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Abstract

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EQUILIBRIUM OF THE REACTION $C_3H_7Br \rightleftarrows C_3H_6 + HBr$

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The reversibility of the hydrobromination reaction of propylene has long been known ([1–4]); however, quantitative measurements of the equilibrium state of this system have not yet been published. Few works devoted to the equilibrium of dehydrohalogenation of alkyl halides are known ([5–10]). In most of them the authors used the static method, and the only criterion for the extent of the process was the change in pressure. In the present work, the equilibrium of dehydrobromination of 2-bromopropane was studied in the interval 110–174°C by the flow-system method.

2-Bromopropane of "pure" grade, as well as 1-bromopropane prepared in our laboratory, were dried with calcium chloride and fractionated on a laboratory column with an efficiency of 20 theoretical plates. After threefold fractionation with selection of the middle fraction, the products had the following properties:

	b.p., °C	n_D^{20}
1-bromopropane	70.0–70.1	1.4338
2-bromopropane	59.3–59.4	1.4260

In the infrared spectrum of 2-bromopropane, no peak corresponding to isomer 1, nor any alcohol peaks, were detected. The glass reactor, on ground joints, had a vapor jacket with a pocket for a thermometer. Vapors of steadily boiling liquids (toluene, brominated isoamyl, chlorobenzene, nonane, and decane) were used for thermostating. The total amount of reaction products passed through the reactor in each experiment was determined from the weight gain in the absorption system and checked by the volume in the dosing device. The discrepancy in the material balance usually did not exceed 0.2 g for a total weight gain of 4–8 g. For each temperature, at different flow rates, two series of experiments were

carried out with separate determination of the content of hydrogen bromide and propylene.

In addition, for several temperatures (132.0; 150.7; 174.3°C), enlarged experiments were carried out with freezing of the reaction products at a temperature of about −70°C, followed by their analysis (infrared spectrum, yield of high-boiling reaction products by fractionation on a microcolumn with an efficiency of 15 theoretical plates). Hydrogen bromide was absorbed by an alcoholic solution of dimethylaniline (DMA) (titration of the solution diluted with water with 0.1 N $AgNO_3$).

It was established by specially performed experiments that an alcoholic solution of DMA does not bind either isopropyl bromide or propyl bromide during 6 hours of joint standing, and quantitatively absorbs hydrogen halide (HCl) both in their absence and in their presence.

After the trap with DMA, a trap with alcohol was placed, cooled to a temperature of −70°C with a mixture of dry ice and alcohol, to capture propylene and the vapors of isopropyl bromide entrained by it.

For determination of propylene, the trap was filled with a solution of bromine-iodine in carbon tetrachloride. After it, a U-shaped tube with anhydrous soda was placed to absorb hydrogen bromide, and the entire absorption system ended with a trap with alcohol placed in a refrigerating mixture. The correction for halogenation of saturated compounds was small and amounted to 0.4-0.6 ml of 0.1 N $Na_2S_2O_3$ (0.2-0.3 ml of 0.1 N NaOH).

by 8 g of the trap packing. The alcoholic solution from the last trap was checked for the content of the ion Br'. The results were always negative.

In experiments up to a temperature of 150.7°C, the amounts of propylene and hydrogen bromide always agreed well. However, already at 150.7 and 174.3°C the amount of propylene in the traps with bromine-iodine was somewhat smaller than that of hydrogen bromide in the DMA traps. One of the simplest explanations was that in the traps with bromine-iodine, during the experiment, competing reactions could proceed according to the schemes

$$C_3H_6 + Br - J \rightarrow C_3H_6Br; \tag{1}$$

$$C_3H_6 + HBr \rightarrow C_3H_7Br. \tag{2}$$

In order to eliminate the significance of the second reaction, a series of experiments was carried out giving the extrapolated consumption of bromine-iodine to zero contact time in the trap, where the effect of the second, slower reaction is eliminated (Fig. 1). The discrepancy between DMA and Br—J with this correction was about 0.3 ml at 150.7°C and 1.2 ml at 174.3°C (per 8 g of trap packing).

Fig. 1

Fig. 2

It is possible that the latter difference corresponds to the consumption of propylene in side reactions. In the condensates of enlarged experiments for temperatures of 132° and 150.7°C, high-boiling products could not be detected; for 174.3°C they amounted to an insignificant value—0.25% of the condensate weight. The content of the 1-isomer only in experiments at 174.3°C was 0.68% and was taken into account in calculating the equilibrium constant. In experiments at 132° and 150.7°C, however, the content of the 1-isomer was 0.3–0.4%, which lay within the error limits of individual experiments.

The catalyst for the reaction was cuprous bromide, promoted with nickel and cadmium (1% each relative to $CuBr_2$), deposited on activated carbon, which had previously been activated at 250°C in a stream of carbon dioxide.

Fig. 3

At 120.6°C the time for the catalyst to reach steady operation was 4 hours (Fig. 2). For temperatures of 132°C and above, the catalyst practically immediately reached its operating regime. A catalyst that had operated steadily at one temperature for 30–40 h was subjected to a change in temperature (it was shifted to a lower one, and then returned to a higher one). The reproducibility of experiments on already used and fresh catalysts was very good. The lowest catalyst operating temperature giving reliable results was 120.6°C. At a temperature of 110.6°C the catalyst did not reach steady operation within 20 h and then ceased to function. This is shown graphically in Fig. 2. Although from these data one can also approximately calculate the equilibrium constant, as some authors do ([6]), and this value fits well on the straight line of the graph (Fig. 3), nevertheless we consider this value to be extrapolated.

At two temperatures (120.7 and 132° C), experiments were carried out to obtain the equilibrium mixture from the synthesis side. For this purpose we set up two reactors in series. In the first reactor, with an isopropyl bromide feeder, a temperature of 139.7° C was maintained. The reaction products from the first reactor, after passing through a connecting tube (the joint was closed with a rubber tube) and a three-way stopcock, could enter either the control system (trap system) or the second reactor, which had a lower temperature (120.7 or 132° C). The reaction products from the second reactor were collected in traps and analyzed as usual.

In this case, however, it turned out that the reaction products, which in the first reactor attained an equilibrium composition corresponding to 139.7° C, after passing through the joint and the three-way stopcock lost part of the components, and a mixture with nonequivalent contents of propylene and hydrogen bromide entered the second reactor. Nevertheless, the values of the equilibrium constants obtained in this way are close to the values of K_p obtained in the decomposition experiments. The results of the experiments are summarized in

Table 1.

Table 1

Temperature, °C	Number of experiments	Space velocity, ml/ml·cat·h, max.	Space velocity, ml/ml·cat·h, min.	Number of moles $\cdot 10^4$ of C_3H_6 and HBr per 8 g trap weight, by DMA, max.	Number of moles $\cdot 10^4$ of C_3H_6 and HBr per 8 g trap weight, by DMA, min.	Number of moles $\cdot 10^4$ of C_3H_6 and HBr per 8 g trap weight, by Br–I, max.	Number of moles $\cdot 10^4$ of C_3H_6 and HBr per 8 g trap weight, by Br–I, min.	$K_p \cdot 10^{31}$, max.	$K_p \cdot 10^{31}$, min.	$K_p \cdot 10^4$, average
120.6	8	0.07	0.04	21.6	20.3	–	–	1.095	1.000	1.03
120.6	3	0.07	0.04	–	–	$\frac{21.4^2}{20.6}$	$\frac{21.2^2}{19.8}$	1.095	1.000	1.03
132.0	6	0.25	0.10	29.5	28.0	–	–	1.905	1.975	1.95
132.0	4	0.25	0.10	–	–	$\frac{29.2^2}{29.4}$	$\frac{28.2^2}{28.5}$	1.905	1.975	1.95
139.7	8	0.20	0.10	36.9	34.4	–	–	3.270	3.060	3.17
139.7	5	0.20	0.10	–	–	$\frac{36.2^2}{36.8}$	$\frac{34.0^2}{34.0}$	3.270	3.060	3.17
150.7	9	0.25	0.10	51.4	50.0	–	–	6.240	6.070	6.13
150.7	5	0.30	0.10	–	–	48.9 $(50.2)^3$	48.4 $(50.2)^3$	6.240	6.070	6.13
174.3	15	0.15	0.15	96.0	93.8	–	–	21.750[4]	21.300[4]	21.57[4]
174.3	5	0.15	0.15	–	–	89.7 $(93.8)^3$	88.9 $(93.8)^3$	21.750[4]	21.300[4]	21.57[4]
Experiments from the synthesis side	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**	**Experiments from the synthesis side**
120.8	5	0.06	0.04	20.3	19.1	23.6	23.0	1.170	1.090	1.12
132.0	8	0.06	0.04	29.8	29.5	27.6	27.2	2.040	1.990	2.01

[1] Max. and min. are not connected with the space velocity.

[2] The numerator is propylene, the denominator hydrogen bromide.
[3] The corrected value according to Fig. 1 is given in parentheses.
[4] The content of the 1-isomer was taken into account.

On the basis of the data in the table of experiments, a graph was constructed (Fig. 3) of the values $\lg K_p \cdot 10^4 - \frac{1}{T} \cdot 10^3$. As can be seen from the graph, all points fall satisfactorily on a straight line, which was drawn through the average values of K_p of the most widely separated, reliably measured points: 120.6 and 150.7° C.

The equation of the straight line has the form $\lg K_p = 7.775 - \frac{19370}{4.575T}$. This corresponds to the values $\Delta H_0^0 = 19370$ cal. and $\Delta S = 35.57$ cal/deg, which should be referred to the mean temperature of the interval, 408.9° K.

For $\Delta Z_{408.9}^0$, a value of 4825 cal. is obtained. In the work of Lacher with a coauthor ([11]), attempts were made to determine directly, by calorimetry, ΔH^0 of this reaction. The authors obtained $\Delta H_{365}^0 = 20\,140 \pm 240$ cal. Kistiakowsky ([10]) and Howlett ([7]), for the hydrobromination of isobutylene, found $\Delta H_T^0 = 18\,900$ cal/mole. The ΔH^0 of our reaction, according to Kistiakowsky, may be estimated as equal to 18,500-18,700 cal.

By combining the value of ΔS_T^0 found by us for the dehydrobromination reaction with the values of S_T^0 for propylene and HBr, the entropy value for 2-bromopropane is obtained: $S_{408.9}^0 = 83.37$ cal/deg.

For the calculation of the thermodynamic functions of 2-bromopropane we used the following data: distances $C—H = 1.1$ Å; $C—C = 1.53$ Å; $C—Br = 1.97$ Å. The angles are tetrahedral.

The assignment of the vibrational frequencies was made by Sheppard [(12)]: 295 (2), 407, 536, 878, 930, 946, 1038, 1126, 1156, 1223, 1325; 1370, 1383, 1442 (2), 1465 (2), 2920 (7).

With these data the moments of inertia are obtained: $I_x = 368.32 \cdot 10^{-40}$ g · cm^2; $I_y = 294.42 \cdot 10^{-40}$ g · cm^2; $I_z = 102.0 \cdot 10^{-40}$ g · cm^2.

The Z axis makes an angle of 14°28′ with the direction of the $C—Br$ bond. The reduced moment of the methyl group is $I_{\text{pr}} = 5.19 \cdot 10^{-40}$ g · cm^2. This gives, for free rotation of two tops at a temperature of 408.9° K, an entropy value $S_{408.9}^0 = 85.63$ cal/deg.

The difference $S_{\text{f.r.}}^0 - S_{\text{h.r.}}^0$ is 2.26 (per one top, 1.13) cal/deg. According to the tables of Pitzer and Gwinn, this corresponds to a potential-barrier height of 3550 cal. In ethyl bromide, radiospectroscopy determines the barrier height as 3567 ± 30 cal. [(13)].

With a barrier of 3550 cal, we calculated the thermodynamic functions of 2-bromopropane (summarized in Table 2).

Table 2

	298.16°K	300°K	400°K	500°K	600°K
S_T^0	75.71	75.83	82.70	89.15	94.94
C_p^0	21.35	21.44	26.57	30.78	34.29
$\frac{H_T^0 - H_0^0}{T}$	13.734	13.781	16.336	18.808	21.085
$-\frac{Z_T^0 - H_0^0}{T}$	51.977	62.046	66.368	70.347	73.352

By combining the value $\Delta H_T^0 = 19370$ cal found by us with the known data for propylene [14] and hydrogen bromide [15], one can also calculate the values of ΔZ_f^0 and ΔH_f^0 for isopropyl bromide.

We found the values $\Delta H_0^0 = -22009$ cal and $\Delta H_{f\,298.16}^0 = 23190$ cal. The latter agrees well with the value $\Delta H_{f\,298.16}^0 = -23550 \pm 460$ cal, calculated from calorimetric data [16].

We studied the equilibrium of the reaction $C_3H_7Br \rightleftarrows C_3H_6 + HBr$ in the temperature range 110—174°C from the decomposition side and, for 120—132°C, from the synthesis side. We calculated the heat of reaction, the change in entropy, and the free energy for 408.9°K. The potential barrier limiting the rotation of methyl groups was estimated as 3550 cal. From molecular and spectral data, the barrier height of 3550 cal and the heats of formation of propylene and hydrogen bromide were used to calculate the values of the thermodynamic functions of 2-bromopropane.

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Note: Figure translations are in progress. See original paper for figures.