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The Entropy Difference between the Rotational Isomers[1]

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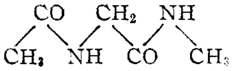
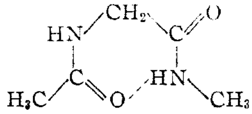
The intensities of two absorption bands, of which one is assigned to the *trans* molecule and the other to the *gauche* molecule of ethylene chlorhydrin have been compared with that of the standard band which is common to the *trans* and the *gauche* molecules in frequency and in molecular absorption coefficient. Such a measurement has been made at different temperatures and from the experimental results the entropy difference between these rotational isomers has been calculated as 3.7 ± 0.4 e.u. This entropy difference has been explained from the structural difference between the *trans* and the *gauche* molecules.

In a previous research on the structure of molecules which can be regarded as structural units of a polypeptide chain we found two configurations of acetylglycine N-methylamide



(E-form) and



(B-form)

which exist in an equilibrium in carbon tetrachloride solutions.[2] There was also found a striking change of the equilibrium ratio with temperature due to the large entropy difference between these two forms.

The large difference in entropy between the two forms of acetylglycine N-methylamide might explain the value of entropy change observed on denaturation of some proteins, since the unfolding of a polypeptide chain on denaturation has been proved by X-ray investigations.

In view of the importance of such a study in protein chemistry, we have made a more exact measurement of entropy difference on ethylene chlorhydrin, a simpler molecule which· has an internal rotation axis and is capable of forming an internal hydrogen bond just as the B-form of acetylglycine N-methylamide.

According to our Raman and infrared investigations ethylene chlorhydrin exists in two molecular forms in the liquid and gaseous states and only in one form in the solid state.[3] These two forms are the *trans* and the *gauche* forms as shown in Fig. 1 and the *gauche* form is the more stable of the two owing to the internal hydrogen bond which will not be formed in the *trans* form. It was also found by these investigations that the energy difference between these two forms amounts to 950 ± 20 cal./mole in the gaseous state.

trans form *gauche* form

Fig. 1.—Stable configurations of $ClH_2C—CH_2OH$ as viewed along the C–C axis. (Full lines denote the bonds in the upper part of the molecule and the dotted lines those in the lower part.)

We shall now try to obtain the entropy difference between these two rotational isomers by the optical method. Let N_t and N_g be the numbers of the *trans* and the *gauche* molecules and $\Delta E = (E_t - E_g)$ and $\Delta S = (S_t - S_g)$ be the differences in energy and in entropy between these two kinds of molecules. Then we have

$$N_t/N_g = {}^1/_2\exp(\Delta S/R)\exp(-\Delta E/RT) \quad (1)$$

Putting the value of ΔE = (950 cal./mole) into this equation, we have

$$N_t/N_g = 0.18\exp(\Delta S/R)$$

as the equilibrium ratio at 200°. If, therefore, the value of ΔS were small as compared with R, the proportion of the *trans* molecule in the equilibrium mixture would be small.

Let us now consider an absorption band at 760 cm.$^{-1}$ assigned to the *trans* molecule (hereafter designated as T-band) and another one at 669 cm.$^{-1}$ assigned to the *gauche* molecule (hereafter designated as G-band).[4] As the intensity of T-band was found not much different from that of G-band, the value of ΔS must be considerably large, unless the molecular absorption coefficient of T-band is much larger than that of G-band.

It is evident that the temperature dependence of the relative intensity of these two bands will give us only the value of ΔE, but not that of ΔS. If, however, there is another absorption band (hereafter designated as S-band meaning standard band) common to the *trans* and the *gauche* molecules in frequency and in molecular absorption coefficient, we can calculate the value of ΔS as follows. According to Eq. (1) we have

$$\frac{N_t}{N_t + N_g} = \frac{1}{1 + 2\exp(-\Delta S/R + \Delta E/RT)} \quad (2)$$

and

$$\frac{N_g}{N_t + N_g} = \frac{1}{1 + {}^1/_2\exp(\Delta S/R - \Delta E/RT)} \quad (3)$$

Let κ be the molecular absorption coefficient and D be the optical density ($D = \ln I_0/I$). Then we have

$$\frac{D_T}{D_S} = \frac{\kappa_T}{\kappa_S}\frac{N_t}{N_t + N_g} = \frac{\kappa_T}{\kappa_S}\frac{1}{1 + 2\exp(-\Delta S/R + \Delta E/RT)} \quad (4)$$

$$\frac{D_G}{D_S} = \frac{\kappa_G}{\kappa_S}\frac{N_g}{N_t + N_g} = \frac{\kappa_G}{\kappa_S}\frac{1}{1 + {}^1/_2\exp(\Delta S/R - \Delta E/RT)} \quad (5)$$

$$2\exp(\Delta E/RT)\exp(-\Delta S/R) - \frac{\kappa_T}{\kappa_S}\frac{D_S}{D_T} + 1 = 0 \quad (6)$$

$${}^1/_2\exp(-\Delta E/RT)\exp(\Delta S/R) - \frac{\kappa_G}{\kappa_S}\frac{D_S}{D_G} + 1 = 0 \quad (7)$$

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(1) Presented at the Twelfth International Congress of Pure and Applied Chemistry.

(2) S. Mizushima, T. Shimanouchi, M. Tsuboi, T. Sugita, E. Kato and E. Kondo, THIS JOURNAL, **73**, 1330 (1951).

(3) S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J. Chem. Phys.*, accepted for publication.

(4) As to these assignments see ref. (3).

The value of ΔE having been obtained as 950 cal./mole in our previous research,[3] that of ΔS can be calculated from Eq. (6) and (7), if we measure the ratio of optical densities D_S/D_T or D_S/D_G at several temperatures. In Table I are shown such experimental values obtained according to the method described in our previous paper, where the band at 2890 cm.$^{-1}$ has been taken as standard.[5] From these values we obtain

TABLE I

OBSERVED RATIO OF OPTICAL DENSITIES

t, °C.	D_S/D_T
127	1.631
129	1.640
130	1.667
133	1.718
245	1.500
250	1.383
251	1.406
255	1.402

$$\Delta S = 3.7 \pm 0.4 \text{ e.u.}^{6}$$

The entropy difference between the rotational isomers can be expressed as the sum of the rotational and vibrational parts

$$\Delta S = \Delta S_{\mathrm{rot}} + \Delta S_{\mathrm{vib}} \qquad (8)$$

where

$$\Delta S_{\mathrm{rot}} = R \ln \left\{\frac{(I_a I_b I_c)_t}{(I_a I_b I_c)_g}\right\}^{1/2} \qquad (9)$$

and

$$\Delta S_{\mathrm{vib}} = R \sum_{t}\left[\frac{w_t \exp(-w_t)}{1 - \exp(-w_t)} - \ln\{1 - \exp(-w_t)\}\right] - R \sum_{g}\left[\frac{w_g \exp(-w_g)}{1 - \exp(-w_g)} - \ln\{1 - \exp(-w_g)\}\right] \qquad (10)$$

In these equations $(I_a I_h I_c)$ is the product of the principal moments of inertia and w denotes $h\nu/kT$, where ν is the normal frequency and the subscripts t and g refer to the *trans* and the *gauche* molecules, respectively.

The values of bond lengths and bond angles being known for these two kinds of molecules, the ratio of the principal moments of inertia is calculated as

$$(I_a I_b I_c)_t/(I_a I_b I_c)_g = 0.85$$

Putting this value into Eq. (9), we obtain

$$\Delta S_{\mathrm{rot}} = -0.16 \text{ e.u.}$$

Of the twenty-one normal frequencies for each of the *trans* and the *gauche* molecules fourteen hydrogen vibrations have much higher frequencies than the skeletal vibrations and can be neglected in our discussion of the entropy difference at lower temperatures. As to the remaining seven skeletal frequencies five of them were determined in our previous paper[3] and by putting their values into Eq. (10), the entropy difference arising from these frequencies is found as 0.24 e.u. at 130° and 0.25 e.u. at 250°. We see, therefore, that the contributions of the rotational motion and of these skeletal vibrations cannot be the main part of the entropy difference which must be contributed by either one or both of the remaining two motions, *i.e.*, the oscillational rotations about the C–C and C–O bonds as axes.

In the *trans* molecule the H-atom of the OH-group has three stable positions with regard to the internal rotation about the C–O axis and the energy difference among these positions would be very small. Similarly, in the *gauche* molecule there are such three stable positions of which, however, one has much lower energy than the other two owing to the internal hydrogen bond. Therefore, the contributions of the other two positions may practically be neglected in the *gauche* molecule and the entropy of this isomer would become considerably smaller than that of the *trans* isomer. Moreover, due to this internal hydrogen bond the frequencies of the oscillational rotations will become higher in the *gauche* molecule than in the *trans* molecule. As these frequencies are of the order of magnitude of 100 cm.$^{-1}$, such changes in their values will make the entropy of *gauche* isomer considerably smaller than that of the *trans* isomer.[7]

Thus we have good reason to believe that the main part of the entropy difference between the rotational isomers of ethylene chlorhydrin arise from the difference in rotational oscillations which is due to the fact that only one of the isomers has an internal hydrogen bond. This would also reasonably explain the entropy difference observed for two forms of acetylglycine N-methylamide.

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[5] It will be seen from the study on hydrocarbons reported by A. Francis, *J. Chem. Phys.*, **18**, 861 (1950), that this band is suitable as standard.

[6] κ_T/κ_S was found as 0.8 ± 0.2.

[7] J. Mizushima, Y. Morino, I. Watanabe, T. Shimanouchi and S. Yamaguchi, *J. Chem. Phys.*, **17**, 591 (1949).