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Note

Thermodynamic functions for 2-chlorocyclobutanone; 2-chloro-2,4,4-trideuterocyclobutanone; 2-bromocyclobutanone; and 2-bromo-2,4,4-trideuterocyclobutanone

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The thermodynamic functions, C_p°, S°, $-(F^\circ-H_0^\circ)/T$ and $(H^\circ-H_0^\circ)/T$, have been computed in the ideal gas state at 1 atm for 2-chlorocyclobutanone; 2-chloro-2,4,4-trideuterocyclobutanone; 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone.

The accessibility of the needed vibrational spectra and structural data[1–3] for 2-chlorocyclobutanone; 2-chloro-2,4,4-trideuterocyclobutanone; 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone has made it possible to continue the calculation of the ideal gas state thermodynamic functions, C_p°; S°; $-(F^\circ-H_0^\circ)/T$; and $(H^\circ-H_0^\circ)/T$, for halogenated small ring compounds[4–6]. The functions for each given compound were calculated by means of the classical statistical mechanical methods.

The obtained results (Table 1) were curve-fitted[7] to eqn (1):

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

where A is the thermodynamic function at the temperature, K. The constants, a, b, c were obtained by means of the common least squares curve fitting methods[7] and are found in Table 2. The needed molecular parameter data are presented in Table 3.

DISCUSSION

2-Chlorocyclobutanone and 2-chloro-2,4,4-trideuterocyclobutanone

The thermodynamic functions of 2-chlorocyclobutanone and 2-chloro-2,4,4-trideuterocyclobutanone (Table 1) were calculated using the fundamental vibration frequency assignments by Durig and Green[1] and the molecular structural data of Frei and Gunthard[2]. During and Green[1] considering the harmonic appearance of the band assigned to the ring-puckering vibration along with the absence of large differences between the liquid and low temperature solid phase spectra concluded that

Thermodynamic function	*Temp. (K)*	*2-Chlorocyclobutanone*	*2-Chloro-2,4,4-trideuterocyclobutanone*	*2-Bromocyclobutanone*	*2-Bromo-2,4,4-trideuterocyclobutanone*
Heat capacity, C_p° (cal mol^{-1} K^{-1})	273.15	18.90	20.93	19.44	21.51
	298.15	20.50	22.70	21.02	23.26
	250.00	23.76	26.18	24.21	26.68
	377.15	25.38	27.87	25.81	28.34
	400.00	26.70	29.21	27.10	29.67
	450.00	29.37	31.92	29.74	32.33
	500.00	31.78	34.33	32.11	34.69
	550.00	33.94	36.47	34.23	36.80
	600.00	35.86	38.38	36.13	38.67
	650.00	37.60	40.08	37.84	40.35
	700.00	39.16	41.62	39.38	41.86
	750.00	40.58	43.00	40.78	43.31
	800.00	41.87	44.24	42.05	44.44
	850.00	43.05	45.37	43.22	45.55
	900.00	44.13	46.40	44.28	46.56
	950.00	45.12	47.33	45.26	47.48
	1000.00	46.04	48.17	46.16	48.31
Entropy, S° (e.u.)	273.15	73.85	75.32	76.88	78.24
	298.15	75.72	77.38	78.79	80.34
	350.00	79.53	81.56	82.68	84.61
	377.15	81.49	83.70	84.67	86.79
	400.00	83.12	85.48	86.33	88.59
	450.00	86.62	89.27	89.87	92.44
	500.00	90.01	92.94	93.30	96.14
	550.00	93.30	96.47	96.62	99.71
	600.00	96.48	99.87	99.83	103.13
	650.00	99.56	103.14	102.92	106.43
	700.00	102.52	106.29	105.90	109.60
	750.00	105.39	109.33	108.78	112.65
	800.00	108.16	112.25	111.56	115.58
	850.00	110.83	115.07	114.25	118.41
	900.00	113.42	117.78	116.84	121.14
	950.00	115.92	120.41	119.35	123.77
	1000.00	118.34	122.94	121.78	126.31

(Continued on p. 262)

TABLE 1 (*continued*)

Thermodynamic function	*Temp. (K)*	*2-Chlorocyclobutanone*	*2-Chloro-2,4,4-trideuterocyclobutanone*	*2-Bromocyclobutanone*	*2-Bromo-2,4,4-trideuterocyclobutanone*
Free energy function, $-(F^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	213.15	60.97	61.64	63.47	64.05
	298.15	62.13	62.87	64.87	65.33
	350.00	64.43	65.33	67.05	67.87
	377.15	65.58	66.58	68.25	69.16
	400.00	66.54	67.61	69.24	70.21
	450.00	68.58	69.80	71.33	72.47
	500.00	70.55	71.94	73.36	74.65
	550.00	72.47	74.01	75.32	76.77
	600.00	74.34	76.02	77.23	78.83
	650.00	76.16	77.98	79.09	80.82
	700.00	77.94	79.89	80.90	82.77
	750.00	79.67	81.75	82.66	84.66
	800.00	81.37	83.57	84.38	86.50
	850.00	83.02	85.34	86.06	88.29
	900.00	84.62	87 07	87.70	90.04
	950.00	86.22	88.75	89.30	91.75
	1000.00	87.77	90.40	90.86	93.41
Enthalpy function, $(H^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	273.15	12.88	13.68	13.41	14.19
	298.15	13.59	14.51	14.12	15.01
	350.00	15.10	16.23	15.63	16.74
	377.15	15.91	17.12	16.42	17.63
	400.00	16.58	17.87	17.09	18.38
	450.00	18.04	19.47	18.54	19.97
	500.00	19.46	21.00	19.94	21.49
	550.00	20.83	22.46	21.30	22.94
	600.00	22.14	23.85	22.60	24.30
	650.00	23.40	25.16	23.83	25.61
	700.00	24.58	26.40	25.00	26.83
	750.00	25.72	27.58	26.12	27.99
	800.00	26.79	28.68	27.18	29.08
	850.00	27.81	29.73	28.19	30.12
	900.00	28.75	30.71	29.14	31.10
	950.00	29.70	31.66	30.05	32.02
	1000.00	30.57	32.54	30.92	32.90

TABLE 2

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

Function	a	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]
2-Chlorocyclobutanone				
C_p°	−0.587	8.210	−3.592	0.2313
$-(F^\circ - H_0^\circ)/T$	48.380	4.920	−9.867	0.0547
S°	51.650	8.670	−2.008	0.0208
$(H^\circ - H_0^\circ)/T$	3.270	3.750	−1.021	0.0526
2-Chloro-2,4,4-trideuterocyclobutanone				
C_p°	0.852	8.580	−3.894	0.2960
$-(F^\circ - H_0^\circ)/T$	48.010	5.320	−1.090	0.0484
S°	50.370	9.580	−2.390	0.0422
$(H^\circ - H_0^\circ)/T$	2.965	4.260	−1.300	0.0302
2-Bromocyclobutanone				
C_p°	0.271	8.080	−3.527	0.2240
$-(F^\circ - H_0^\circ)/T$	50.430	5.120	−1.081	0.0639
S°	54.310	8.840	−2.103	0.0302
$(H^\circ - H_0^\circ)/T$	3.830	3.730	−1.022	0.0481
2-Bromo-2,4,4-trideuterocyclobutanone				
C_p°	1.800	8.430	−3.821	0.2940
$-(F^\circ - H_0^\circ)/T$	49.990	5.510	−1.178	0.0554
S°	53.480	9.770	−2.495	0.0558
$(H^\circ - H_0^\circ)/T$	3.490	4.250	−1.317	0.0282

[a] Standard error is the number S where: $S = \sum_{i=1}^{n} (Y_i - \bar{Y}_i)^2/n-m-1$; such that n is the number of observations, m is the number of independent variables; Y_i is the calculated value of Y (Table 1) and $\bar{Y}_i$ is the extrapoted value of Y (eqn (1)).

there is but only one equilibrium conformation of these molecyles and that the ring is very nearly planar. In view of these conclusions, the presented thermodynamic functions (Table 1) were calculated assuming that indeed for both of these molecules the structure is planar with one stable equilibrium conformation.

2-Bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone

The thermodynamic functions for 2-bromocyclobutanone and 2-bromo-2,4,4-trideuterocyclobutanone were calculated using the fundamental frequency values as assigned by During and Morrisey[3]. These authors as a result of their Raman and infrared spectra analysis of both molecules did conclude that these molecules are planar or very nearly so, and that there is serious doubt as to the existence of conformers[4] for these molecules. Consequently, the presented thermodynamic functions (Table 1) were calculated assuming that both molecules are planar and have only one stable equilibrium conformer.

ACCURACY

Since the literature search did not reveal any experimental data on thermodynamic functions of these compounds in the gaseous state, it was not possible to

TABLE 3

SUMMARY OF DATA

2-Chlorocyclobutanone	*2-Chloro-2,4,4-trideuterocyclobutanone*	*2-Bromocyclobutanone*	*2-Bromo-2,4,4-trideuterocyclobutanone*
Fundamental frequencies (cm^{-1})[a]			
3013, 2995, 2967, 2954, 2940, 1799, 1448, 1394, 1251, 1225, 1204, 1188, 1165, 1069, 1034, 1002, 975, 893, 872, 746, 687, 598, [illegible], 412, 307, 275, 178	3013, 2966, 2247, 2213, 2185, 1797, 1447, 1110, 1224, 893, 975, 952, 1143, 1075, 1037, 798, 973, 835, 649, 745, 619, 556, 488, 362, 301, 253, 170	3010, 2980, 2965, 2965, 2934, 1789, 1445, 1393, 1245, 1212, 1196, 1177, 1155, 1063, 1029, 990, 964, 892, 852, 737, 686, 555, 513, 379, 270, 225, 152	3010, 2244, 2963, 2213, 2184, 1785, 1442, 1084, 1228, 885, 945, 945, 1140, 1063, 1033, 780, 963, 826, 653, 711, 614, 498, 480, 345, 266, 210, 151
Principal moments of inertia[b] I_A, I_B *and* I_C, $g\text{-}cm^2 \times 10^{39}$			
$I_A = 20.24$	$I_A = 21.24$	$I_A = 21.09$	$I_A = 22.11$
$I_B = 30.34$	$I_B = 33.00$	$I_B = 47.28$	$I_B = 50.92$
$I_C = 47.53$	$I_C = 49.25$	$I_C = 68.67$	$I_C = 71.31$
Molecular symmetry number[c]			
1	1	1	1

[a] All frequencies from refs. 1 and 3. [b] Moments of inertia values calculated, this work, using structural data of ref. 2. [c] Molecular symmetry members taken from data of refs. 1, 3.

directly compare the experimental results with the calculated thermodynamic function (Table 1) values. Indirectly, however, if we consider the overall accuracy of the structural and molecular data used (Table 3) as well as the statements regarding the existing planarity of the ring structures, it may well be thought that the presented results would fall within an experimental measurement accuracy range, i.e., 1–2% error estimate limit.

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