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An Electron Diffraction Study of the *anti-gauche* Ratio as a Function of Temperature for Ethylene Chlorohydrin, 2-Chloroethanol

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In order to investigate the possibility of more accurate determination of energy and entropy differences between conformers using gas electron diffraction techniques, gaseous ethylene chlorohydrin has been studied at five different temperatures (37, 125, 170, 200, and 250 °C). While the less stable *anti* conformer contributes only 6 – 8 % at the lowest temperature, the gas contains as much as 20 – 30 % at the highest temperature.

The temperature dependence of the *gauche*/*anti* ratio (K) is studied by various approaches, including a graphical procedure comparing area ratios on the radial distribution curves.

The best values for the energy and entropy differences between *gauche* and *anti* conformers are $\Delta E = -2.4(2)$ kcal mol^{-1} and $\Delta S = -2.8$ (3) cal mol^{-1} deg^{-1}, respectively.*

Earlier studies [1–7] have demonstrated that the halogenated ethylene hydrins exhibit two coexisting conformers in the gaseous state. At room temperature the *gauche* conformer prevails to the extent that *anti* can hardly be recognized. At higher temperatures the contribution of the *anti* conformer is easily demonstrated by the increase of the O···X peak corresponding to this conformer in the radial distribution curve. The *gauche*/*anti* ratio (K) may be studied considering K as one of the parameters, in addition to the geometric and vibrational parameters, in a least squares refinement of the intensity curve. This procedure was applied using data obtained at two temperatures in the previous study.[1] The main scope of the present study was to extend the experimental bases by including data from three more temperatures, and thereby study in detail the influence of the temperature on the part of the radial distribution curves most sensitive to conformational changes.

EXPERIMENTAL AND DATA REDUCTION

The sample of chlorohydrin, obtained from Merck, was used without further purification. In addition to the recordings described in the previous paper [1], electron diffraction photographs were made at three new nozzle temperatures: 125, 170 and 250 (°C), with the Oslo apparatus [9] under conditions as summarized in Table 1. Selected plates were traced with a microdensitometer, and the data reduced in the usual way,[10] to yield an intensity curve for each plate. The intensities were modified with the function

$$s/|f_{Cl}||f_O|$$

The theoretical molecular intensities were calculated according to eqn. 11 of Ref. 10. The scattering amplitudes were calculated by the partial wave method,[10, 11] using Hartree Fock atomic potentials.[12]

The average for each set of plates was calculated, and composites made for each temperature by scaling corresponding pairs of curves and averaging the intensities in the overlap region. Due to the low symmetry of the molecule, reproducible intensity values are obtained in a more limited s-range than normal.

STRUCTURE ANALYSIS

Radial distribution curves (RD-curves) calculated from the corresponding intensities from the 48 cm data by a Fourier transformation,

* 1 cal = 4.184 J.

Table 1. Experimental conditions and photographic plate data.

Temperature (°C)	37		125		170	200		250	
Nozzle-to plate distance (mm)	479.33	260.54	480.72	250.78	480.63	478.73	198.78	480.42	250.63
Electron wavelength (Å) [a]	0.064802	0.064846	0.064580	0.064580	0.06580	0.064732	0.064732	0.064598	0.065574
Range of data (s) [b]	1.5–20.0	5.0–35.0	1.5–18.5	5.0–35.0	1.5–18.5	1.5–20.0	7.0–45.0	1.5–18.5	5.0–30.5
Data interval (Δs)	0.125	0.250	0.125	0.250	0.125	0.125	0.250	0.125	0.250
Number of plates used	4	5	4	7	5	4	4	4	5
Corresponding curves in Fig. 1	A		B		C	D		E	

[a] Determined in separate experiments by calibration to gold. [b] $s = 4\pi\lambda^{-1}\sin\theta$, 2θ is the scattering angle, λ is the electron wavelength

are shown in Fig. 1. (See Ref. 1 for more detailed discussions.) The five different bond distances contribute to the first three peaks. The peak complex between 2 and 3 Å corresponds to all the non-bonded torsional independent distances. The torsional dependent H···Cl and H···O distances make a negligible contribution to the RD-curves, and the outer complex consists mainly of the torsional dependent O···Cl peaks, at 3.2 Å for *gauche* and 4.0 Å for the *anti* conformer. The area of these two peaks varies with the temperature, and Fig. 1 shows a systematic increase in the peak area at 4.0 Å with the temperature and a corresponding decrease in the *gauche* peak at 3.2 Å.

For practical reasons a theoretical tail was added to the experimental intensities in the outer s-region ($s = 18.5 - 45.0$ Å^{-1}) in addition to the theoretical contribution in the inner, unobserved region. Since the vibrational amplitudes for the conformational dependent distances are fairly large ($u(\mathrm{O}\cdots\mathrm{Cl})_a = 0.08$ and $u(\mathrm{O}\cdots\mathrm{Cl})_g = 0.12 - 0.16$ Å), the main contribu-

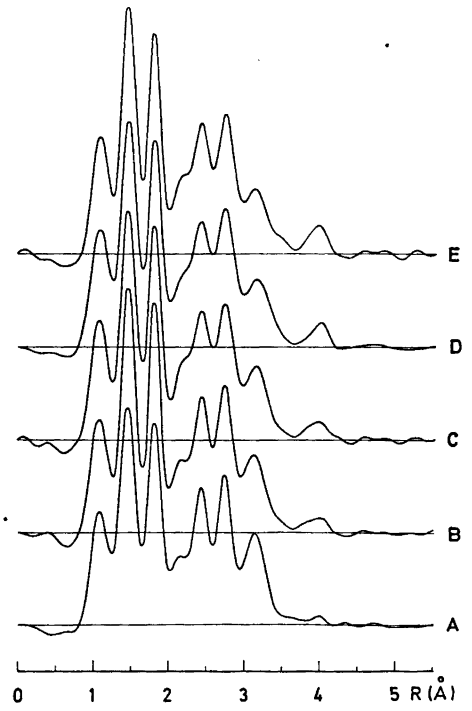

Fig. 1. Experimental radial distribution curves, calculated from the corresponding 48 cm intensity curves with $B = 0.0020$ Å^2.

tions to the total intensity from these distances will be within the experimental *s*-region of the 48 cm plates. The torsional dependent peaks should therefore be relatively independent of the theoretical contribution added to the experimental intensities.

Because of the similarities between the C – C, C – O and C – H, O – H distances, a mean of these two types and the difference were chosen as geometry parameters in the molecular model.[1] The independent geometry parameters thus used in least squares refinement are ⟨C – C,O⟩ (the average of the C – C and C – O bond), Δ(C – C, O) (the difference between these two bond lengths), ⟨C, O – H⟩, Δ(C, O – H), R(C – Cl), ∠CCO, ∠CCCl, ∠HCH, ∠COH and the torsional angle, ϕ, around the C – C axis. ϕ is defined as 180° in *anti*, and is refined in *gauche* for each temperature.

The torsional independent parameters of the two conformers are assumed to be nearly the same and are therefore put equal. The hydroxyl group has for the sake of simplicity in both conformers been fixed at a *gauche* position with respect to the C – O axis ($\phi' = 60°$), even though an *ab initio* calculation on fluorohydrin[13] has

Table 2. Molecular parameters. Distances (r_a) and amplitudes (u) in Å, angles ($\angle_a$) in degrees.

Temp. (°C)	37	125	170 [a]	200	250	[f]
⟨C – C,O⟩	1.466(1) [b]	1.465(1)	1.475(1)	1.473(1)	1.464(1)	
Δ(C – C,O)	0.106(2)	0.083(3)	0.10 –	0.106(2)	0.079(4)	
⟨C,O – H⟩	1.063(2)	1.059(3)	1.068(3)	1.067(2)	1.066(3)	
Δ(C,O – H)	0.06 –	0.06 –	0.06 –	0.06 –	0.06 –	
r(C – Cl)	1.801(1)	1.796(1)	1.801(1)	1.807(1)	1.794(2)	1.800(2)
∠CCCl	110.7(1)	110.5(2)	109.8(2)	109.9(2)	110.9(3)	110.4(2)
∠CCO	113.8(3)	112.0(3)	110.7(3)	110.6(3)	110.5(4)	111.5(6)
∠HCH	108 –	108 –	108 –	108 –	108 –	
∠HOC	125 –	125 –	125 –	125 –	125 –	
ϕ	62.4(6)	66.3(7)	67.9(6)	70.2(8)	70.0(10)	67.3(14)
r(C – O) [c]	1.413(2)	1.424(4)	1.425(1)	1.420(3)	1.424(4)	1.421(2)
r(C – C)	1.519(2)	1.507(4)	1.525(1)	1.526(3)	1.504(4)	1.516(2)
r(C – H)	1.093(2)	1.089(3)	1.098(3)	1.097(2)	1.096(3)	1.094(2)
r(O – H)	1.033(2)	1.029(3)	1.038(3)	1.037(2)	1.036(3)	1.034(2)
u(C – C)	0.050 [e] –	0.050 –	$0.029(5)_1$ [d]	0.050 –	0.050 –	0.052
u(C – O)	0.050 –	0.050 –	$0.029(5)_1$	0.050 –	0.050 –	0.051
u(C – Cl)	0.052(1)	0.042(2)	0.026(5)	0.050(1)	0.055(2)	0.057
u(C – H)	0.090 –	0.090 –	0.090 –	0.090 –	0.090 –	0.078
u(O – H)	0.070 –	0.070 –	0.070 –	0.070 –	0.070 –	0.070
$u(C_1 \cdots Cl_9)$	0.061(2)	0.068(2)	0.070(4)	0.080(2)	0.079(3)	0.091
$u(C_3 \cdots O_4)$	$0.082(2)_1$	$0.067(3)_1$	$0.061(4)_2$	$0.092(3)_1$	$0.078(3)_1$	0.078
$u(Cl_9 \cdots H_7)$	$0.106(2)_1$	$0.101(3)_1$	$0.085(4)_2$	$0.116(3)_1$	$0.102(3)_1$	0.111
$u(O_4 \cdots H_2)$	$0.132(6)_2$	$0.094(5)_2$	0.110 –	$0.109(6)_2$	$0.099(7)_2$	0.105
$u(C_1 \cdots H_5)$	$0.132(6)_2$	$0.094(5)_2$	0.110 –	$0.109(6)_2$	$0.099(7)_2$	0.101
$u(C_1 \cdots H_7)$	$0.132(6)_2$	$0.094(5)_2$	0.110 –	$0.109(6)_2$	$0.099(7)_2$	0.111
$u(O_4 \cdots Cl_9)_g$	0.125(3)	0.148(5)	0.120 –	0.153(6)	0.169(9)	0.159
$u(Cl_9 \cdots H_2)_g$	0.121(25)	0.056(23)	0.120 –	0.081(26)	0.067(33)	0.113
$u(O_4 \cdots Cl_9)_a$	0.077 –	0.083 –	0.087 –	0.089 –	0.091 –	0.086

[a] Data from refinement only on 48 cm data, since 19 cm was not observed. [b] Standard deviations, given in parentheses, are from least squares and do not include estimates of correlation or systematic error. –, parameters which were not refined. [c] Dependent distances calculated from ⟨C – C,O⟩, Δ(C – C,O) and ⟨C,O – H⟩, Δ(C,O – H), respectively. [d] Refined in groups, the suffix number indicates which u's are in the same groups. [e] Calculated by Cyvin [18] when not refined. [f] Mean of the geometry parameters in the temperature range. Standard deviations, in parentheses, are calculated from the deviations from the mean by $\sigma_{\bar{R}} = [\sum_n (R_n - \bar{R})^2/n(n-1)]^{1/2}$ where $n = 5$. Calculated u-values for 250 °C.

given $\phi' = 180°$ for the *anti* isomer. Due to low contribution to the total intensity from distances dependent on ϕ', this assumption will not affect the conclusions of this investigation.

The composition in the gas phase is thus determined from the torsional dependent distances, the O···Cl distance in *gauche* and *anti* being the most important.

In general some of the independent parameters [Δ(C, O–H), $\angle$HCH and $\angle$COH] as well as certain of the vibrational amplitudes did not refine, and were kept at reasonable assigned values.

Table 2 gives the results obtained from refinements at the different temperatures on average composite curves, assuming a reasonable *gauche*/*anti* ratio, changed by an iterative procedure as the structure analysis proceeded. The lack of molecular symmetry had the largest effect on the 19 cm plates and refinements on 48 cm data have been carried out as well. The overall agreement with the parameters listed in Table 2 was reasonably good.

A simplified valence force field was established for chlorohydrin, applying a program by Gwinn,[14] extended by Stølevik *et al.*[15] to calculate vibrational amplitudes. The force constants (given in Table 3) were chosen from chlorohydrin,[4] 1,2-dichloroethane,[16] and CH_3-OH,[17] and slightly modified to get a better agreement with the observed frequencies.[3] The small discrepancies in the off-diagonal elements as compared to the forcefield given by Giguère,[4] are believed to originate mainly from the different numbers of coupling constants included. The calculated vibrational amplitudes (u-values) from this force field (given in Table 4) agree excellently with those calculated in *anti* by Cyvin [18] from symmetry coordinates.

Although there are some discrepancies between the assumed u-values used in the least squares refinement and the calculated values, we felt that a repeated refinement, based upon the force-field calculations, was not necessary. Since the u-values kept constant are insensitive to temperature, as shown in Table 4, the assigned values should not influence the conclusions that may be drawn from the refinements. The unrealistic small u-values for the bond distances at 170 °C arise from the short s-interval of observations, since that refinement is performed only on 48 cm data.

Table 3. Force constants.[a]

Stretch		Interaction	
f_{CC}	4.94	$f_{CC,CCl}$	0.73
f_{CCl}	3.50	$f_{CC,CO}$(*anti*)	0.73
f_{CO}(*anti*)	4.45	$f_{CH,CH}$	0.06
f_{CH}	4.91	$f_{CC,CCH}$	0.26
f_{OH}(*anti*)	7.49	$f_{CC,CCCl}$	0.29
f_{CO}(*gauche*)	5.00	$f_{CC,CCO}$	0.29
f_{OH}(*gauche*)	7.33	$f_{CCl,HCCl}$	0.33
$f_{Cl\cdots H}$(*gauche*)	0.10	$f_{CCl,CCCl}$	0.55
Bending		$f_{CO,HCO}$	0.44
		$f_{CO,CCO}$	0.55
f_{CCH}	0.68	$f_{CC,CO}$(*gauche*)	0.50
f_{HCH}	0.50		
f_{CCCl}	0.75		
f_{HCCl}	0.79		
f_{CCO}	1.09		
f_{HCO}	0.80		
f_{COH}(*anti*)	0.68		
$f_{\tau(C-C)}$(*anti*)	0.10		
$f_{\tau(C-O)}$	0.03		
f_{COH}(*gauche*)	0.86		
$f_{\tau(C-C)}$(*gauche*)	0.16		

[a] Stretching constants in mdyn Å^{-1}, stretch-bend in mdyn rad^{-1} and bending in mdyn Å rad^{-2}.

Table 4. Vibrational amplitudes (u), calculated from a valence force field.

		R (Å)	u (Å) 37 °C	125 °C	170 °C	200 °C	250 °C
	C–C	1.52	0.050	0.051	0.051	0.052	0.052
	C–O	1.42	0.048	0.049	0.050	0.050	0.051
	C–Cl	1.80	0.051	0.053	0.054	0.055	0.057
	C–H	1.10	0.078	0.078	0.078	0.078	0.078
	O–H	1.04	0.070	0.070	0.070	0.070	0.070
	$C_1 \cdots Cl_9$	2.73	0.075	0.082	0.085	0.088	0.091
	$C_6 \cdots O_4$	2.42	0.067	0.072	0.074	0.075	0.078
	$Cl_9 \cdots H_7$	2.40	0.106	0.108	0.109	0.110	0.111
	$O_4 \cdots H_2$	2.07	0.102	0.103	0.103	0.104	0.105
	$C_1 \cdots H_5$	2.19	0.098	0.099	0.099	0.100	0.101
	$C_1 \cdots H_7$	2.15	0.107	0.108	0.109	0.110	0.111
↑	$H_2 \cdots H_3$	1.78	0.127	0.127	0.128	0.128	0.128
	$H_2 \cdots H_5$	3.04	0.120	0.121	0.121	0.122	0.123
	$H_3 \cdots H_5$	2.57	0.194	0.204	0.210	0.214	0.220
	$C_6 \cdots H_5$	2.83	0.189	0.205	0.213	0.218	0.226
gauche	$O_4 \cdots Cl_9$	3.14	0.125	0.140	0.147	0.151	0.159
	$O_4 \cdots H_7$	2.63	0.155	0.163	0.168	0.171	0.176
	$O_4 \cdots H_8$	3.36	0.103	0.105	0.106	0.107	0.109
	$Cl_9 \cdots H_2$	3.70	0.104	0.108	0.110	0.111	0.113
	$Cl_9 \cdots H_3$	2.85	0.171	0.183	0.189	0.193	0.200
↓	$Cl_9 \cdots H_5$	2.93	0.191	0.206	0.213	0.218	0.227
	$H_5 \cdots H_7$	3.05	0.310	0.340	0.354	0.364	0.379
↑	$H_5 \cdots H_8$	3.87	0.168	0.177	0.181	0.184	0.189
	$H_2 \cdots H_7$	2.53	0.169	0.174	0.177	0.179	0.182
	$H_2 \cdots H_8$	2.43	0.165	0.169	0.171	0.173	0.175
	$O_4 \cdots Cl_9$	4.01	0.071	0.077	0.081	0.083	0.086
anti	$O_4 \cdots H_7$	2.67	0.163	0.175	0.181	0.184	0.191
	$Cl_9 \cdots H_2$	2.90	0.181	0.196	0.204	0.208	0.216
	$Cl_9 \cdots H_5$	4.52	0.174	0.188	0.195	0.199	0.207
	$H_5 \cdots H_7$	2.67	0.280	0.304	0.316	0.324	0.336
↓	$H_5 \cdots H_8$	3.12	0.328	0.361	0.377	0.388	0.405
	$H_2 \cdots H_7$	3.05	0.128	0.129	0.130	0.130	0.131
	$H_2 \cdots H_8$	2.49	0.180	0.186	0.190	0.192	0.196

Since the aim of the present work is to study the reliability of the deduced thermodynamic functions, a series of computing approaches were tried out. Data reduced from 48 cm plates were studied independently for each temperature, as well as the composites made from various nozzle-to-plate distances. The various approaches may be divided into two types, one based upon conventional least squares refinement, and one based upon area studies of the radial distribution curve.

Because of the rather small percentage of *anti* at low temperatures, in addition to the low symmetry of the molecule, determination of the *gauche*/*anti* ratio by the conventional least squares method is problematic. We will therefore emphasize the discussion in this work on the second procedure.

The peaks on the RD-curve of particular interest for conformational analysis are those marked W and w in Fig. 2, corresponding to the O···Cl distance in *gauche* and *anti*, respectively. The area under peak w is nearly proportional to the percentage of the *anti* conformer, whereas the peak W is somewhat more complex, due to contributions from other distances.

Fig. 2 presents, for sake of illustration, a theoretical curve based upon a set of well established structure parameters and a chosen, representative, percentage of *anti* (15 %). The line diagram indicates the positions of the interatomic distance, the length of each is a measure of the relative contribution of the corresponding distance to the total area of the radial distribution curve. The solid lines corre-

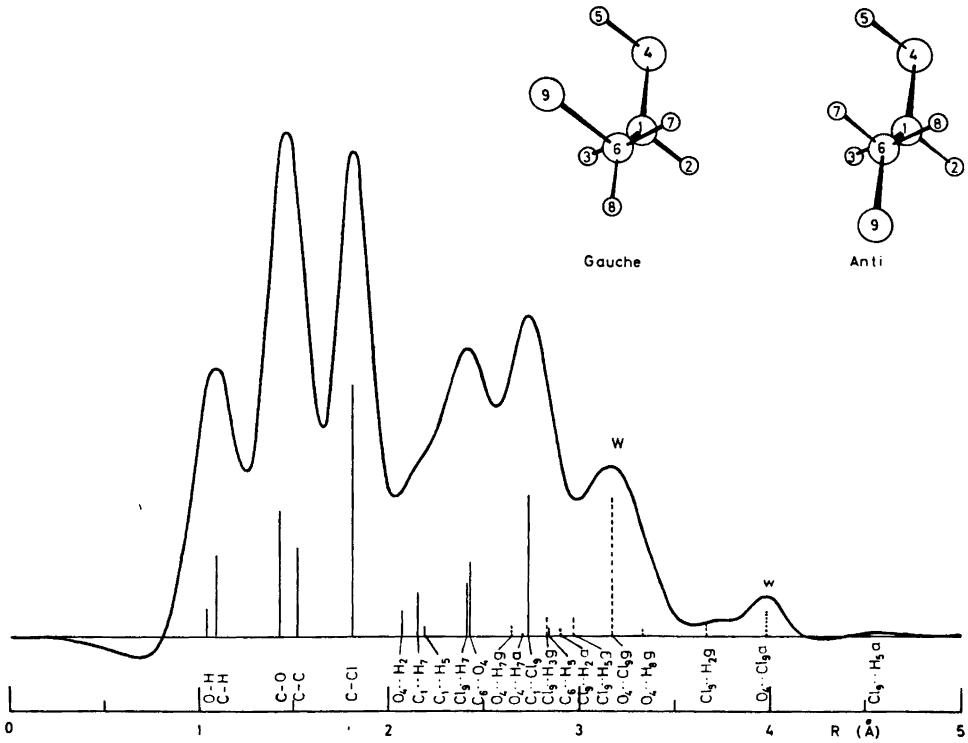

Fig. 2. Theoretical radial distribution curve, calculated from the structural parameters of Table 2 and 15 % of *anti*.

spond to those distances which do not vary explicitly with the torsion. The other lines correspond to distances varying with the torsional angle, the dashed ones are *gauche* contributions, the dotted ones *anti*.

The area under the peaks *W* and *w* are designated *WA* and *wA*, respectively. The total area under the RD-curve is *totA*. *WA* is calculated between 3.1 and 3.6 Å, of *wA* between 3.7 and 4.2 Å and *totA* from 0.8 to 4.2 Å. This type of integration is performed for both experimental and theoretical curves. The theoretical curves are based upon the refined structural parameters of Table 2 and calculated for different *anti/gauche* ratios (5 %, 10 %, 15 % *etc.* of *anti*). The fractions between the different areas, *WA/wA*, *WA/totA* and *wA/totA* are calculated for both experimental and theoretical data. The experimental *anti/gauche* ratios are determined by comparison between the different area ratios, as a function of the *anti* percentage. The estimated percentages of the *anti* conformer are given in Table 5, as well as the thermodynamic quantities.

Inspection of Table 5 reveals some differences between the three outlined approaches. As expected the *WA/totA* values are less able to reproduce the conformational ratio, due to the small percentage change with temperature in this quantity. *WA/wA* and *wA/totA* give nearly identical results, which is quite reasonable because they are essentially the same quantity on different normalization. The discussion in this study is based upon the *WA/wA* values, because we feel that weighting *wA* to the total area (*totA*) will be dominated by the comparatively large value of *totA*, even though *W* (see Fig. 2) is a shoulder in a peak complex and not so easily defined.

Column *f* of Table 2 gives the average values of the geometry parameters in the temperature interval. These values agree excellently with the means presented in the previous paper.[1] Contrary to what is found for halogenated

Table 5. Percentage of *anti* (n_a) and thermodynamic differences.

Temp (°C)	Connected curves				48 cm curves		
	$\frac{WA}{wA}$	$\frac{WA}{totA}$	$\frac{wA}{totA}$	Refined [a]	$\frac{WA}{wA}$	$\frac{WA}{totA}$	$\frac{wA}{totA}$
37	7.10	8.57	6.95	–	6.70	1.50	7.60
125	19.03	15.04	20.55	–	17.30	12.30	19.20
170	–	–	–	–	21.62	17.92	23.10
200	22.65	19.55	23.95	21.2(2.3)	25.43	22.20	27.06
250	28.02	24.08	30.25	25.1(1.2)	30.32	22.60	34.80
ΔE^b(kcal mol^{-1})	−2.4(2)	−1.8(1)	−2.6(4)		−2.7(1)	−4.7(6)	−2.7(1)
ΔS (cal mol^{-1} deg^{-1})	−2.8(3)	−1.1(2)	−3.4(9)		−3.6(2)	−7.3(16)	−3.9(3)

[a] Standard deviations as obtained in the least squares refinement are given in parentheses. [b] For explanations see text.

ethanes, the *gauche* torsional angle for chlorohydrin increases systematically. This indicates that the stabilizing energy of the Cl···H interactions in *gauche* decrease with the temperature.

DISCUSSION

The most interesting results of this investigation are the measurements of the composition as a function of the temperature. If we consider the conformational equilibrium *anti* ⇌ *gauche*, the difference in energy, $\Delta E = E_g - E_a$, and the difference in entropy, $\Delta S = S_g - S_a$, of the two conformers are obtainable from the effect of the temperature on composition by use of the formula

$$K = \frac{n_g}{n_a} = e^{-(\Delta E - T\Delta S)/RT} = \frac{2Q_g}{\sigma Q_a} e^{-\Delta E^\circ/RT} \quad (1)$$

where n is the percentage of the conformers *gauche* (g) and *anti* (a). Q is the vibrational-rotational partition function, ΔE° is the energy difference between *gauche* and *anti* at the absolute zero point. The factor 2 is the statistical weight from the two identical *gauche* forms, while σ is a statistical weight of the different *anti* forms, arising from the difference in acceptable hydroxy-hydrogen positions in the two conformers. Because of the three nearly identical staggered positions around the C···O axis in *anti*, compared to the one in *gauche* pointing towards the Cl atom to form an internal hydrogen bond, σ is set equal to 3 in this analysis. Even though the calculated partition functions show a slight temperature dependence of ΔE and ΔS, this effect is fairly small ($RT\partial/\partial T \ln (Q_g/Q_a) = -0.5$ cal mol^{-1} deg^{-1}), and a straight line is fitted by a least squares method to the $R \ln K$ *versus* $1/T$ points, giving the mean of ΔE as the slope and ΔS as the intersection of the $R \ln K$-axis in the actual temperature interval.[19] Selecting the values of column WA/wA, connected curves, of Table 5, the ($R \ln K$, $1/T$) points appear as the Δ given in Fig. 3. The vertical lines give the range of each point as obtained from the different set of values given in Table 5, connected curves. The straight line fit to the WA/wA gave $\Delta E = -2.4(2)$ kcal

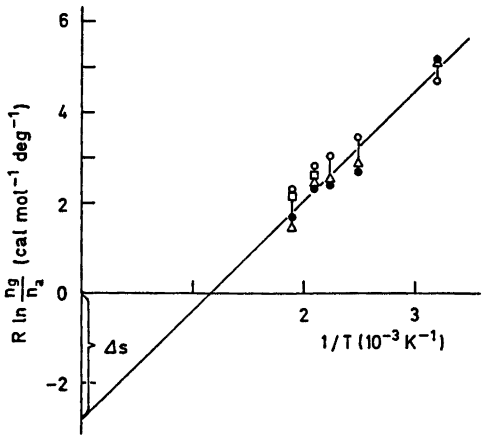

Fig. 3. $R \ln K$ as a function of $1/T$, estimated from the area ratios. Δ, from WA/wA; ●, from $wA/totA$; ○, from $WA/totA$; □, refined values.

Table 6. Thermodynamic quantities.[a]

	I	II[b]	III
ΔE(kcal mol^{-1})	−2.4(.2)	−2.4	−2.6(−1.9,0.8)
ΔS(cal mol^{-1} deg^{-1})	−2.8(.3)	−2.2 [−2.08−(−2.29)]	−2.2
$R \ln (2Q_g/3Q_a)$(cal mol^{-1} deg^{-1})	−2.3	−1.7 [−1.52−(−1.80)]	
$RT\frac{\partial}{\partial T}(\ln Q_g/Q_a)$(cal mol^{-1} deg^{-1})	−0.5	−0.5 [−0.49−(−0.56)]	

[a] For explanations see text. [b] The values inside the brackets give the temperature variation. $(I_A I_B I_C)_g = 9.956 \times 10^5$ and $(I_A I_B I_C)_a = 8.213 \times 10^5$ a.w.Å.^{2}

mol^{-1} and $\Delta S = -2.8(3)$ cal mol^{-1} deg^{-1} (Table 6, column I). An analysis based on *wA/totA* would have changed ΔE insignificantly, where as ΔS would have decreased to −3.4(9) cal mol^{-1} deg^{-1}.

The partition functions are calculated from the moments of inertia and vibrational frequencies.[16] The thermodynamic quantities can also be calculated from these, combined with the observed values for the *gauche/anti* ratios (K). These results are presented in column II of Table 6. In column III of that table are presented the results from the previous investigation.[1] (Actually the value given there for the entropy is $\Delta S' = \Delta S - R \ln 2 = -3.6$ (−2.5,1.8) cal mol^{-1} deg^{-1}.)

Table 6 demonstrates the excellent agreement between the electron diffraction results based on *WA/wA* and the spectroscopic observed frequencies. Under the assumption of a statistical weight of 3 for the *anti* form, the straight line fitted ΔS value corresponds to a torsional frequency in *anti* of 82 cm^{-1} (observed 115 cm^{-1} in crystal phase) when the torsion in *gauche* (156 cm^{-1}) is considered as the correct one. A difference well within the error limits of the two methods.

Also the agreement with the estimates in the first paper[1] is reasonable. The conclusions drawn in that investigation are therefore verified. The results may be interpreted in terms of a rather strong intramolecular hydrogen bond favouring the *gauche* conformer.

Compared with the energy differences for fluoro[7] and bromo[8] hydrins (less than −2.8 and −1.3 kcal mol^{-1}, respectively), it is demonstrated that the strength of the internal hydrogen bond is between that of H···F and H···Br. This is contrary to the observations by Buckley *et al.*[3] They observe rather more stabilization of the H···Br bond than the H···Cl, the difference in energy is −1.45 and −1.20 kcal mol^{-1}, respectively, as calculated from the intensity difference of the CX bonds (which are the numbers to compare with the electron diffraction results).

The rather large, negative entropy difference between *gauche* and *anti* can be accounted for from the statistical factor of 3 for the essential equally probable positions of the hydroxy-hydrogen in *anti*. Also the conformational entropy difference ($\Delta S_c = \Delta S - R \ln 2/3 = -2.0$ cal mol^{-1} deg^{-1}), however, is fairly large, about 5 times what is found in 1,2-dichloroethane.[19] This must reflect a higher degree of order in *gauche*, introduced by the formation of the internal hydrogen bond. This estimate of ΔS_c is of course dependent on the assumption of $\sigma = 3$, but a value close to 3 seems reasonable from the theoretical calculations from the partition functions, and the estimate of the torsional frequency in *anti*. σ less than 3 would in fact lead to an even more ordered structure in *gauche*. The large, negative conformational entropy also conflicts with the interpretation of the difference in ΔE obtained from the temperature dependence of the OH and CX bond intensities,[3] as due to the presence of a third conformer, a non-hydrogen bonded *gauche* form. This again would introduce a higher degree of statistical disorder in *gauche*, thus making ΔS_c even more negative than the above value of −2.0 cal mol^{-1} deg^{-1}, which means there is an even higher degree of conformational order in *gauche*. This seems unlikely when the hydrogen bond is formed to a smaller extent.

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