Conformational Analysis. 1. The Temperature Effect on the Structure and Composition of the Rotational Conformers of 1,2-Dichloroethane as Studied by Gas Electron Diffraction. Additional Remarks.

KARI KVESETH

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Gaseous 1,2-dichloroethane has been studied by electron diffraction at 2 °C. The ratio between the amounts of *anti* and *gauche* conformers is determined and the results compared with the values obtained in the previous investigation [1] of this compound.

The temperature dependency of the thermodynamical differences for the conformational equilibrium *anti*⇌*gauche*, ΔE and ΔS, is discussed in detail.

The temperature average of ΔS is determined fitting the best straight line to the $R \ln(1/K)$ *versus* $1/T$ data, and the slope gives ΔE. The results obtained in this investigation are $\Delta E = 1.05(.10)$ kcal mol^{-1} and $\Delta S = 0.90(.29)$ cal mol^{-1} deg^{-1}.

In the previous investigation on 1,2-dichloroethane,[1] some uncertainties were introduced because the observation at -13 °C did not seem to represent the conformational equilibrium at that temperature. The deviation from the best straight line fitted to the other observed ($R \ln 1/K$, $1/T$)-points was too large to originate from the temperature dependency of the thermodynamical terms, and was believed to be caused by some condensing phenomena in the nozzle, favouring the *anti* conformer.

Partly to check this, but also to present a more complete analysis of the temperature dependency of the thermodynamical quantities ΔE and ΔS, the molecule has been studied at 2 °C by gas electron diffraction.

EXPERIMENTAL AND STRUCTURE ANALYSIS

The sample of 1,2-dichloroethane was obtained from British Drug Houses (> 98.9 %) and used without further purification. Electron-diffraction photographs were obtained with the Balzer Eldigraph KDG-2 [2,3] unit, the experimental conditions being summarized in Table 1. The data corrections and analysis are performed as described in Ref. 1.

D and u values calculated from the force field [4] at 2 °C are given in Table 2, and the refined structure in Table 3. The distances are all R_a-values, the angles correspond to R_α-values.[5] The standard deviations, given in parentheses, are those calculated by the least-squares procedure, using off-diagonal elements in the applied weight matrix and adding 0.1 % as contribution from systematic errors in the wavelength.

RESULTS AND DISCUSSION

The structural parameters (Table 3) agree well with the previous results,[1] although the $R(C-H)$ and CCH-angle are definitely smaller than the means in the latter (Table 4, column c of Ref. 1). The better values for $u(C-C)$ and $u(C-Cl)$, indicates that a more correct blackness correction has been used.

If $R \ln (1/K)$ varies linearly with $1/T$ in the actual temperature interval, this means that $R \ln (2Q_g/Q_a)$ is temperature independent, or at least that the temperature derivative of $\ln (Q_g/Q_a)$ is so small that it can be neglected in the calculations of ΔE and ΔS (eqn. 1)

Table 1. Experimental conditions and photographic plate data.

Temp (°C)	2	
Apparatus	Balzer	
Nozzle-to-plate distance (mm)	579.93	189.91
Electron wavelength (Å) [a]	0.058550	0.058534
Number of plates used	5	5
Range of data (s) [b]	1.125 – 13.500	5.500 – 32.250
Data interval (Δs)	0.125	0.250

[a] Determined in separate experiments by calibration to benzene. [b] $s = 4\pi/\lambda \sin \theta$; 2θ is the scattering angle.

Table 2. The difference, D, between R_a and R_α and vibrational amplitudes, u, calculated from valence force field for $t = 2$ °C.

	D (Å)	u (Å)
(C−C)	0.00008	0.052
(C−Cl)	− 0.00439	0.052
(C−H)	− 0.01123	0.078
(C···Cl)$_a$[a]	− 0.00291	0.068
(C···Cl)$_g$	− 0.00035	0.068
(C···H)$_a$	− 0.00192	0.109
(C···H)$_g$	− 0.00523	0.109
(Cl···H)	− 0.00713	0.109
(H···H)	− 0.01133	0.128
(Cl···Cl)$_a$	0.00100	0.066
(Cl···H)$_{a,g}$	0.00055	0.163
(Cl···H)$_{a,g}$	0.00055	0.163
(H···H)$_{a,a}$	− 0.00246	0.128
(H···H)$_{a,g}$	0.00162	0.178
(H···H)$_{a,g}$	0.00162	0.178
(Cl···Cl)$_g$	0.00614	0.144
(Cl···H)$_g$	0.00263	0.159
(Cl···H)$_{g,a}$	− 0.00218	0.102
(H···H)$_{g,g}$	− 0.00354	0.170
(H···H)$_{g,g}$	− 0.00520	0.174
(H···H)$_{g,a}$	− 0.00686	0.129

[a] The suffix a and g refers to *anti* and *gauche* respectively. In the double suffix the first letter gives the conformation, the second the type of distance involved.

$$\Delta E = \Delta E^\circ + RT^2(\partial/\partial T)[\ln(Q_g/Q_a)] \quad (1)$$
$$\Delta S = R \ln 2 + R \ln(Q_g/Q_a) + RT(\partial/\partial T)[\ln(Q_g/Q_a)]$$

where Q is the vibrational-rotational partition function, ΔE° is the energy-difference between *gauche* and *anti* at the absolute zero point. $\Delta E = \Delta H$ and ΔS are the thermodynamical quantities for the reaction. The factor 2 is the statistical weight of the *gauche* form.

This usual assumption can be tested by calculating the partition functions from the moments of inertia and vibrational frequencies. Combined with the observed values of K, the thermodynamical quantities are calculated according to eqns. 1 and 2, and the results given in Tables 4 and 5.

$$K = \frac{n_g}{n_a} = \frac{2Q_g}{Q_a} e^{-\Delta E^\circ/RT} = e^{-(\Delta E - T\Delta S)/RT} \quad (2)$$

where n is the percentage of the conformers *gauche* (g) and *anti* (a).

The calculated values for ΔE° agree very well except the ΔE° value at − 13 °C which deviates significantly from the mean. Since this point

Table 3. Molecular parameters for 1,2-dichloroethane. Distance (R_a) and amplitudes (u) in Å, angles ($\angle\alpha$) in degrees.

Temp.	2 °C
R(C−C)	1.510 (6)[a]
R(C−Cl)	1.788 (2)
R(C−H)	1.081 (8)
$\angle$CCCl	109.21(.28)
$\angle$CCH	110.93(.43)
ϕ_a	72.36(3.05)
u(C−C)	0.052 (6)
u(C−Cl)	0.053 (2)
u(C···Cl)	0.080 (3)
u(Cl···H)	0.078 (9)
u(Cl···Cl)$_a$	0.068 (3)
u(Cl···Cl)$_g$	0.148 (30)
%-*anti*	81.4 (3.8)

[a] The distances are corrected for shrinkage. Standard deviations obtained from the refinement using off-diagonal elements in the weight-matrix, are given in parentheses.

Table 4. Thermodynamical terms calculated from measured equilibrium mol fractions (n_a) and calculated partition functions (Q).

Temp (°C)	(−13)	2	40	140	140 B	300
%-anti [a]	89.4(4.4)	81.4(3.8)	78.7(3.4)	67.9(3.6)	67.0(5.1)	63.9(5.8)
$R \ln (2Q_g/Q_a)$ (cal mol^{-1} deg^{-1}) [b]	1.453	1.437	1.395	1.313	1.313	1.228
$RT(\partial/\partial T)[\ln (Q_g/Q_a)]$ (cal mol^{-1} deg^{-1}) [b]	−0.330	−0.326	−0.314	−0.281	−0.281	−0.236
$\Delta E°$ (kcal mol^{-1})	1.48(.25)	1.26(.14)	1.25(.13)	1.16(.14)	1.12(.19)	1.35(.27)
ΔE (kcal mol^{-1}) [c]	1.15	1.14	1.13	1.10	1.10	1.05
ΔS (cal mol^{-1} deg^{-1})	1.12	1.11	1.08	1.03	1.03	0.99

[a] Determined from electron diffraction in Ref. 1 and this investigation, standard deviations from the structure determination in parentheses (σn_a). [b] Calculated from the valence force field of Snyder and Schachtschneider[4] with torsional force constants $f_{t,g} = 0.253$ ($\nu_{t,g}$ 117 cm^{-1}) and $f_{t,a} = 0.174$ (mdyn Å rad^{-2}) ($\nu_{t,a} = 125$ cm^{-1}), and products of principal moments $(I_A I_B I_C)_a = 2.954 \times 10^6$ and $(I_A I_B I_C)_g$ 2.109 × 10^6 (a.w.Å^2). [c] The mean of $\Delta E°$ is applied ($\Delta E° = 1.22$ kcal mol^{-1}). Standard deviations in $\Delta E°$, given in parentheses are calculated acccording to $[\partial(\Delta E°)]^2 = \left(\dfrac{\partial}{\overline{\partial n_a}} \Delta E° \right) [\sigma(n_a)]^2$

Table 5. Thermodynamical quantities.

	I	II
ΔE (kcal mol^{-1})	1.11(.04)	1.05(.10)
$R \ln(2Q_g/Q_a)$ (cal mol^{-1} deg^{-1})	1.33	1.19 (.29)
$RT\ \partial/\partial T \ln(Q_g/Q_a)$ (cal mol^{-1} deg^{-1})	−0.29	−0.29
ΔS (cal mol^{-1} deg^{-1})	1.04	0.90(.29)

I. The results obtained applying K from electron diffraction and calculating the partition functions, when $\nu_{t,g} = 117$ cm^{-1} and $\nu_{t,a} = 125$ cm^{-1}. The values are the mean of those in Table 4, the standard deviation for ΔE in parenthesis, is calculated from the deviations from the mean.

II. The results obtained by fitting a straight line to the $(R \ln(1/K), 1/T)$-points. $\Delta S = 0.90$ corresponds to $\nu_{t,g}/\nu_{t,a} = 1.02$ (giving $\nu_{t,} = 128(20)$ cm^{-1}, if $\nu_{t,a}$ is kept at the experimental value 125 cm^{-1}). The standard deviations as obtained from the least squares fitting are given in parentheses. The observations at -13 °C are excluded in this treatment of the data.

also is off the line around which the other points are grouped (Fig. 1), this observation is excluded in the further treatment of the data.

Table 4 demonstrates quite clearly that $(\partial/\partial T)[\ln(Q_g/Q_a)]$ is *not* sufficiently small to be neglected in the calculations of ΔS, while considering ΔE as temperature independent, is sufficiently accurate within the experimental error limits. Still the least squares fitting of a straight line to $R \ln (1/K)$ *versus* $1/T$ seems to give a slope which is a reasonable good estimate of ΔE, and the temperature mean of $-\Delta S$ as
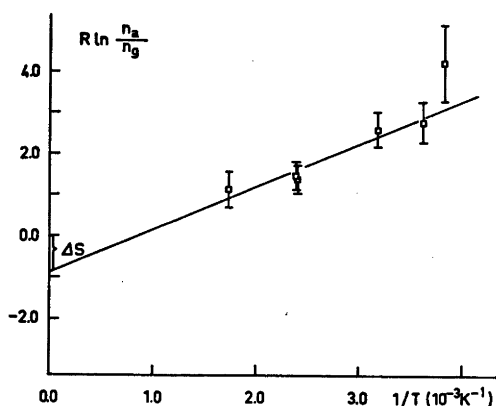

Fig. 1. $R \ln(1/K) = R \ln(n_a/n_g) = \Delta E/T - \Delta S$ as a function of $1/T$. $\Delta E = 1.05$ kcal mol^{-1} is the slope of the straight line drawn, $\Delta S = 0.90$ cal mol^{-1} deg^{-1} is the "constant". The standard deviations marked in each point by vertical lines are calculated from those obtained on n_a in the least squares refinement on the total structure.

the intersection of the $R \ln(1/K)$-axis (see Fig. 1). This can be demonstrated by applying the least squares method to theoretically calculated $R \ln(1/K)$-points. The determined coefficients in the assumed straight line then agree with the temperature average of ΔE and ΔS rather than $\Delta E°$ and $R \ln(2Q_g/Q_a)$ (see eqn. 2).

The best fitted straight line gave $\Delta S = 0.90(.29)$ cal mol^{-1} deg^{-1}, (Table 5, column II). If the usual assumption that the temperature derivative, $RT(\partial/\partial T)[\ln(Q_g/Q_a)]$, can be neglected, is applied, then $R \ln(2Q_g/Q_a) = \Delta S$ gives $\nu_{t,g} = 147$ cm^{-1} when $\nu_{t,a} = 125$ cm^{-1} is considered as the correct value (see below).

Even though $R \ln(2Q_g/Q_a)$ is temperature dependent, Table 4 shows that $RT(\partial/\partial T)[\ln(Q_g/Q_a)]$ is fairly temperature independent. The mean value of $R \ln(2Q_g/Q_a)$ can therefore be calculated from the least squares ΔS-value, substracting the average $RT(\partial/\partial T)[\ln(Q_g/Q_a)]$ calculated from the experimental frequencies (with $\nu_{t,g} = 117$ cm^{-1} and $\nu_{t,a} = 125$ cm^{-1}).

Table 5 demonstrates the excellent agreement between the results obtained from the electron diffraction data and the spectroscopic torsional frequencies. The least squares determined $R \ln(2Q_g/Q_a) = 1.19$ cal mol^{-1} deg^{-1} corresponds to a ratio of 1.02 between the torsional frequencies in *gauche* and *anti*, giving $\nu_{t,g} = 128(20)$ cm^{-1} if $\nu_{t,a} = 125$ cm^{-1} is considered as the correct value. The experimental frequencies are respectively 123 cm^{-1} and 125 cm^{-1}, with a reasonable liquid/ gas shift in *gauche* down to 117 cm^{-1}, ratio 0.94, which agrees both with the above straight line approach and the u-value estimate at 300 °C

(Ref. 1). Very reliable torsional frequencies [6] have not yet been obtained in the gas phase. Within an uncertainty of 10 cm^{-1} in the frequency, the experimental $\nu_{t,g}/\nu_{t,a}$ ratio may be shifted to a value close to 1.02. Unfortunately this shift in frequency ratio does not change the u values significantly compared to the experimental refined results and error limits. On the other hand it is possible that the correction terms because of anharmonicity may be a bit larger in *gauche*, where the potential is much more asymmetric. This will move the calculated $\nu_{t,g}$ closer to $\nu_{t,a}$, more in accordance with the experiment, although the effect probably is small.

This uncertainty in the calculated partition functions has minor influence on the obtained ΔE value.

Since any changes in the torsional frequencies mainly will influence the $R \ln(2Q_g/Q_a)$ term $[RT(\partial/\partial T)[\ln(Q_g/Q_a)]$ does only change from -0.29 to -0.40 (cal mol^{-1} deg^{-1}) when $\nu_{t,g}/\nu_{t,a}$ goes from 0.93 to 1.18] the uncertainty in the thermodynamical estimate of ΔS originates only from the uncertainty of $R \ln(2Q_g/Q_a)$.

According to Table 5 this means that ΔS for the conformational equilibrium should be close to 0.9 cal mol^{-1} deg^{-1}. The two outlined procedures give in the case of 1,2-dichloroethane equally good estimates of ΔE and ΔS. Which one to apply depends on the quality of the experimental $R \ln(1/K)$-points on one hand, and the quality of the observed vibrational and torsional frequencies on the other. A combination of the two sets of information is a method to check the consistency of the obtained results.

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