.6
5	0.113 g	0.014 g	11.0	10.00	16.40	12.0
6	0.098 g	0.014 g	12.5	10.00	16.47	12.7
7	0.108 g	0.028 g	20.6	10.00	15.62	20.4
8	0.076 g	0.027 g	26.2	10.00	15.87	23.1
9	0.096 g	0.055 g	36.4	10.00	14.30	32.4
10	0.172 g	0.107 g	38.4	10.02	12.08	30.5
11	0.086 g	0.086 g	50.0	10.00	13.07	40.0
12	0.090 g	0.106 g	54.1	10.04	11.37	49.5
13	0.086 g	0.104 g	54.8	9.99	11.90	45.9
14	0.084 g	0.117 g	58.2	10.00	10.55	54.2
15	0.062 g	0.088 g	58.6	10.00	12.75	49.2
16	0.087 g	0.124 g	58.8	10.02	10.70	50.8
17	0.046 g	0.076 g	62.2	10.00	12.98	57.5
18	0.067 g	0.121 g	64.4	10.04	11.36	51.7
19	0.019 g	0.098 g	83.8	10.00	11.82	75.8
20	0.020 g	0.113 g	85.0	10.00	11.23	73.9
21	0.000 g	0.106 g	100.0	9.79	8.83	82.
22	0.000 g	0.088 g	100.0	10.13	13.14	81.
23	0.000 g	0.144 g	100.0	10.06	10.08	82.

CURVE I

Analysis of Known Mixtures of the Bromobutanes at 22°.

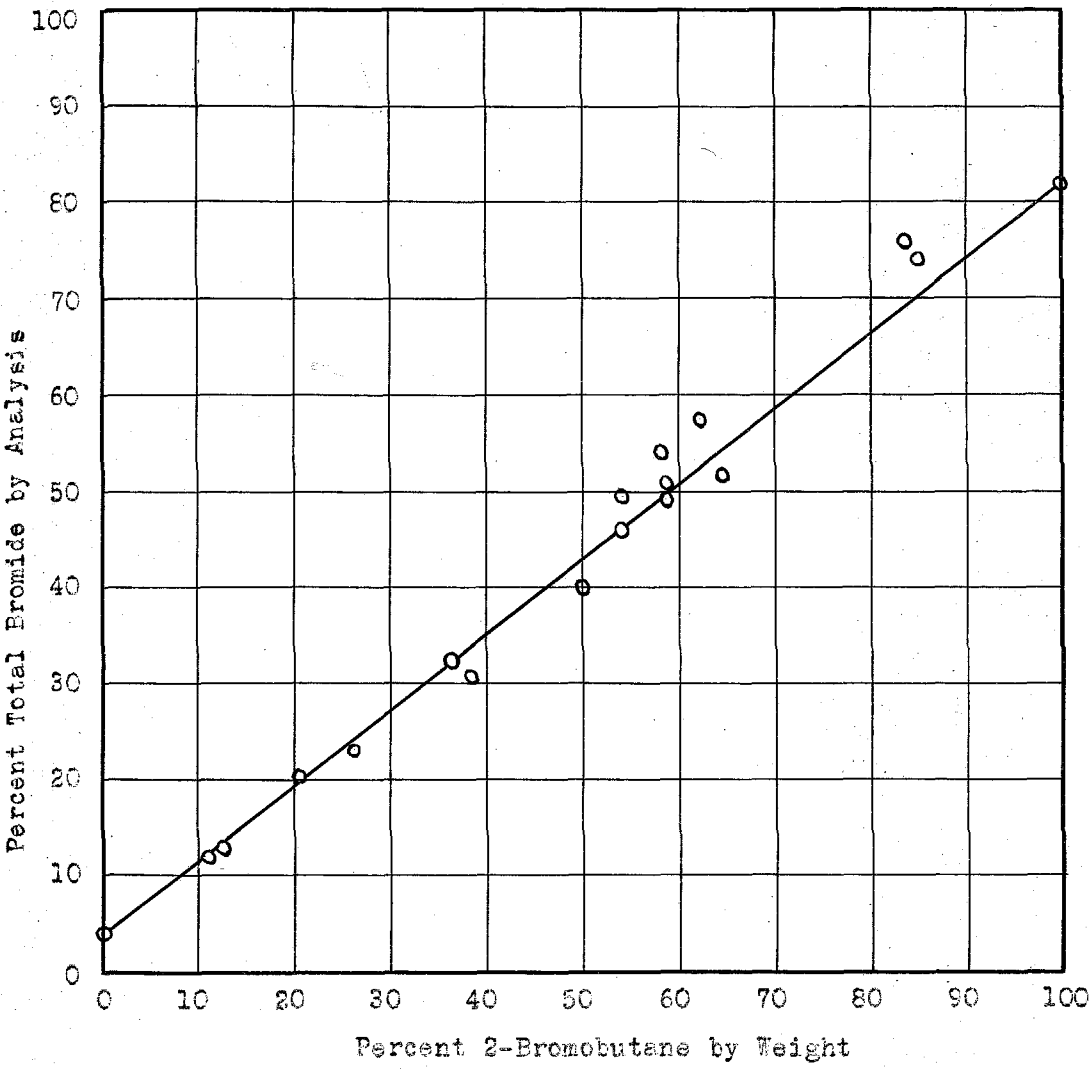

TABLE II

Rearrangement of 1-Bromobutane at 248°.

No.	Hours Heated	Wt. of Sample Taken for Analysis	Cu. cm. of 0.2049 N $AgNO_3$	Cu. cm. of 0.08869 N KSCN	Percent Total Bromide by Analysis	Percent 2-Bromobutane Found	K, for Monomolecular Reaction	Remarks
1	3	0.105	10.0	21.24	21.5	22	.038	
		0.101	10.0	21.28	22.9	24		
2	$3\frac{2}{3}$ a	0.074	10.0	21.80	21.4	$22\frac{1}{2}$	.027	a colorless after heating. Liq. had same surface as b. Same quantity of liq. in all tubes.
		0.091	10.0	21.58	20.3	21		
	b	0.104	10.0	21.47	19.0	$19\frac{1}{2}$		Liquid much charred by heating. Tube b had 3 times the free volume of a and c.
		0.094	10.0	21.62	19.2	20		
	c	0.096	10.0	21.49	20.4	21		Liquid colorless. Tube c had same free volume as a, but 3 times the liq. surface of a and b.
		0.094	10.0	21.52	20.4	21		
3	7	0.106	10.0	19.74	38.5	44	.037	
		0.098	10.0	19.84	40.5	47		
4	19	0.128	10.0	17.66	52.	62	.023	
		0.101	10.0	18.58	54.	64		
5	20	0.108	10.0	18.40	53.	63	.022	
		0.112	10.0	18.05	54.8	65		
6	27	0.118	10.0	18.17	50.8	60	.015	The liquid in this tube was very dark brown after heating.
		0.080	10.0	19.51	54.5	65		
7	29	0.091	10.0	17.82	71.	86	.031	Very little free volume in tube during heating. The analysis was confirmed by fractionation.
		0.091	10.0	17.65	73.	89		
8	50	0.092	10.1	17.32	79.5	97	.029	Dissociation during heating determined by titrating HBr in wash water Dissociation: 3.1%
		0.067	10.0	18.77	78.5	96		
9	80	0.097	10.0	16.66	80.8	98	.021	Exact time of heating unknown. Dissociation determined as above: 4.2%
		0.094	10.0	16.85	80.8	98		

CURVE II Rearrangement of 1-Bromobutane at 248°.