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## Abstract

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# EQUILIBRIUM OF THE ISOMERIZATION OF BROMOPROPANES

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The cheapest methods for obtaining alkyl halides consist in the direct halogenation of hydrocarbons and in the addition of a hydrogen halide to a double bond. Although certain rules have been established for the preferential formation of particular isomers, it is nevertheless not possible to obtain individual alkyl halides in pure form. Approximate thermodynamic calculations, based on empirically obtained energy relationships (heats of addition of hydrogen halides), indicate that Markovnikov’ s rule is consistent with the thermodynamic probability of reactions proceeding in two directions.

However, there is also a clear influence here of kinetic factors on the yield of one product or another. A striking example is the fact discovered by Kharash (ˆ1) that, in the presence of peroxides (ascaridole), addition of hydrogen bromide proceeds predominantly in the opposite direction. This can be explained by a radical mechanism of the reaction.

It should be noted that, when the reaction proceeds normally according to Markovnikov’ s rule, both factors—the thermodynamic and the kinetic—act in the same direction. Thus, addition of hydrogen bromide to propylene with formation of 2-bromopropane is a more exothermic reaction than formation of 1-bromopropane under the same conditions.

In accordance with the inverse relationship between the magnitude of the thermal effect and the activation energy, the rate of formation of 2-bromopropane should be greater than the rate of formation of 1-bromopropane.

Direct halogenation leads to the formation of a considerable amount of the 1-isomer. Here the course of the process is evidently determined by kinetic factors.

Unfortunately, there are still no reliable data for thermodynamic calculations that could indicate what limiting ratio of isomers can be obtained by introducing a halogen into hydrocarbons by one route or another.

The isomerization of alkyl halides was first observed by A. M. El’tekov (ˆ2) in the examples of isobutyl and isoamyl bromides. For the case of the isomerization of primary isobutyl bromide into tertiary, A. M. El’ tekov even observed a conversion limit at 230–240°, corresponding to 80% tertiary bromide, although later he expressed uncertainty that equilibrium had been reached here.

Aronshtein (^3) observed the conversion of propyl bromide at 280° and noted that the reaction did not proceed to completion.

A. E. Favorskii (^4), together with coworkers, firmly established the presence of isomerization of alkyl halides, including bromopropanes, at temperatures above 200°.

Somewhat later Michael and Leupold (^5) published a large work on the isomerization of alkyl bromides. For propyl bromides in the vapor phase at 237°, the authors found the content of normal bromide to be 3.80% after 2 hours, 4.47% after 3 hours, and 5.72% after 5 hours.

These results raise doubts, since as the reaction proceeds the rate of isomerization should decrease and—since by the third hour the content of the normal bromide had increased by 0.67%—over the subsequent 2 hours the yield of this bromide could hardly have increased by 1.25%.

In the thirties, Brouwer and Wibaut (6) reported that at a temperature of about 250° equilibrium was reached by them within 96 hours. They found that at 250° the equilibrium mixture contains 70% secondary bromide and 30% primary, while at 275° it contains 33% primary and 67% secondary. However, these results cannot be considered correct. Although the heat of isomerization calculated from these equilibrium data in the given temperature range leads to an acceptable value—3200 cal.—for lower temperatures the formation of small amounts of the 2-isomer (1–1.5%) has always been observed.

If one assumes that the order of magnitude of the content of the 2-isomer at low temperatures corresponds to the equilibrium to some extent, then, by an analogous calculation, the heat of reaction over a broader temperature range (367–523° K) should be of the order of 800 cal., which is unlikely.

These overestimated contents of primary bromopropane may be explained by the unsuitability of the method of determining the isomers, adopted by the authors, from refraction. In experiments on high-temperature isomerization, other authors noted the formation of higher alkyl halides (probably by dimerization of the olefin through which the isomerization proceeds). In this case there should be a sharp change in refraction, even with small contents of the impurities formed.

As for the heat of isomerization, it can be approximately estimated by the method of G. B. Kistyakovskii (7), according to whose data the heats of addition of a hydrogen atom to primary and secondary carbons are respectively 16.3 and 13.5 kcal, and the heats of addition of a bromine atom are 14.5 and 14.9 kcal. Hence the heat of isomerization for the process 1-bromopropane → 2-bromopropane is 3200 kcal.

The heat of hydrobromination of propylene (with formation of 2-bromopropane)

Fig. 1

Figure 1: Fig. 1

according to these data will be −18.8 kcal. The experimentally determined heat of hydrobromination according to Lacher (8) is −20140 cal.

In our laboratory, work was undertaken to study the isomerization equilibrium of bromopropanes: at the boiling point of 2-bromopropane, 60° (in the liquid phase), and at 250° (in the vapor phase). At the low temperature, the catalyst used was $AlBr_3$ (in an amount of 5% by weight) in the form of snow-white crystals (a melt) stored in a sealed ampoule. Equilibrium was reached at a content of 1.3% 1-bromopropane in the liquid phase. At 250°, in a sealed ampoule under a nitrogen atmosphere, equilibrium was reached without a catalyst. The large volume of the ampoules ensured complete vaporization of the bromides (filling 8% of the ampoule volume).

The equilibrium content of 1-bromopropane at this temperature was found to be 5.2%, and $K_{523^\circ\mathrm{K}} = 18.5$. Knowing the liquid-phase equilibrium at 60°, one can calculate the vapor-phase equilibrium at the same temperature.

The heat of vaporization of 1-bromopropane according to Trouton' s constant is 7220 cal.; using the integrated Clapeyron-Clausius equation, this gives at 60° a vapor pressure of 526 mm. The ratio of isomers in the vapor phase is

$$\frac{760 \cdot 98.7}{526 \cdot 1.3} = \frac{99 \cdot 1}{0.9} \simeq 110.$$

Thus, we have found the equilibrium constants in the vapor phase for two temperatures: $K_{333^\circ\mathrm{K}} = 110$; $K_{523^\circ\mathrm{K}} = 18.5$.

Hence the change in free energy of the reaction $CH_3CH_2CH_2Br \rightleftarrows CH_3CHBrCH_3$ is $\Delta Z^0_{333^\circ\mathrm{K}} = -3110$ cal/mol; $\Delta Z^0_{523^\circ\mathrm{K}} = -3020$ cal/mol, or in general form: $\Delta Z^0_T = -3270 + 0.474\,T$, which gives a heat of isomerization $\Delta H^0_T = -3270$ cal/mol in agreement with Kistyakovskii' s rule and $\Delta S^0_T = -0.474$ entropy units.

## Experimental Part

Both 1-bromopropane and its isomer were obtained by the action of phosphorus tribromide on narrow fractions of the corresponding alcohols. The fraction of normal alcohol had a boiling interval of 97.5—98.5°, and that of isopropyl alcohol 82.4—83.0°.

After repeated fractionation, the bromopropanes obtained were distilled in the intervals 71.4—71.7° (1-bromopropane) and 59.45—59.55 (2-bromopropane).

**Fig. 1**

Special attention was devoted to obtaining 2-bromopropane, and only as a result of repeated refractionations was it possible to obtain a product spectrally free from the impurity of the 1-isomer.

The purity of the preparation, as well as the determination of the content of the 1-isomer in mixtures, was monitored from the intensity (peak *a*) in the infrared spectrum of the line with frequency 1282 $\text{cm}^{-1}$ (Fig. 1, *I*). As is seen from Fig. 1, *II*, 2-bromopropane does not contain an impurity of its isomer (peak *a*).

The spectra were obtained on an IKS-14 double-beam instrument.

In experiments in the liquid phase, equilibrium was attained from both sides. First, pure 1-bromopropane was taken in a flask with a reflux condenser connected to a constant-pressure gasometer, and after the addition of aluminum bromide and several drops of water, heating was carried out to gentle boiling. The duration of these experiments was 2, 6, and 12 h.

In all these experiments no gas evolution was observed. After cooling, the catalyst complex was decomposed with water, and after washing, drying with calcium chloride, and distillation, the product was subjected to spectral measurements. It was established that 6 h was sufficient to attain equilibrium. This is seen from the identical height of peak *a* in Fig. 1, *III*, *IV*.

To attain equilibrium from above, a previously prepared mixture containing 98.5% 2-bromopropane and 1.5% 1-bromopropane was taken. After

After 6 hours of heating, the peak height was almost the same as in the preceding experiments with pure 2-bromopropane, but after 12 hours of heating the peak height coincided completely with the previous ones and no longer changed (Fig. 1, *V, VI*).

From the calibration curve of standard mixtures, the content of 1-bromopropane in the liquid phase is estimated at $1.30 \pm 0.5\%$ (for a temperature of 60°).

Equilibrium in the vapor phase was attained in sealed ampoules, previously filled with nitrogen, without catalyst, and placed in a furnace at a temperature of 250°.

Here the equilibrium was also approached from two sides. In addition to pure 2-bromopropane, a mixture of both isomers containing 11.1% 1-bromopropane was taken. After 100 hours the ampoules were opened, the product was filtered (although no increased pressure was observed when the ampoules were opened, coke deposition was noted on the walls of the ampoules) and distilled. We observed the formation of a small amount (1–2 drops from a 25 $\text{cm}^3$ charge) of a higher-boiling residue during distillation of the equilibrium mixture.

From the heights of peaks *a* for both liquids it was found that the mixture obtained from pure 2-bromopropane contained $5.2 \pm 0.2\%$ 1-bromopropane, while the previously prepared artificial mixture (with 11.1%) contained $6.7 \pm 0.2\%$ of the same isomer (Fig. 1, *VI, VII*).

Both liquids were again placed in ampoules for another 100 hours at the same temperature. In this case the mixtures were found to contain 5.2 ± 0.2% and 5.2 ± 0.2% 1-bromopropane (Fig. 1, *VIII, IX*).

The spectral determinations were carried out by L. P. Shadrin. V. M. Aleksandrova took part in the preparative portion of the work.

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