

Conformational Analysis

The Structure, Composition, and *trans-gauche* Energy and Entropy Differences for Ethylene Chlorohydrin as Determined by Electron Diffraction

A. ALMENNINGEN, O. BASTIANSEN, L. FERNHOLT, and
KENNETH HEDBERG*

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

Gaseous ethylene chlorohydrin has been studied by electron diffraction at temperatures of 37°C and 200°C. The analysis revealed substantially more of the *trans* conformer present at the higher temperature (15–25 % *trans*) than at the lower (less than 10 % *trans*) and led to the estimates $E_T - E_G = 2.6 (+1.9, -0.8)$ kcal mol⁻¹ and $S_T - S_G = 3.6 (+2.5, -1.8)$ cal mol⁻¹deg⁻¹. The energy of the O···Cl hydrogen bond is estimated to be roughly 3.8 (+2.0, -1.0) kcal mol⁻¹. The following values for distances (r_a) and angles with errors given as 2σ are appropriate for the structure at both temperatures: $\langle C-C, O \rangle = 1.45_s$ Å (0.01_s), $\Delta(C-C, O) = 0.10$ Å (0.02), C-C = 1.51_s Å (0.02), C-O = 1.41_s Å (0.02), $\langle C, O-H \rangle = 1.08_s$ Å (0.01_s), $\Delta(C, O-H) = 0.10$ Å (assumed), C-H = 1.10₇ Å, O-H = 1.00₇ Å, C-Cl = 1.80_s Å (0.01_s), $\angle CCl = 110.6^\circ$ (2.1), $\angle CCO = 111.8^\circ$ (3.2), $\angle HCH = 108^\circ$ (assumed). The angle between the CCl and CCO planes was found to be 60.6° (3.9) at 37°C, and 70.2° (2.0) at 200°C. Root-mean-square amplitudes (u_a) were also determined: $u(C-C) = u(C-O) = 0.060$ Å (0.017), $u(C-H) = u(O-H) + 0.02 = 0.093$ Å (0.012), $u(C-Cl) = 0.057$ Å (0.004), $u(C\cdots Cl) = 0.076$ Å (0.027), $u(C\cdots O) = 0.086$ Å (0.014), $u(O\cdots Cl) = 0.125$ Å (0.015) at 37°C, and 0.170 Å (0.019) at 200°C.

It has long been recognized that rotation about single bonds in organic molecules may lead to the coexistence of two or more conformers in the liquid and gas phases. Some thirty-five years ago, for example, the Raman spectra of a series of liquid 1,2-disubstituted ethanes were interpreted by Kohlrausch and Ypsilanti¹ in terms of a mixture of *cis* and *trans* conformers. Likewise, Zumwalt and Badger² interpreted their gas-phase infrared spectra of certain OH bands of substituted alcohols in terms of *cis* and *trans* con-

* Visiting Professor 1969–70. Permanent address: Department of Chemistry, Oregon State University, Corvallis, Oregon 97331, USA.

formers, and concluded from the effect of temperature on band intensities that the *trans* forms were of higher energy. (It is not clear whether these authors' use of "*cis*" was meant, in the cases of propanol and ethylene chlorohydrin, in a broad sense to include *gauche*.) An early electron diffraction investigation of ethylene glycol, ethylene chlorohydrin and glycerol, based on data taken at the lowest possible temperatures,³ revealed no substantial amounts of the *trans* form in any of these cases. Nor did the diffraction results conform to the eclipsed *cis* form. In all cases, the angle of twist about the C—C bond was about 70–75°, corresponding closely to a *gauche* conformation. Mizushima and coworkers⁴ concluded from Raman spectra of the gas, liquid, and solid phases of ethylene chlorohydrin that *gauche* and *trans* forms (Fig. 1) were present in the first two, but only *gauche* in the last; like Zumwalt and Badger they assigned the *trans* form a higher energy from analysis of the intensity changes in certain infrared bands as a function of temperature.

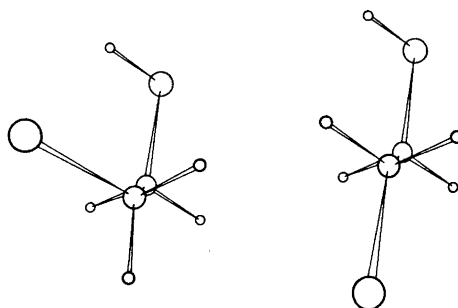


Fig. 1. *gauche* and *trans* Conformers of ethylene chlorohydrin.

Recently, a more extensive study of the four ethylene halohydrins by infrared spectroscopy led Wyn-Jones and Orville-Thomas⁵ to the same conclusion. Yamaha,⁶ in a reinvestigation of the ethylene chlorohydrin structure by electron diffraction at temperatures in the range 25–35°C, found no positive evidence of the presence of a *trans* conformer, but concluded that it could coexist in minor proportion with the *gauche* form. His results, including the torsional angle for the *gauche* form, were in satisfactory agreement with those from the earlier work.³ To summarize the foregoing evidence: it seems very likely that ethylene chlorohydrin in the liquid and gaseous states at room temperature contains the *trans* conformer, but probably in such small amounts as to have been undetectable with the electron-diffraction methods available to the early workers. Further, the amount of *trans* form can be increased markedly by modest increases in temperature, suggesting it to be of higher energy than the *gauche* form, but not greatly so.

Our interest in conformational analysis has led us to reconsider the ethylene chlorohydrin problem. Firstly, the electron-diffraction methods of today are much more sensitive than those used in the earlier studies, and secondly, even though the amount of *trans* conformer present at room temperature might be too small to be detectable, that at the much higher, currently attainable temperatures could well be substantial. Moreover, identification of the *trans*

conformer should be simple through the appearance of a peak corresponding to the *trans* O...Cl distance in a region of the distance spectrum free from other peaks. We decided to carry out experiments at two temperatures as widely separated as possible. The difference in the compositions, could it be detected, would provide a basis for evaluation of the energy difference between the *trans* and *gauche* forms.

Experimental and data reduction. The sample of ethylene chlorohydrin, obtained from Merck, was used without further purification. Electron-diffraction photographs were made at nozzle temperatures of 37°C and 200°C in the Oslo apparatus,⁷ under conditions as summarized in Table 1. Selected plates were traced with a microdensitometer, and

Table 1. Experimental conditions and photographic plate data.

	37°C			200°C	
Nozzle-to-plate distance, mm	1301.50	479.33	260.54	478.73	198.78
Electron wavelength, Å ^a	0.06480	0.06480	0.06485	0.06473	0.06473
Exposure times, sec	30	30	60	30	60
Number of plates used	4	4	4	4	4
Range of data, in s ^b	0.5–6.0	1.5–20.0	5.0–35.0	1.5–20.0	7.0–45.0
Data interval, Δs	0.25	0.25	0.25	0.25	0.25

^a Determined in separate experiments by calibration against gold.

^b $s = 4\pi\lambda^{-1}\sin\theta$, θ is one-half the scattering angle.

the data reduced in the usual way⁸ to yield an intensity curve for each plate. From these curves, composites were formed (four at each temperature) by arbitrarily selecting a representative from each distance group, and averaging the intensity values in the overlap region after scaling and small background adjustments. An overall average curve for each temperature was then formed by averaging the composite intensities; these overall average curves are shown in Fig. 2. The range and quality of the data are somewhat lower than is usually obtained. However, this may be inherent in the compound, which has a distance multiplicity of only 1.0 for each of the important terms. They are in the form represented by

$$I(s) = \text{const} \sum_{ij} g_{ij} k_l(s) \exp(-u_{ij}^2 s^2 / 2) \sin(r_{ij}s) / r_{ij} \quad (1)$$

where

$$g_{ij} k_l = \frac{|f_i(s)| |f_j(s)|}{|f_k(s)| |f_l(s)|} \cos|\eta_i(s) - \eta_j(s)| \quad (2)$$

The electron scattering amplitudes $f_i(s)$ and phases $\eta_i(s)$ were calculated from partial waves,⁹ using Hartree-Fock atomic potentials.¹⁰ The symbols u^2 , r , and s are, respectively, the mean square amplitude of vibration, the interatomic distance, and diffraction variable ($s = 4\pi\lambda^{-1}\sin\theta$).

STRUCTURE ANALYSIS

Experimental radial distribution curves. Radial distribution curves were calculated from the average curves according to

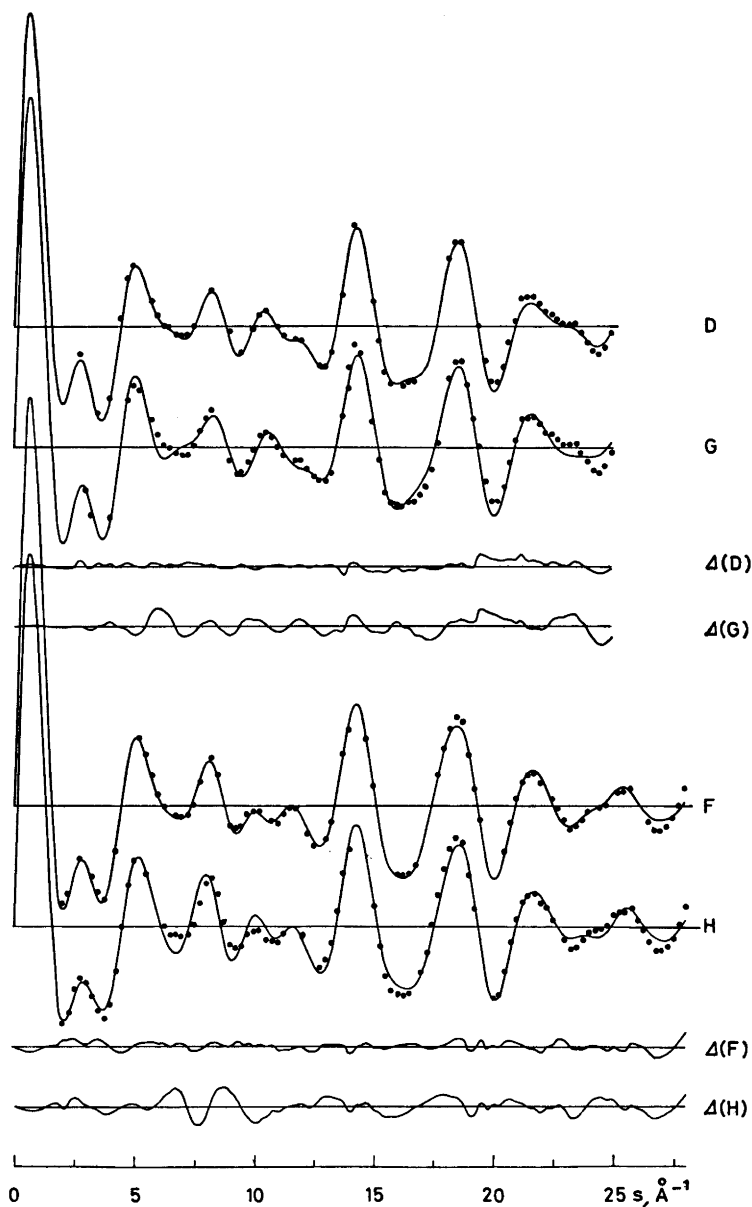


Fig. 2. Intensity curves and difference curves. The experimental values are given as ●. The solid curves are theoretical. The difference curves are the experimental minus the theoretical. The upper curves correspond to 37°C, the lower to 200°C. The curves D and F correspond to the data given under column D and F in Table 2. The curves G and H correspond to the data given in Table 3.

$$\sigma(r)/r = \sum I(s) \exp(-Bs^2) \sin(rs) \Delta s \quad (3)$$

with $\Delta s = 0.25$, and $B = 0.0020$, in order to reduce the errors introduced by series termination. These curves are shown in Fig. 3. The most obvious difference between them is found in the region at about 4.0 Å: the peak seen in

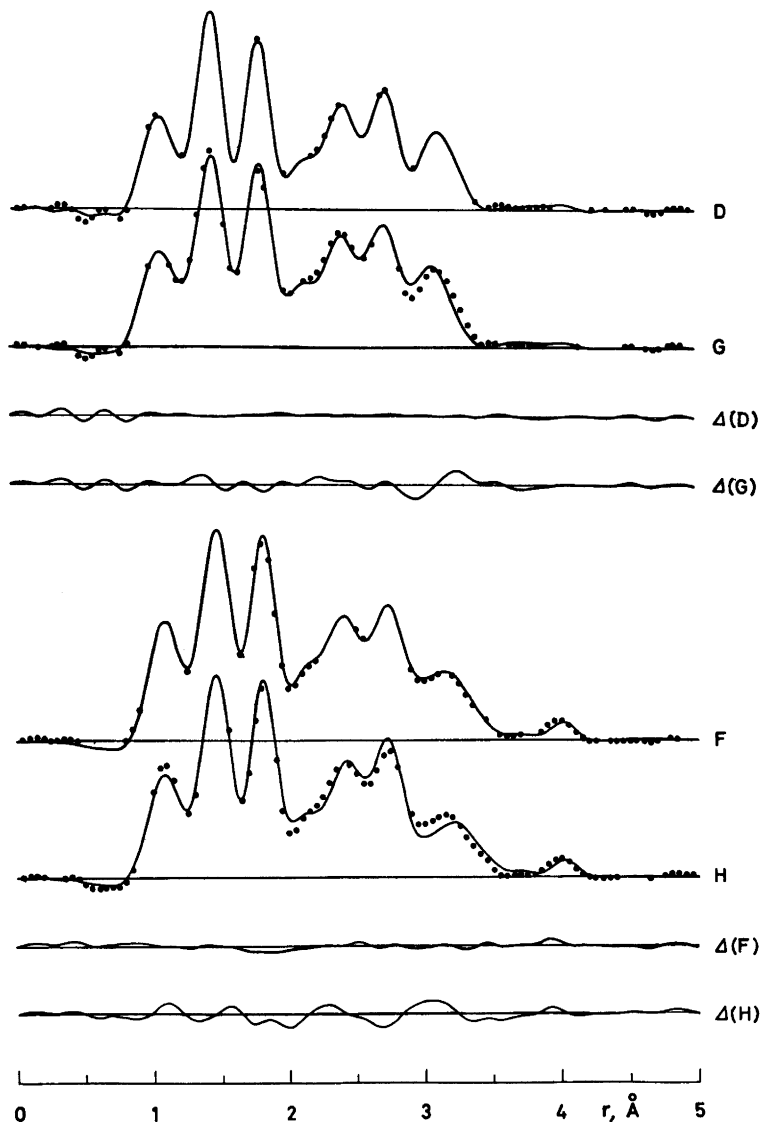


Fig. 3. Radial distribution curves and difference curves. The experimental values are given as ●. The solid radial distribution curves are theoretical, and calculated from the intensity curves of Fig. 2 with $B = 0.0020$. The difference curves are the experimental minus the theoretical.

the higher temperature curve corresponds to the O \cdots Cl distance in the *trans* form of the ethylene chlorhydrin molecule, and its very much smaller size (if indeed present at all) in the lower temperature curve gives clear evidence of the effect of temperature on the composition of the sample.

The radial distribution curves were easily interpreted, as follows. The various bond distances in the molecule are responsible for the peaks at 1.1 Å (C–H and O–H), 1.4 Å (C–C and C–O), and 1.8 Å (C–Cl). Non bond distances through one bond angle contribute strongly to the peaks at 2.4 Å (C \cdots O and Cl \cdots H), and 2.7 Å (C \cdots Cl), and to the shoulder at 2.2 Å (C \cdots H and O \cdots H). The distances through two bond angles, generally speaking, contribute throughout the region > 2.8 Å. The most important of these is the O \cdots Cl distance, which in the *gauche* conformation of the molecule is found at approximately 3.2 Å and is the principal contributor to the peak seen at that location, and in the *trans* conformation is found at about 4.0 Å, as mentioned above. Theoretical radial distribution curves calculated for *gauche* trial structures having approximate O–H, C–H, C–O, C–C, and C–Cl bond lengths of 1.04, 1.10, 1.42, 1.52, and 1.81 Å, respectively, approximately tetrahedral bond angles, and torsion angles of about 70° (with the *cis* conformation of O \cdots Cl taken as zero) were in satisfactory agreement with the observed low-temperature curve. To obtain equally satisfactory agreement for the high temperature curve, it was necessary to divide the contribution of rotation-sensitive distances to correspond to about 85 % *gauche* and 15 % *trans*.

Structure refinement. The analysis of the radial distribution curves provided the basis for refinement of the structure, which was carried out by least squares, based upon intensity curves.¹¹ The model for the structure was constructed with the following geometrical assumptions: 1) the planes of the two –CH₂ groups are perpendicular to the planes of their respective XCY groups and bisect the XCY angles; 2) the two HCH angles are equal; and 3) the *gauche* and *trans* conformers have identical structures, except for the ClCCO torsion angle. Although none of these can be strictly correct, departures of reasonable magnitude could not significantly affect the values of the principal parameters. The final results tend to support the last assumption, in that the *trans* O \cdots Cl distance, calculated as a "dependent" quantity, agrees well with that observed. As results were accumulated, and as the effect of varying the H(O) position by changing the torsion angle around the C–O bond was ascertained to be small, this torsion angle was fixed at 60° (with the coplanar CCOH conformation taken as zero); the values correspond to a favourable hydrogen-bonding position for molecules in the *gauche* conformation. Root-mean-square amplitudes for non-bond distances involving hydrogen atoms were given plausible values and not refined; for the *gauche* form these were, for distances through one bond angle, $u(\text{Cl}\cdots\text{H}_\text{C}) = u(\text{O}\cdots\text{H}_\text{C}) = u(\text{C}\cdots\text{H}_\text{C}) = u(\text{C}\cdots\text{H}_\text{O}) = 0.110$ Å, and for distances through two bond angles $u(\text{Cl}\cdots\text{H}_\text{C}) = u(\text{O}\cdots\text{H}_\text{C}) = u(\text{C}\cdots\text{H}_\text{O}) = 0.150$ Å, $u(\text{O}\cdots\text{H}_\text{C}') = 0.120$ Å, and $u(\text{Cl}\cdots\text{H}_\text{O}) = 0.200$ Å. For the *trans* form, the values were the same, except for those involving the oxygen and chlorine atoms through two bond angles.

A large number of refinements were carried out, in which selected combinations of parameters were allowed to vary, while others which experience

Table 2. Results of various refinements of ethylene chlorohydrin.^a

	37°C			200°C		
	A	B	C	D ^b	E	F
	$r_a, u_{a_i} / \sigma_{I_i}$	$r_a, u_{a_i} / \sigma_{I_i}$	$r_a, u_{a_i} / \sigma_{I_i}$	$r_a, u_{a_i} / \sigma_{I_i}$	$r_a, u_{a_i} / \sigma_{I_i}$	$r_a, u_{a_i} / \sigma_{I_i}$
$\langle C-C-O \rangle$	1.452	1.452	1.450	1.445	1.466	1.466
$\Delta(C-C_iO)$	(0.100)	(0.100)	(0.080)	.092	(0.100)	(0.100)
$\langle C_iO-H \rangle$	1.080	1.079	1.078	1.076	1.085	1.085
$\Delta(C_iO-H)$	(0.060)	(0.060)	(0.060)	0.075	(0.060)	(0.060)
$r(C-Cl)$	1.796	1.795	1.798	1.797	1.808	1.808
$\angle CCl$	111.6	111.7	112.1	112.2	109.8	109.6
$\angle CCO$	113.3	113.3	114.3	111.9	110.6	110.3
$\angle HCH$	(108.0)	(108.0)	(108.0)	(108.0)	(108.0)	(108.0)
$\angle HOC$	97.2	97.5	90.3	106.0	131.7	126.8
ϕ^c	60.6	60.9	58.5	63.0	69.6	70.2
% gauche	1.37	(85.0)	1.44	(95.0)	78.8	85.7
<i>gauche</i>						
$u(C-C)$	0.0531	0.0517	0.0631	0.0427	0.0657	0.0666
$u(C-O)$	0.0531	0.0517	0.0631	0.0557	0.0657	0.0666
$u(C-Cl)$	0.0570	0.0556	0.0580	0.0581	0.0574	0.0579
$u(C-H)$	0.0950	0.0939	0.0945	0.0941	0.0904	0.0910
$u(O-H)$	0.0750	0.0739	0.0745	0.0938	0.0704	0.0710
$u(C \cdots Cl)$	0.0628	0.0630	0.0622	0.0661	0.0865	0.0886
$u(C \cdots O)$	0.0869	0.0850	0.0880	0.1237	0.0871	0.0853
$u(O \cdots Cl)$	0.1250	0.1164	0.1274	0.1235	0.1683	0.1702
<i>trans</i>						
$u(O \cdots Cl)$	0.0175	(0.0500)	0.0179	0.0441	(0.1000)	(0.0500)
Rd	15.94	17.06	16.09	10.40	9.35	9.70

^a Distance and mean amplitudes in Ångström units; angles in degrees. Parenthesized values were assumed. Standard deviations are from least squares and do not include estimates of correlation or systematic error.

^b Amplitudes and distances are refined in consecutive cycles.

^c Angle of torsion; $\phi = 0$ for the eclipsed conformation of the C-Cl and C-O bonds.

^d $R = \sum w_i A_i^2 / \sum w_i |I_i^{obs} - I_i^{calc}|^2$, where A_i is the difference $I_i^{obs} - I_i^{calc}$, and w_i is a weight.

suggested could not be refined, either because they were weak or because they were likely to be strongly affected by correlation, were held constant at plausible values. Models were defined in terms of the geometrical parameters $\langle C-C,O \rangle$ (the average of the C-C and C-O bond lengths), $\Delta(C-C,O)$ (the difference between these bond lengths), $\langle C,O-H \rangle$, $\Delta(C,O-H)$, $r(C-Cl)$, $\angle CCO$, $\angle CCCL$, $\angle HCH$, $\angle HOC$, and ϕ (the OCCCl torsion angle for the *gauche* conformer). Of these, the parameters $\langle C-C,O \rangle$, $\langle C,O-H \rangle$, C-Cl, $\angle CCO$, $\angle CCCL$, and ϕ were generally allowed to vary, while $\Delta(C-C,O)$, $\Delta(C,O-H)$, $\angle HCH$, and certain of the vibrational amplitude parameters were generally assigned reasonable values. Also adjusted was a composition parameter, the per cent of *trans* form. Both the average intensity curves and the individual curves were used, in order to help with error estimation. The weight matrix was diagonal with elements given by $\exp[-0.100(s_{\min}-s)^2]$ over the range $s_{\min} \leq s \leq 5.75$, 1 over the range $6.00 \leq s \leq 24.00$, and $\exp[-0.005(s-s_{\max})^2]$ over the range $24.25 \leq s \leq s_{\max}$, where s_{\min} had the value 2.75 and 2.00, and s_{\max} the value 25.00 and 28.00 at the low and high temperatures, respectively. Table 2 shows the results of some of the many refinements.

Because of the complexity of the ethylene chlorohydrin structure and the rather small range of the diffraction data, our conclusions about structural details are necessarily limited. However, comparisons among the results of the many refinements do allow some broad generalizations, as follows.

In agreement with the qualitative indications of the radial distribution curves, the composition of the samples at the two temperatures differed substantially. We estimate the amount of *trans* conformer in ethylene chlorohydrin at 200°C to be 15–25 %, and at 37°C as less than 10 %. More precise estimates are difficult, because the composition parameter proved to be strongly correlated with certain other parameters, such as $u(O \cdots Cl)$ for the *trans* distance (compare refinements E and F).

The values of the CCCL and CCO angles, and the $\langle C-C,O \rangle$ distance are found to be different at the two temperatures by amounts considerably greater than can reasonably be accounted for on the basis of a temperature effect alone. This puzzling discrepancy led us to carry out some new, check diffraction experiments, which indicate that the differences mentioned are not real: data from composites of three of the new plates at each temperature led to the same values for these parameters to within experimental error and, moreover, the individual values tended to be about the average of those first obtained. We have no plausible explanation.

The value of the C-Cl distance and that for the $\langle C-C,O \rangle$ distance are insensitive to refinement conditions at either temperature. Because the quality of agreement, as judged from the *R* values, changes only very slowly with $\Delta(C-C,O)$ (compare refinements B and C), the value of this parameter can be only roughly determined. The parameter $\langle C,O-H \rangle$ is very insensitive to $\Delta(C,O-H)$, as might be expected.

Most of the amplitude values appear to be reasonable. Although the uncertainties in the relative values of the geometric parameters mentioned earlier inspire no confidence in the amplitude values, it is comforting that the latter, taken as a group, is larger for the high temperature experiment than for the

low-temperature one. The value of $u(\text{O}\cdots\text{Cl})$ for the *gauche* molecule is especially interesting, reflecting, as it does, the torsional vibration about the C—C bond. The value of $u(\text{O}\cdots\text{Cl})$ for the *trans* form, when refined, has no significance for the 37°C experiments (refinements A and C), undoubtedly due to the very small amount of *trans* conformer present. At 200°C, the values 0.05–0.07 Å with standard deviations of about 0.01 Å are obtained, which probably are still unreasonably small. Again, the low values probably derive from errors in the intensity data which reflect themselves especially strongly in this parameter, due to the small amount of *trans* conformer present.

Table 3. Final results for ethylene chlorohydrin.^a

	r_a	2σ	u_a	2σ	Angle	2σ
$\langle\text{C}-\text{C},\text{O}\rangle$	1.45 ₉	0.01 ₅			$\angle\text{CCCl}$	110.6 2.1
$\Delta(\text{C}-\text{C},\text{O})$	0.10	0.02			$\angle\text{CCO}$	111.8 3.2
C—C	1.51 ₆ ^b	0.02	0.060 ^c	0.017	$\angle\text{HCH}$	(108.0)
C—O	1.41 ₆ ^b	0.02	0.060 ^c	0.017	$\phi, 37^\circ\text{C}$	60.6 3.9
$\langle\text{C},\text{O}-\text{H}\rangle$	1.08 ₂	0.01 ₀			$\phi, 200^\circ\text{C}$	70.2 2.0
$\Delta(\text{C},\text{O}-\text{H})$	(0.100)					
C—H	1.10 ₇ ^b		0.093 ^d	0.012	% <i>trans</i> , 37°C	< 10
O—H	1.00 ₇ ^b		0.073 ^d	0.011		
C—Cl	1.80 ₂	0.01 ₃	0.057	0.004	% <i>trans</i> , 200°C	15–25
C \cdots Cl			0.076	0.027		
C \cdots O			0.086	0.014		
O \cdots Cl (<i>gauche</i> , 37°C)			0.125	0.015		
O \cdots Cl (<i>gauche</i> , 200°C)			0.170	0.019		
O \cdots Cl (<i>trans</i>)			0.06	0.02		

^a Distances and amplitudes in Ångström units, angles in degrees.

^b Calculated from average and difference values assuming weights equal to $n_{ij}Z_iZ_j$.

^c Refined under the condition $u(\text{C}-\text{C})-u(\text{C}-\text{O})=0$.

^d Refined under the condition $u(\text{C}-\text{H})-u(\text{O}-\text{H})=0.02$.

Final results. Table 3 is a listing of our final results for the structure of ethylene chlorohydrin. Considerations outlined above suggested that the apparent differences in the geometry of the molecule at the two temperatures should be disregarded, and accordingly we have taken the average of corresponding values from refinements A and F as an appropriate measure for bond distances, non-rotation sensitive distances, and bond angles. The refinements are themselves, respectively, representative of the average results obtained at each temperature. The values of the rotation angle ϕ and the O \cdots Cl distance dependent upon it are reported for both temperatures, although it can hardly be argued that these are really significantly different. The value for the parameter $\Delta(\text{C}-\text{C},\text{O})$ requires explanation. It was arrived at by observing the effect of changing the value assigned to it (and held constant during a given refinement) on the *R* factor. As with some of the other parameters, the results differed slightly for the two temperatures; a value slightly less than

0.100 seemed to give the best fit to the 37°C data, and one slightly greater the 200°C data. The approximate average is listed with a rather arbitrary error guessed from intercomparisons of refinement results. Although a similar approach was used with the parameter $\Delta(\text{C},\text{O}-\text{H})$, the results were even less conclusive, and we have chosen to indicate its value as assumed; it was ascertained, however, that the assumption has very little effect on the value of the other parameters.

The amounts of *trans* conformer are listed as a range for each temperature; this form expresses better our opinion about the compositions than would the value-plus-error type of representation.

The amplitude values are also shown as average values, except for that associated with the *gauche* $\text{O}\cdots\text{Cl}$ distance: it was felt that although the amplitudes at the high temperature are as a group appropriately larger than at the lower temperature, the individual pairs of values do not differ by consistently reasonable amounts. The *gauche* $\text{O}\cdots\text{Cl}$ amplitude values, however, differ by so much more than the calculated standard deviations from the least squares procedure (in contrast to the non-torsion dependent amplitudes), that presentation of both seems justified.

The errors of Table 3, except for that associated with $\Delta(\text{C}-\text{C},\text{O})$, have been estimated from the formulas

$$2\sigma_r = 2[2\sigma_{\text{LS}}^2 + (0.0005r)^2 + \langle\delta^2\rangle]^{1/2} \quad (4)$$

$$2\sigma_u = 2[2\sigma_{\text{LS}}^2 + (0.02u)^2 + \langle\delta^2\rangle]^{1/2} \quad (5)$$

$$2\sigma_{\text{angle}} = 2[2\sigma_{\text{LS}}^2 + \langle\delta^2\rangle]^{1/2} \quad (6)$$

The meaning of the various terms, except for $\langle\delta^2\rangle$, has been discussed.¹² We felt it wise to include $\langle\delta^2\rangle$ as an expression of errors, suggested by the large and otherwise unaccountable differences between the measured value of the parameters at the two temperatures. The quantities $\langle\delta^2\rangle$ are the mean square deviation of the parameter values from selected refinements; we have taken them from refinements A and F of Table 2, which are representative. The error for $\Delta(\text{C}-\text{C},\text{O})$ is an estimate obtained from appropriate *R* factors.

Figs. 2 and 3 show theoretical intensity and radial distribution curves calculated for models D and F of Table 2 and the corresponding difference curves. Similar curves are also shown for the models corresponding to the final results of Table 3, with $\angle\text{HOC} = 105^\circ$.

DISCUSSION

The electron-diffraction results reveal nothing very unusual in the geometry or vibrational properties of ethylene chlorohydrin. The C-Cl, C-C, and C-O bond distances are very close to those found in ethyl chloride¹³ (C-Cl = 1.788 Å, C-C = 1.520 Å) and in ethanol¹⁴ (C-C = 1.524 Å, C-O = 1.428 Å); the CClCl bond angle also agrees well with the ethyl chloride value (111°2'), but the CCO angle seems to be larger than the 107°36' found in ethanol. Our parameter values also seem to be in satisfactory agreement with those from the electron-diffraction studies of Bastiansen³ (C-C = 1.54 Å, C-Cl = 1.76 Å,

C-O = 1.43 Å, $\phi = 74^\circ$) and Yamaha ⁶ (C-O = 1.46 ± 0.02 Å, $\angle \text{CCCl} = 111 \pm 2^\circ$, $\angle \text{CCO} = 110 \pm 2^\circ$); however, detailed comparisons are difficult, because the early studies include some assumptions not involved in our work.

The most interesting results are the measurements of the isomeric composition of the samples at the two temperatures which in agreement with the interpretations of the spectra, clearly show the *trans* conformer to be of greater energy than the *gauche*. In principle, the difference in energy $\Delta E = E_T - E_G$, and the difference in entropy $\Delta S = S_T - S_G$ of the two conformers are obtainable from the effect of temperature on composition by use of the formula

$$N_T/N_G = \frac{1}{2} \exp(\Delta S/R) \exp(-\Delta E/RT) \quad (7)$$

where the factor $\frac{1}{2}$ takes into account the two-fold degeneracy of the *gauche* conformation relative to the *trans*. Unfortunately, as Table 4 shows, the combinations of possible compositions corresponding to our final results lead to

Table 4. Calculated energy and entropy differences for conformers of ethylene chlorohydrin. Differences are *trans* minus *gauche*.

200°C	% <i>trans</i>	37°C	ΔE kcal/mol	ΔS cal mol ⁻¹ deg ⁻¹
25		2	5.0	9.6
25		5	4.5	6.1
25		8	2.4	4.5
25		10	2.0	3.3
20		2	4.4	8.0
20		4	3.2	5.3
20		5	2.8	4.4
20		8	1.9	2.5
20		10	1.4	1.6
15		2	3.8	6.0
15		3	3.1	4.5
15		5	2.2	2.5
15		6	1.8	1.8
15		8	1.3	0.6
15		10	0.8	-0.3

values for both ΔE and ΔS over a rather large range. However, conclusions based on Table 4 alone are probably too pessimistic, because certain of the combinations of the extremes of the permissible ranges are surely very much less likely than others. For example, experience with the analysis of radial distribution and intensity curves suggests that if the true composition at 200°C corresponds to 15% *trans*, then it is very unlikely indeed that the composition at 37°C corresponds to as much as 10% *trans*. The sense of this statement may be felt from comparison of the *trans* Cl...O peaks in the radial distribution curves from the high and low temperatures: if the high-temperature peak corresponds to a composition of 15% *trans*, it is difficult to see how

the nearly absent low-temperature peak can correspond to a composition of 10 % *trans*; on the other hand, 25 % *trans* at the high temperature might conceivably allow 8–10 % *trans* at the low. The situation then might perhaps be best expressed by stating the range of a ratio of compositions $C_T(200^\circ)/C_T(37^\circ)$ which, solely based on the type of experience cited, we feel to be in accord with the data. We take this range to be $2.5 \leq C_T(200^\circ)/C_T(37^\circ) \leq 5.0$, and thus the compositions 25–2, 20–2, 20–10, 15–2, 15–8, and 15–10, given in Table 4, may be eliminated from further consideration. The remaining compositions lead to values for ΔE and ΔS in the ranges 4.5–1.8 kcal/mol and 6.1–1.8 cal mol⁻¹deg⁻¹. A fair statement of our results for these thermodynamic functions is $\Delta E = 2.6 (+1.9, -0.8)$ kcal/mol, and $\Delta S = 3.6 (+2.5, -1.8)$ cal mol⁻¹deg⁻¹, where the deviations for one function are correlated sign-wise with those for the other.

Two quite different values have been reported for ΔE , 2.0 ± 0.5 kcal/mol^{2b} and 0.95 ± 0.02 kcal/mol,⁴ both obtained by optical methods using infrared spectroscopy. Because the former involved intensity measurements of OH bands, and the latter intensity measurements of skeletal stretching vibrations, the meaning of the thermodynamic quantities is slightly different: the value based on the OH intensities may be interpreted as the energy difference between the hydrogen-bonded *gauche* conformer and the average energy of nonhydrogen-bonded *gauche* conformers (obtained by rotations about the C–O bond) plus *trans* conformers; the value based on skeletal band intensities corresponds best to the difference between the mean energies of the *gauche* and *trans* conformers. Our value for ΔE is derived from direct measurements of the *trans-gauche* composition, and ought therefore to be compared with the optical results based on skeletal band intensities. The agreement with the result from the OH intensity measurement is much better, however.

It might be thought that the large uncertainties associated with our ΔE measurement make it less likely than the others to be correct. Nevertheless, we feel our value is probably the best one available. Consider, for example, the value $\Delta S = 3.7 \pm 0.4$ cal mol⁻¹deg⁻¹ obtained from optical studies¹⁵ (and incidentally in good agreement with ours) by a method which made use of the previously determined value of ΔE (0.95 ± 0.02 kcal mol⁻¹deg⁻¹). There appears to be an error in this work, which we assume to be in the value of κ_T/κ_S . Using the value 0.8 ± 0.2 , given by the authors, one calculates ΔS in the range 5.7–7.4 cal mol⁻¹deg⁻¹, while its reciprocal leads to the ΔS value reported by them. These ranges of values for ΔE and ΔS used with eqn. (7) lead to predictions of composition corresponding to approximately 41 ± 5 and 54 ± 6 % of the *trans* conformer at the low and high temperatures, respectively. Such predicted compositions are completely incompatible with the diffraction measurements. Moreover, we know of no types of error which, should they be present in the diffraction work, could upon correction lead to compositions corresponding to so much *trans* conformer.

The fact that the *gauche* form of ethylene chlorohydrin is more stable than the *trans* is due mostly to the formation of a weak hydrogen bond between the oxygen and chlorine atoms. If one assumes that the intramolecular forces apart from the hydrogen bond are not greatly different from those in 1,2-dichloroethane, where, in contrast to ethylene chlorohydrin the *trans* conformer

is about 1.2 kcal mol⁻¹ more stable than the *gauche*,¹⁶ then the energy of the hydrogen bond is about 3.8 (+2.0, -1.0) kcal/mol. This value is roughly that found for intermolecular hydrogen bonds for gaseous aliphatic alcohols.¹⁷

The rather large entropy difference between the *trans* and *gauche* conformers has been plausibly attributed¹⁵ to the existence of three essentially equally probable species in the *trans* case, corresponding to rotation of the hydrogen atom around the C-O bond, compared to essentially only one species (the stable, hydrogen-bonded one) in the *gauche*.

After completion of this manuscript, Azrak and Wilson's detailed report¹⁸ of their microwave study of ethylene chloro- and bromohydrin appeared. Their accurate values for the important structural parameters of ethylene chlorohydrin are in excellent agreement with our final results. Their values calculated from Kraitchman coordinates are as follows:

C-Cl = 1.7886 ± 0.0038 Å, C-C = 1.5191 ± 0.0009 Å, C-O = 1.4107 ± 0.0014 Å, O-H = 1.0077 ± 0.0030 Å, ∠CCCl = 110°5' ± 20', ∠CCO = 112°46' ± 6', ∠CCO, CCl = 63°15' ± 35', ∠CCO, COH = 58°22' ± 60' (compare Table 3).

We feel that this excellent agreement concerning the molecular geometry lends support to our deductions of compositions and hence to our conclusions about the thermodynamic quantities.

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