Values for the Gas-phase Thermodynamic Functions of Conjugated Compounds existing as a Mixture of Conformers

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The conformational analysis of *trans*-but-2-enal, propenal, propenoyl chloride, propenoyl bromide, ethanedial, ethanedioyl chloride, and ethanedioyl bromide has been summarised. Values for the entropy, heat capacity, and enthalpy ($H^{\ominus} - H_0^{\ominus}/T$) have been calculated for all these compounds in the gaseous phase, except ethanedioyl bromide, over a range of temperatures by statistical methods, allowing for increase in these values due to mixing of low and high energy conformers. The concentration of high energy conformer at each temperature has been calculated.

THERMODYNAMIC data on chemical compounds is important both theoretically and practically, but unfortunately the available information has not been tabulated for many types of compounds. Statistical calculation of data for the gaseous phase is comparatively straightforward for simple systems if a full vibrational assignment is available for a compound, and the results agree with measured values.

Many compounds exist in the gaseous phase in more than one conformer, and the mixing of conformers gives an increase in energy of the system. In the compounds of interest to this work the conjugated double bonds are found to be stabilised in the planar *s-trans* conformer, with a second high energy conformer present in the liquid and gaseous phases. The structure of this high energy form is often difficult to elucidate due to the low concentration present, and may be planar *s-cis* or non planar *gauche* (which gives two equivalent structures).

Thermodynamic and spectroscopic measurements [1] were used to obtain evidence that both buta-1,3-diene and 2-methylbuta-1,3-diene (isoprene) exist as a mixture of *s-trans* and *s-cis* (not *gauche*) conformers, and the extra enthalpy of the *s-cis* conformer was found to be 10.4 and 4.6 KJ mol^{-1} respectively.

An experimental value of $\Delta H^{\ominus}$ was used to calculate values of the gas phase thermodynamic functions of 2-methylbuta-1,3-diene over a range of temperatures, and the calculated *s-cis* concentration of 2-methylbuta-1,3-diene at room temperature (11%) was higher than the 3% calculated for *s-cis*-buta-1,3-diene.

No reported values were found for the thermodynamic functions of the seven compounds reported here except for *trans*-but-2-enal,[2] but the values reported for this compound were calculated for the *s-trans* form only. Values are presented for six compounds, but it was not found possible to give values for ethanedioyl bromide, possibly because the existing data is inaccurate.

In statistical calculations wherever possible data given for the gaseous phase have been used in preference to other data, and all the available data have been critically examined before selecting the values used.

The evidence for the structure of the high energy conformers of the compounds studied is incomplete. Microwave studies indicate that the high energy conformers of propenoyl fluoride [3] and ethanedial [4] are *s-cis* and Raman work on propenal [5] concludes that this is also present in the *s-cis* high energy form. Electron diffraction studies on ethanedioyl chloride [6] and bromide [7] indicate that the high energy forms are both *gauche*. In this work it is assumed that both *trans*-but-2-enal and propenoyl chloride have *s-cis* high energy conformers.

A review of the statistical method of calculating thermodynamic functions was written by Frankiss and Green.[8] Contributions to the thermodynamic functions by the methyl rotor in but-2-enal were calculated using

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[1] D. A. C. Compton, W. O. George, and W. F. Maddams, *J.C.S. Perkin II*, 1976, 1666.

[2] J. R. Durig, S. C. Brown, V. F. Kalasinsky, and W. O. George, *Spectrochim. Acta*, 1976, **32A**, 807.

[3] J. J. Keirns and R. F. Curl, jun., *J. Chem. Phys.*, 1968, **48**, 3773.

[4] J. R. Durig, C. C. Tong, and Y. S. Li, *J. Chem. Phys.*, 1972, **57**, 4425.

[5] L. A. Carriera, *J. Phys. Chem.*, 1976, **80**, 1149.

[6] K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, 1973, **95**, 1003.

[7] K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, 1973, **95**, 4796.

[8] S. G. Frankiss and J. H. S. Green in 'Chemical Thermodynamics,' Chem. Soc. Specialist Periodical Report 1973, vol. 1, ch. 8.

the Tables of Pitzer and Gwinn reproduced in refs. 9 and 10.

The error involved in such calculations is not easy to establish. The results are quoted to 0.1 J K^{-1} mol^{-1} in all Tables but may not be this accurate. The main sources of error are in the vibrational assignments, which are usually tentative and rarely complete for the high energy conformer, and the values of $\Delta H^{\ominus}$ used which are normally associated with a high experimental error. These sources of error will also affect the accuracy of the concentration of high energy conformer in Table 2, but no definite error limit can be quoted.

TABLE 1

Selected values for the principal moments of inertia of conformers and the enthalpy differences between conformers

	Low energy conformer				High energy conformer				Enthalpy difference[b]	
		I_A[a]	I_B[a]	I_C[a]		I_A[a]	I_B[a]	I_C[a]	$\Delta H^{\ominus}$	$\Delta H_0^{\ominus}$
trans-But-2-enal	*s-trans*	2.571 3	38.437	40.476	*s-cis*	4.543 6	31.390	35.403	7 110	6 880
Propenal	*s-trans*	1.772 7	18.016	19.785	*s-cis*	3.785 4	12.989	16.775	6 990	6 810
Propenoyl fluoride	*s-trans*	7.944 0	18.854	26.798	*s-cis*	7.691 3	19.954	27.639	380	590
Propenoyl chloride	*s-trans*	15.182	22.061	37.248	*s-cis*	8.806 8	33.458	42.265	2 510	2 230
Ethanedial	*s-trans*	1.512 5	17.529	19.042	*s-cis*	3.140 3	13.533	16.642	13 450	13 460
Ethanedioyl chloride	*s-trans*	16.786	55.725	72.512	*gauche*	26.212	44.200	60.210	5 780	4 780
Ethanedioyl bromide	*s-trans*	17.221	144.44	161.66	*gauche*	36.300	98.295	118.27	2 640	1 940

[a] In 10^{-39} g cm^2. [b] In J mol^{-1}.

TABLE 2

Concentration of high energy conformer (%)

T/K	273.15	298.15	300.0	400.0	500.0	600.0	700.0	800.0	900.0	1 000.0
trans-But-2-enal	5.3	6.7	6.9	13.1	18.8	23.6	27.6	30.8	33.5	35.7
Propenal	5.9	7.5	7.6	14.2	20.3	25.3	29.3	32.6	35.3	37.6
Propenoyl fluoride	43.1	43.5	43.5	44.4	45.0	45.3	45.5	45.6	45.7	45.8
Propenoyl chloride	28.6	30.5	30.7	36.3	40.1	42.7	44.6	46.1	47.2	48.1
Ethanedial	0.47 *	0.56	0.58	2.20	4.8	8.0	11.4	14.7	17.7	20.5
Ethanedioyl chloride	32.8	38.1	38.5	54.4	54.0	70.0	74.8	76.9	78.9	80.5

* 289 K.

TABLE 3

Entropy ($S^{\ominus}$/J K^{-1} mol^{-1})

T/K	273.15	298.15	300.0	400.0	500.0	600.0	700.0	800.0	900.0	1 000.0
trans-But-2-enal	309.9	318.0	318.6	349.0	376.8	402.5	426.4	448.7	469.6	489.2
Propenal	275.6	281.7	282.1	304.9	325.7	344.9	362.7	379.1	394.5	408.9
Propenoyl fluoride	296.5	302.8	303.3	327.0	348.8	368.8	387.4	404.5	420.5	435.4
Propenoyl chloride	310.5	317.8	318.3	345.0	368.7	390.1	409.5	427.3	443.7	458.9
Ethanedial	270.5 *	272.4	272.7	291.9	309.1	324.9	339.3	352.6	364.9	376.2
Ethanedioyl chloride	334.7	343.5	344.1	374.4	398.8	419.4	437.3	453.2	467.4	480.3

* 289 K.

TABLE 4

Heat capacity ($C_P^{\ominus}$/J K^{-1} mol^{-1})

T/K	273.15	298.15	300.0	400.0	500.0	600.0	700.0	800.0	900.0	1 000.0
trans-But-2-enal	90.2	95.4	95.8	115.8	133.5	148.7	161.7	172.7	182.3	190.5
Propenal	67.5	71.5	71.8	87.0	99.9	110.6	119.6	127.3	133.8	139.4
Propenoyl fluoride	69.8	74.1	74.4	90.7	104.4	115.6	124.7	132.3	138.6	143.9
Propenoyl chloride	81.1	85.3	85.6	100.3	112.3	122.0	129.9	136.5	142.1	146.9
Ethanedial	59.9 *	60.9	61.1	72.3	82.3	90.3	96.8	102.0	106.3	109.7
Ethanedioyl chloride	99.8	102.1	102.2	107.6	111.4	114.7	117.6	120.0	121.9	123.5

* 289 K.

TABLE 5

Enthalpy [$(H^{\ominus} - H_0^{\ominus})T^{-1}$/J K^{-1} mol^{-1}]

T/K	273.15	298.15	300.0	400.0	500.0	600.0	700.0	800.0	900.0	1 000.0
trans-But-2-enal	60.4	63.0	63.2	73.9	84.1	93.6	102.5	110.6	118.0	124.9
Propenal	47.1	49.0	49.1	56.7	64.1	71.0	77.3	83.1	88.4	93.2
Propenoyl fluoride	49.6	51.5	51.6	59.4	67.1	74.3	80.9	86.8	92.2	97.2
Propenoyl chloride	55.8	58.1	58.2	67.0	74.9	81.9	88.2	93.9	98.9	103.5
Ethanedial	59.9	60.9	61.1	72.4	82.3	90.3	96.8	102.0	106.3	109.7
Ethanedioyl chloride	66.2	69.1	69.3	78.3	84.6	89.3	93.1	96.4	99.1	101.5

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[9] D. R. Stull, E. F. Westram, and G. C. Sinke, ' Chemical Thermodynamics of Organic Compounds,' Wiley, New York, 1969.

[10] G. N. Lewis and M. Randall, ' Thermodynamics,' McGraw-Hill, New York, 1961.

In Tables 3—5 values of entropy $S^\ominus$, heat capacity $C_p^\ominus$, and enthalpy $(H^\ominus - H_0^\ominus/T)$ are reported for six compounds. Calculation of the Gibbs free energy is done using equation (1).

$$(G^\ominus - H_0^\ominus)/T = (H^\ominus - H_0^\ominus)/T - S^\theta \qquad (1)$$

Table 1 shows the selected values of the data parameters used. To calculate values of $\Delta H_0^\ominus$ using equation (3) the average value of $T\Delta C_p^\ominus$ was calculated over the same temperature range that quoted values of $\Delta H^\ominus$ were calculated in the original works. The calculated values of $\Delta H_0^\ominus$ are listed in Table 1.

Table 2 gives the calculated concentrations of the high energy conformer for each compound over the range of temperatures used.

THEORY

The method of calculation given refers to the general case of conformational equilibrium where m equivalent types of low energy conformer A are in equilibrium with n equivalent types of conformer B; *i.e.* $[A] \rightleftharpoons [B]$ where [A] is the total concentration of all types of conformer A. The entropy change of the equilibrium must take into account the statistical weights of conformers A and B, and is given by equation (2). The free energy change is calculated in equations (5) and (6) from the statistical values by including a term for the enthalpy difference between conformers at absolute zero, $\Delta H_0^\ominus$. An approximate expression for the relationship between $\Delta H_0^\ominus$ and the experimental $\Delta H^\ominus$ is given in equation (3), but due to the relatively high errors in the calculation of $\Delta H^\ominus$ any approximation in the relationship is negligible.

$$\Delta S^\ominus = S_B^\ominus - S_A^\ominus + R\ln(n/m) \qquad (2)$$

$$\Delta H^\ominus = \Delta H_0^\ominus + T\Delta C_p^\ominus \qquad (3)$$

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus \qquad (4)$$

$$\begin{aligned}\Delta G^\ominus &= T\left[\left(\frac{H_B^\ominus - H_0^\ominus{}_{,B}}{T}\right) - \left(\frac{H_A^\ominus - H_0^\ominus{}_{,A}}{T}\right) - S_B^\ominus + S_A^\ominus - R\ln(n/m)\right] + \Delta H_0^\ominus \\ &= T\left[\left(\frac{G_B^\ominus - H_0^\ominus{}_{,B}}{T}\right) - \left(\frac{G_A^\ominus - H_0^\ominus{}_{,A}}{T}\right) - R\ln(n/m)\right] + \Delta H_0^\ominus \qquad (5) \\ &= -RT\ln K \qquad (6)\end{aligned}$$

From the free energy change the concentration of high energy conformer, X_B, can be calculated by equation (7).

$$X_B = K/(1 + K) \qquad (7)$$

Values of X_B calculated are given in Table 1. Using the value of X_B calculated at any temperature the final values for the thermodynamic functions of the mixture, given in Tables 3—5, are calculated by equations (8)—(10), first reported by Aston *et al.*[11]

$$S^\ominus = X_A S_A^\ominus + X_B S_B^\ominus - R[X_A\ln(X_A/m) + X_B\ln(X_B/n)] \qquad (8)$$

$$C_P^\ominus = X_A C_P^\ominus{}_{,A} + X_B C_P^\ominus{}_{,B} + \left(\frac{X_A X_B}{R}\right)\left[\frac{\Delta H_0^\ominus}{T} + \left(\frac{H_B^\ominus - H_0^\ominus{}_{,B}}{T}\right) - \left(\frac{H_A^\ominus - H_0^\ominus{}_{,A}}{T}\right)\right]^2 \qquad (9)$$

$$\left(\frac{H^\ominus - H_0^\ominus}{T}\right) = X_A\left(\frac{H_A^\ominus - H_0^\ominus{}_{,A}}{T}\right) + X_B\left[\left(\frac{H_B^\ominus - H_0^\ominus{}_{,B}}{T}\right) + \frac{\Delta H_0^\ominus}{T}\right] \qquad (10)$$

DISCUSSION

trans-*But-2-enal*.—Thermodynamic functions for *trans*-but-2-enal have recently been calculated[2] for the *s-trans* conformer in the gas phase. A full vibrational assignment for *trans*-but-2-enal was given, and bands present at 395 and 1 690 cm^{-1} in the Raman spectrum of the liquid were assigned to a high energy conformer. A value of $\Delta H^\ominus$ of 7.1 kJ mol^{-1} was given.

The structure of *trans*-but-2-enal was determined in two laboratories independently using microwave spectroscopy,[12] and shown to be *s-trans*. Both works gave similar values for the moments of inertia and methyl torsion barrier height, but neither work could detect any peaks due to a high energy conformer. In this work the results of Suzuki and Kozima[12a] were used, and using their value of 7 240 ± 40 J mol^{-1} for the methyl torsion barrier height a value of 171 cm^{-1} was calculated for the torsion in the gaseous phase.

Using the *s-trans* structure proposed[12a] moments of inertia were calculated for the *s-cis* conformer, as it was assumed that *trans*-but-2-enal has the *s-cis* high energy conformer like propenal.[5]

The relatively low concentration of *s-cis* conformer calculated at room temperature (7%) explains why efforts to locate evidence of the *s-cis* conformer in the microwave spectrum[12] failed.

Propenal.—Cherniak and Costain[13] examined the microwave spectrum of propenal and ten isotopically substituted molecules and assigned peaks to *s-trans* conformers in each case, giving principal moments of inertia. They searched for evidence of a high energy conformer (either *s-cis* or *gauche*) but could find none, indicating a high energy conformer concentration probably well below 10%, if at all.

Carriera examined the Raman spectrum of gaseous propenal and assigned weak peaks as torsional overtones of both the *s-trans* and high energy conformer.[5] The torsional potential function was calculated and this led to assignment of the high energy conformer as *s-cis* 584 ± 180 cm^{-1} above the *s-trans*.

A complete vibrational assignment for *s-trans*-propenal

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[11] J. G. Aston, G. Szasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, 1946, **14**, 67.

[12] (*a*) M. Suzuki and K. Kozima, *Bull. Chem. Soc. Japan*, 1969, **42**, 2183; (*b*) S. L. Hsu and W. H. Flygare, *Chem. Phys. Letters*, 1969, **4**, 317.

[13] E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 1966, **45**, 104.

was given by Bowles *et al.*,[14] using low frequency data reported by Harris,[15] but no evidence for a high energy conformer was found. Recently Krantz *et al.* observed the i.r. spectrum using matrix isolation techniques,[16] and noted weak bands which increased in intensity on photoradiation of the matrix. These bands were assigned to the *s-cis* conformer as redeposition of the matrix gave the original spectrum.

Propenoyl Fluoride.—A microwave study of propenoyl fluoride [3] located peaks due to two different conformers which were shown to be both planar. The extra enthalpy of the *s-cis* conformer was calculated as 375 ± 420 J mol^{-1}.

If the inertial defect Δ is known for both the ground state, Δ_0, and the first torsional level, Δ_1, then the torsion can be calculated [17] by equation (11). Using the

$$\Delta_1 - \Delta_0 = -4(h/8\pi^2c)\,(1/\nu) \qquad (11)$$

data reported by Keirns and Curl [3] this predicts the *s-trans* torsion at 93 cm^{-1} and the *s-cis* torsion at 85 cm^{-1}, for the gaseous phase.

The complete vibrational assignment for *s-trans*-propenoyl fluoride was made by Carlson *et al.*[18] who obtained a value of $\Delta H^{\ominus}$ in CS_2 solution of 625 ± 420 J mol^{-1} and estimated *ca.* 50% *s-cis* at room temperature. Later Redington [19] altered the assignments, and using matrix isolation and high resolution gas-phase i.r. techniques, gave a complete assignment for both conformers. Redington assigned a weak gas band at 115 cm^{-1} which showed a sharp Q branch as the *s-trans* torsion in agreement with the earlier work. Also a very weak gas band at 195 cm^{-1} showing no central Q branch under the resolution available was assigned by Redington as the corresponding *s-cis* torsion.[19] However Carlson *et al.*[18] reported that this band was present in the annealed solid at 182 cm^{-1}. If this band was due to the out-of-plane torsion then it should disappear from the solid spectrum and also show a C contour gas structure with a sharp central Q branch. Therefore it is assumed that assignment of the *s-cis* torsion at 195 cm^{-1} is incorrect. Hence in the present calculations the assignments of Redington [19] have been used, but the *s-cis* torsion has been given a value of 115 cm^{-1}.

Propenoyl Chloride.—The microwave spectrum of propenoyl chloride was examined by Kewley *et al.*,[17] but only peaks due to the predominant *s-trans* conformer were assigned. Moments of inertia were given for molecules containing both ^{35}Cl and ^{37}Cl and in these calculations a mean value was taken using the normal isotopic ratio of 0.755 : 0.245. Using the *s-trans* model moments of inertia were calculated for the *s-cis* conformer. Using equation (11) above the *s-trans* torsion was calculated [17] to be 95 ± 25 cm^{-1} which is close to the observed value [20] of 106 cm^{-1}.

Katon and Feairhellar [21] examined the i.r. spectrum of gaseous propenoyl chloride over the temperature range 276—361 K and obtained a value of 2 510 J mol^{-1} for $\Delta H^{\ominus}$.

Redington and Kennedy examined the i.r. spectrum of propenoyl chloride [20] using matrix isolation techniques and gave a complete assignment for both conformers. Their values were used in this work except the value of the *s-cis* torsion. This was assigned on the basis of a similar value given to the *s-cis* torsion of propenoyl fluoride,[19] which is considered to be in error.

Ethanedial.—The *s-trans* conformer of ethanedial has a centre of symmetry and therefore exhibits no microwave spectrum, whereas a high energy conformer will give a spectrum due to lower symmetry. Durig *et al.*[4] examined the microwave spectrum and assigned peaks to a high energy conformer which had only a small inertia defect and so was determined to be the planar *s-cis* form. The *s-cis* torsion was assigned a value of 114 ± 8 cm^{-1}. An electron diffraction study [22] assigned the predominant conformer as *s-trans* and we have calculated moments of inertia from their proposed structure. Currie and Ramsay [23] examined an electronic band of ethanedial at 488 nm under high resolution and measured the rotational spacings which they assigned to the *s-cis* conformer. They obtained a value of $\Delta H^{\ominus}$ of 1 125 ∓ 100 cm^{-1}. Fundamental frequencies were assigned by Harris,[15] and Cole and Osborne [24] have given more accurate values. The concentration of *s-cis*-ethanedial calculated is only *ca.* 0.5% at room temperature which explains why neither vibrational spectroscopy nor electron diffraction gave evidence of the *s-cis* conformer. In the electronic study [23] it was noted that the band due to the *s-cis* conformer was *ca.* 1 000 times weaker than a similar *s-trans* band, which points to a very low concentration. It is interesting to note that even such a low concentration of *s-cis* raises the entropy and heat capacity relative to the pure *s-trans* conformer by 0.3 and 1.2 J K^{-1} mol^{-1} respectively.

Ethanedioyl Chloride.—The vibrational spectrum of ethanedioyl chloride was examined in gas, liquid, and solid states using i.r. and in liquid and solid states using Raman by Durig and Hannum.[25] Complete vibrational assignments were given for both *s-trans* and *s-cis* conformers except for the *s-cis* torsion, and a value of $\Delta H^{\ominus}$ given as 9.1 ± 0.8 kJ mol^{-1} for the liquid state. How-

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[14] A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc.* (*B*), 1969, 810.

[15] R. K. Harris, *Spectrochimica Acta*, 1964, **20**, 1129.

[16] A. Krantz, T. D. Goldfarb, and C. Y. Lin, *J. Amer. Chem. Soc.*, 1972, **94**, 4022.

[17] R. Kewley, D. C. Hemphill, and R. F. Curl, jun., *J. Mol. Spectroscopy*, 1972, **44**, 443.

[18] G. L. Carlson, W. G. Fateley, and R. E. Witkowski, *J. Amer. Chem. Soc.*, 1967, **89**, 6437.

[19] R. L. Redington, *J. Chem. Phys.*, 1975, **62**, 4927.

[20] R. L. Redington and J. R. Kennedy, *Spectrochim. Acta*, 1974, **30***A*, 2197.

[21] J. E. Katon and W. R. Feairheller, jun., *J. Chem. Phys.*, 1967, **47**, 1248.

[22] K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, 1967—1968, **1**, 463.

[23] G. N. Currie and D. A. Ramsay, *Canad. J. Phys.*, 1971, **49**, 317.

[24] A. R. H. Cole and G. A. Osborne, *Spectrochim. Acta*, 1971, **27***A*, 2461.

[25] J. R. Durig and S. E. Hannum, *J. Chem. Phys.*, 1970, **52**, 6089.

ever no reason for selecting *s-cis* as the high energy form instead of *gauche* was given. An electron diffraction study of ethanedioyl chloride in the gas was carried out by Hagan and Hedberg,[6] who concluded that the molecule existed predominantly as the *s-trans* conformer, but the high energy conformer was *gauche*, some 55° off the *s-cis* structure. They calculated the concentration of *gauche* conformer at 0, 80, and 190 °C to be 0.324, 0.487, and 0.576 respectively, from which they calculated $\Delta H^\ominus$ as 5.8 kJ mol^{-1} and $\Delta S^\ominus$ as 9.6 J mol^{-1} K^{-1}. They gave proposed structures for both conformers and these were used to calculate the values of the moments of inertia given in Table 1.

The calculations in this work gave results which agreed well with those of Hagen and Hedberg.[6] The value of $\Delta S^\ominus$ (measured statistically at 298 K) and the concentration of *gauche* form at 273 K were calculated as 11.3 (+5.8) J K^{-1} mol^{-1} and 0.33, which compare well with their values of 9.6 and 0.32 respectively.

Ethanedioyl Bromide.—The vibrational spectrum of ethanedioyl bromide was examined by Durig *et al.*[26] in the gas, liquid, and solid states using i.r. and the liquid and solid states using Raman. A complete assignment was given for the predominant *s-trans* conformer and nearly all the high energy conformer bands were assigned, and a value of $\Delta H^\ominus$ of 12.1 ± 0.4 kJ mol^{-1} was obtained for the liquid state. Hagen and Hedberg[7] studied ethanedioyl bromide in the gas phase using electron diffraction. They concluded that the high energy form was *gauche* like ethanedioyl chloride, but that $\Delta H^\ominus$ was only 2.63 kJ mol^{-1} and $\Delta S^\ominus$ 4.6 (+ 5.8) J K^{-1} mol^{-1}. These results contrast greatly with those reported by Durig *et al.*[26] and cannot be easily explained by difference between gas and liquid states.

In this work the vibrational assignment given by Durig *et al.*[26] was used and moments of inertia were calculated from the results of Hagen and Hedberg.[7] The calculated concentration of *gauche* conformer was 74% at room temperature which cannot be correct, as the vibrational spectrum indicates *s-trans* predominating. The *s-trans* conformer has a centre of symmetry which results in application of the mutual exclusion rule for vibrations due to this conformer. Bands which disappear on freezing are due to the asymmetric *gauche* form and are present in both Raman and i.r., whereas bands which remain in the solid are due to the centrosymmetric *s-trans* conformer and so are found in either Raman or i.r., but not both. However at room temperatures the *s-trans* bands are strongest and this would indicate that the concentration of *gauche* is $< 50\%$.

Because the calculations give results which are clearly inconsistent, the thermodynamic values are not tabulated. It appears that the value of $\Delta H^\ominus$ obtained by electron diffraction[7] for ethanedioyl bromide is too low, especially as the liquid value[26] differs so greatly.

It can be seen that this method of calculating thermodynamic functions can also be a useful method for checking experimental values of $\Delta H^\ominus$ and pointing out discrepancies.

[6/1948 *Received, 18th October,* 1976]

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[26] J. R. Durig, S. E. Hannum, and F. G. Baglin, *J. Chem. Phys.*, 1971, **54**, 2367.