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Note

Thermodynamic functions for 2-chloro- and 2-bromopropionitrile

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Using the spectroscopic data by Klaboe and Grundnes[1]; the rotational isomerism data taken from work by Wyn-Jones and Orville-Thomas[2], and the molecular-structural data given by Lerner and Dailey[3] and Bondi and Lielmezs[4]; it was possible to estimate the thermodynamic functions, C_p°, S°, $(H^\circ - H_0^\circ)/T$ and $-(F^\circ - H_0^\circ)/T$, for the isomeric equilibrium mixtures (*trans* and *gauche* stable isomers) of 2-chloro and 2-bromopropionitriles in the ideal gas state at 1 atm pressure.

Table 1 presents the obtained thermodynamic functions calculated by means of the well-established statistical mechanical thermodynamic calculation methods[5]. The associated interval rotational contribution was treated, however, by means of the Lielmezs–Bondi method[6–7]. The results given in Table 1 are correlated to eqn (1):

$$A = a + bT + cT^2 \qquad (1)$$

where A is the thermodynamic function at temperature T (K). The curve fitted constants a, b and c (eqn (1)) were obtained using the linear squares regression

TABLE 1

HEAT CAPACITY, ENTROPY, AND FREE ENERGY AND ENTHALPY FUNCTIONS

Thermodynamic function	*Temp. (K)*	*Isometric mixture of trans & gauche 2-chloropropionitrile*	*Isometric mixture of trans & gauche 2-bromopropionitrile*
Heat capacity, C_p° (cal mol^{-1} K^{-1})	298.15	19.94	20.64
	400.00	24.06	24.67
	500.00	27.57	28.09
	600.00	30.50	30.93
	700.00	32.95	33.30
	800.00	35.02	35.31
	900.00	36.78	37.03
	1000.00	38.29	38.49

(*Table continued on p. 422*)

TABLE 1 (*continued*)

Thermodynamic function	*Temp. (K)*	*Isometric mixture of trans & gauche 2-chloropropionitrile*	*Isometric mixture of trans & gauche 2-bromopropionitrile*
Entropy, S° (e.u.)	298.15	78.08	79.41
	400.00	84.52	86.06
	500.00	90.28	91.96
	600.00	95.57	97.34
	700.00	100.47	102.30
	800.00	105.01	106.89
	900.00	109.24	111.15
	1000.00	113.19	115.13
Free energy function, $(F^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	64.00	64.90
	400.00	68.42	69.46
	500.00	72.22	73.38
	600.00	75.68	76.93
	700.00	78.88	80.20
	800.00	81.86	83.26
	900.00	84.67	86.12
	1000.00	87.33	88.83
Enthalpy function, $(H^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	14.08	14.51
	400.00	16.10	16.60
	500.00	18.06	18.58
	600.00	19.89	20.41
	700.00	21.59	22.10
	900.00	23.15	23.63
	700.00	24.57	25.03
	1000.00	25.86	26.30

TABLE 2

CALCULATED CONSTANTS *a*, *b* AND *c* IN EQN (1)

Function	*a*	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]
Isomeric mixture of *trans*- and *gauche*-2-chloropropionitrile				
C_p°	5.8114	5.41	−2.176	0.1278
$(H^\circ - H_0^\circ)/T$	7.2012	2.48	−6.163	0.0293
$-(F^\circ - H_0)/T$	50.2316	5.05	−1.349	0.1221
S°	57.4329	7.53	−1.965	0.0949
Isomeric mixture of *trans*- and *gauche*-2-bromopropionitrile				
C_p°	6.8720	5.28	−2.128	0.1322
$(H^\circ - H_0^\circ)/T$	7.4399	2.57	−6.859	0.0161
$-(F^\circ - H_0^\circ)/T$	50.6726	5.23	−1.421	0.1278
S°	58.1125	7.80	−2.107	0.1163

[a] Standard error of Y is the number S, where:

$$S = \sqrt{\sum_{i=1}^{n} (Y_i - \bar{Y}_i)/n - m - l}$$

such that n is the number of observations; m is the number of independent variables; Y_i is the ith calculated value of Y (Table 1) and $\bar{Y}_i$ is the interpolated value of Y (eqn (1)).

TABLE 3

SUMMARY OF DATA

trans-2-chloro-propionitrile			*gauche-2-chloro-propionitrile*			*trans-2-bromo-propionitrile*			*gauche-2-bromo-propionitrile*		
Fundamental frequencies, cm^{-1}											
2984[a]	2898	771	2984[a]	2938	686	2982[a]	2857	679	2982[a]	2926	579
2260	1447	1430	2260	1447	1430	2252	1439	1415	2252	1439	1415
1336	1308	1019	1336	1308	1000	1329	1279	1025	1321	1276	958
210	826	495	210	826	545	245	800	475	220	800	540
313	3010	2972	313	3010	2972	285	3038	2962	285	3038	2962
1216	1183	919	1216	1183	919	1227	1105	896	1206	1150	896
885	372	(106)	885	372	(106)	822	374	(90)	822	374	(90)
Product of principal moments of inertia[b], $g^3\ cm^6 \times 10^{117}$											
$I_A I_B I_C = 10164$			$I_A I_B I_C = 13929$			$I_A I_B I_C = 21513$			$I_A I_B I_C = 30139$		
Isomerization energy ΔE_{iso}[c], $cal\ mol^{-1}$											
380						540					
Symmetry number, σ											
1			1			1			1		
Molecular weight											
89.53						133.98					

[a] All frequency values obtained from ref. 1. [b] Moment of inertia values calculated, this work. Structural data taken from refs. 3 and 4. [c] Isomerization energies taken from ref. 2.

methods[8] and are found in Table 2. The values of spectroscopic data and molecular–structural parameters used for the calculation of the presented thermodynamic functions are given in Table 3.

There are no available experimental data. However, the overall reliability of the spectroscopic and molecular–structural data[1–4] suggests that the calculated thermodynamic property values should be within the limits of the experimental accuracy.

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