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IDEAL GAS STATE THERMODYNAMIC FUNCTIONS FOR MONOHALOGENATED CYCLO-ALKANES

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ABSTRACT

The thermodynamic functions, C_p°, S°, $-(F^\circ - H_0^\circ)/T$ and $(H^\circ - H_0^\circ)/T$, have been calculated in the ideal gas state at 1 atm for the following monohalogenated cycloalkanes: bromocyclopropane, bromocyclobutane, chlorocyclobutane, fluorocyclobutane, bromocyclopentane. The effect of pseudorotation of the cyclobutanes and bromocyclopentane on the thermodynamic function values was considered to be negligible.

INTRODUCTION

The published spectroscopic and structural data for several halogenated monocycloalkanes[1–11], have made it possible to calculate the thermodynamic functions—heat capacity, enthalpy, entropy, and free energy for bromocyclopropane, bromocyclobutane, chlorocyclobutane, fluorocyclobutane and bromocyclopentane in the ideal gas state at a pressure of 1 atm. The functions for each given compound were calculated by means of the well-known statistical mechanical methods.

The results presented in Table 1 were fitted[12] to eqn (1)

$$\Lambda = a + bT + cT^2 \tag{1}$$

where Λ is the thermodynamic function at temperature T (K). The constants a, b and c (eqn 1) were obtained using least squares curve fitting methods[12] and are found in Table 2 and Figs. 1–4. Table 2 also lists a, b and c values for iodocyclobutane. These a, b and c values of iodocyclobutane were estimated from Figs. 1–4 extrapolating the corresponding a, b and c values of bromo-, chloro- and fluorocyclobutanes. Table 3 presents the values of the molecular parameters used in thermodynamic function calculations.

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DISCUSSION

Bromocyclopropane

The thermodynamic functions (Table 1) for bromocyclopropane were calculated using the fundamental vibration frequency assignments made by Rothschild[1] and the structural data of Lam and Dailey[2].

Halocyclobutanes

The structural configurations and the vibrational spectra of halocyclobutanes have been studied by several investigators[3–9]. In this work to calculate the thermo-

TABLE 1

HEAT CAPACITY, ENTROPY, FREE ENERGY AND ENTHALPY FUNCTION

	Temperature (K)	*Bromo-cyclo-propane*	*Bromo-cyclo-butane*	*Chloro-cyclo-butane*	*Fluoro-cyclo-butane*	*Bromo-cyclo-pentane*
Heat capacity, C_p° (cal mol^{-1} K^{-1})	273.15	15.51	18.57	17.57	16.42	24.27
	298.15	16.91	20.30	19.29	18.13	26.37
	350.00	19.77	23.85	22.85	21.70	30.69
	400.00	22.35	27.09	26.13	25.03	34.63
	450.00	24.69	30.04	29.15	28.12	38.26
	500.00	26.77	32.70	31.88	30.94	41.56
	550.00	28.60	35.09	34.34	33.48	44.55
	600.00	30.22	37.24	36.55	35.78	47.25
	650.00	31.65	39.17	38.55	37.85	49.71
	700.00	32.92	40.93	40.37	39.74	51.95
	750.00	34.05	42.54	42.03	41.46	54.00
	800.00	35.07	44.01	43.55	43.03	55.89
	850.00	35.98	45.37	44.95	44.48	57.63
	900.00	36.81	46.61	46.24	45.81	59.23
	950.00	37.56	47.77	47.43	47.04	60.72
	1000.00	38.24	48.84	48.5	48.17	62.09
Entropy, S_0° (e.u.)	273.15	69.73	74.53	69.12	68.75	84.51
	298.15	71.30	76.38	70.88	70.40	86.87
	350.00	74.50	80.18	74.52	73.85	91.71
	400.00	77.53	83.80	78.00	77.19	96.29
	450.00	80.49	87.36	81.45	80.52	100.80
	500.00	83.38	90.84	84.84	83.80	105.10
	550.00	86.18	94.22	88.16	87.03	109.40
	600.00	88.88	97.52	91.39	90.19	113.50
	650.00	91.49	100.70	94.12	93.27	117.60
	700.00	94.01	103.80	97.57	96.27	121.40
	750.00	96.43	106.80	100.50	99.18	125.20
	800.00	98.77	109.70	103.40	102.00	128.90
	850.00	101.00	112.50	106.20	104.80	132.40
	900.00	103.20	115.20	108.90	107.40	135.80
	950.00	105.30	117.90	111.50	110.00	139.20
	1000.00	107.30	120.40	114.00	112.60	142.40

TABLE 1 (*continued*)

	Temperature (K)	*Bromo-cyclo-propane*	*Bromo-cyclo-butane*	*Chloro-cyclo-butane*	*Fluoro-cyclo-butane*	*Bromo-cyclo-pentane*
Free energy function, $-(F^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	273.15	58.59	61.76	56.95	57.23	68.56
	298.15	59.59	62.91	58.05	58.27	70.00
	350.00	61.56	65.18	60.22	60.32	72.86
	400.00	63.37	67.28	62.22	62.22	75.50
	450.00	65.11	69.32	64.17	64.07	78.06
	500.00	66.79	71.30	66.07	65.88	80.55
	550.00	68.43	73.23	67.92	67.66	82.98
	600.00	70.02	75.11	69.75	69.40	85.36
	650.00	71.57	76.96	71.53	71.12	87.68
	700.00	73.08	78.77	73.28	72.81	89.96
	750.00	74.56	80.54	75.00	74.47	92.18
	800.00	76.00	82.27	76.69	76.10	94.36
	850.00	77.41	83.97	78.34	77.71	96.50
	900.00	78.78	85.63	79.96	79.29	98.59
	950.00	80.12	87.25	81.55	80.24	100.60
	1000.00	81.43	88.85	83.12	82.36	102.60
Enthalpy function, $(H^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	273.15	11.14	12.77	12.17	11.52	15.95
	298.15	11.71	13.47	12.83	12.13	16.87
	350.00	12.94	15.00	14.30	13.53	18.85
	400.00	14.16	16.52	15.78	14.97	20.79
	450.00	15.38	18.04	17.28	16.45	22.71
	500.00	16.59	19.54	18.77	17.92	24.60
	550.00	17.75	20.99	20.24	19.37	26.43
	600.00	18.86	22.41	21.64	20.79	28.19
	650.00	19.92	23.75	22.59	22.15	29.88
	700.00	20.93	25.03	24.29	23.46	31.49
	750.00	21.87	26.25	25.53	24.71	33.04
	800.00	22.77	27.42	26.71	25.92	34.52
	850.00	23.61	28.53	27.84	27.06	35.92
	900.00	24.42	29.59	28.92	28.15	37.26
	950.00	25.18	30.62	29.95	29.20	38.54
	1000.00	25.90	31.58	30.93	30.21	39.77

dynamic properties for bromo-, chloro- and fluorocyclobutane (Table 1) we used the vibrational assignments of Durig et al.[8]. The atomic coordinates for chlorocyclobutane with the halogen in the equatorial position have already been calculated by Kim and Gwinn[4]. However, they did not observe the halogen (X = Cl) in the axial position. On the other hand, Kim and Gwinn[4] indicated that the structure for fluorocyclobutane is similar to that for chlorobutane; and so they recommended a bond length of 1.37 Å for the C–F bond. Additional to this, in this work we assume that such is the case also for bromocyclobutane (Fig. 1) and we have adopted[3,9] a bond length of 1.939 Å for the C–Br bond to calculate the atomic coordinates of bromine.

Since Kim and Gwinn[4] did not observe the axial position of the halogen atom and since the potential barrier to pseudorotation appears to be high[4], only the classi-

cal thermodynamic function values for the isomer with the halogen (X = Br, Cl, F) in the equatorial[4] position have been calculated (Table 1).

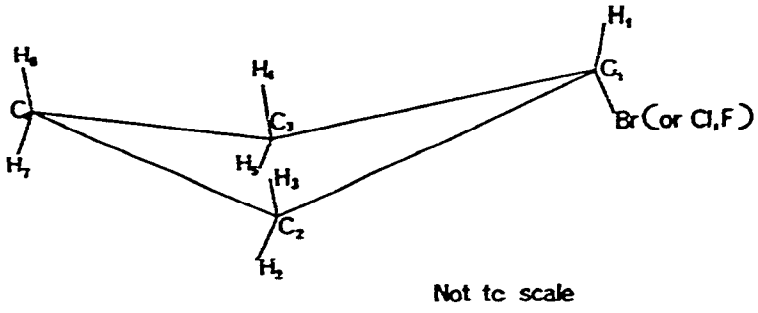

Fig. 1. Structure of bromocyclobutane.

The variation of the coefficients *a*, *b* and *c* describing eqn (1) with the atomic weight of the substituent halogen atom (X = Br, Cl, F), is shown in Figs. 2–5 for each of the calculated thermodynamic functions.

Since the obtained curves (Figs. 2–5) show smooth monotonic behavior, it is possible to extend these curves and by extrapolation to estimate the *a*, *b*, and *c* values for the iodocyclobutane (Table 2). However, for none of the listed compounds (Tables 1 and 2) we have supporting experimental evidence.

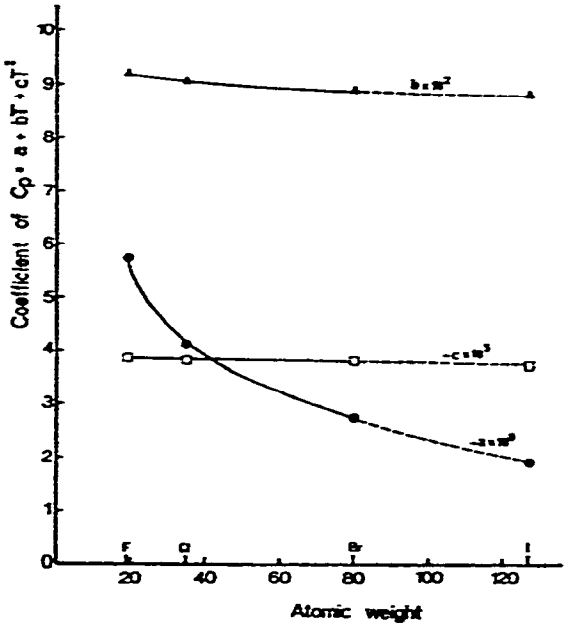

Fig. 2. Variation of the heat capacity coefficients (Table 2) with the atomic weight of substituent atom.

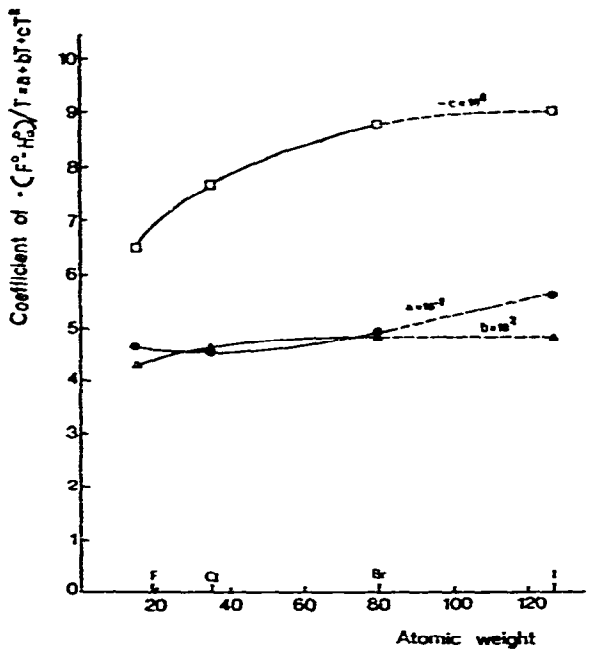

Fig. 3. Variation of the free energy function coefficients (Table 2) with the atomic weight of the substituent atom.

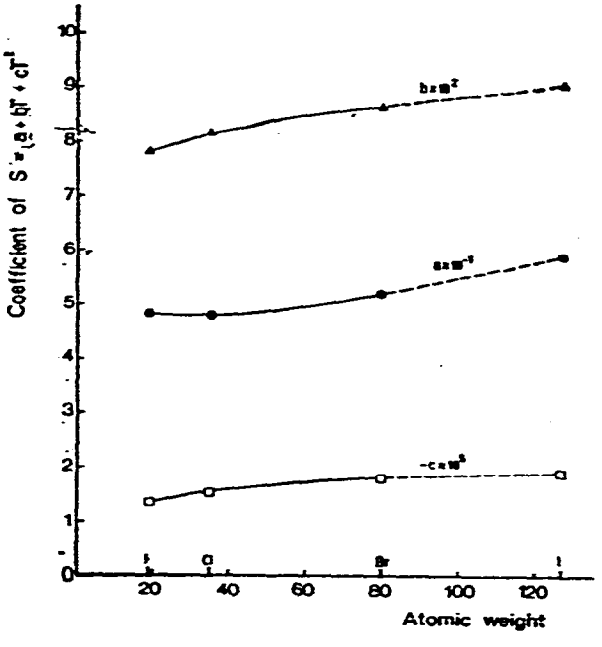

Fig. 4. Variation of the entropy coefficients (Table 2) with the atomic weight of the substituent atom.

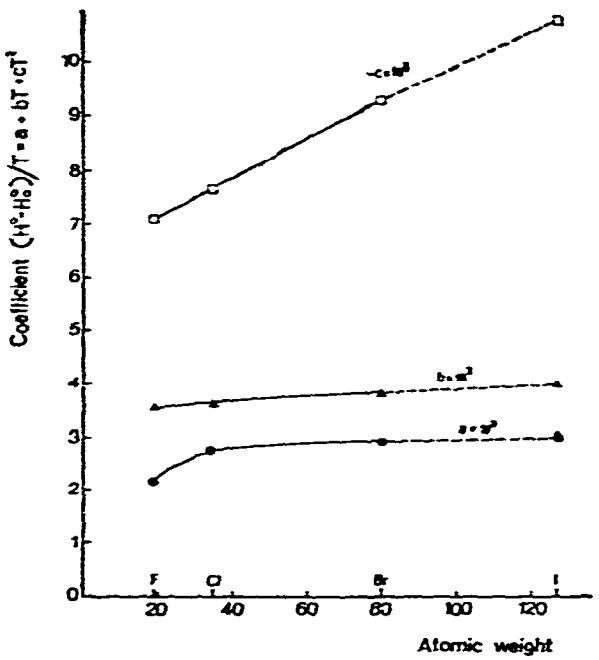

Fig. 5. Variation of the enthalpy function coefficients (Table 2) with the atomic weight of substituent atom.

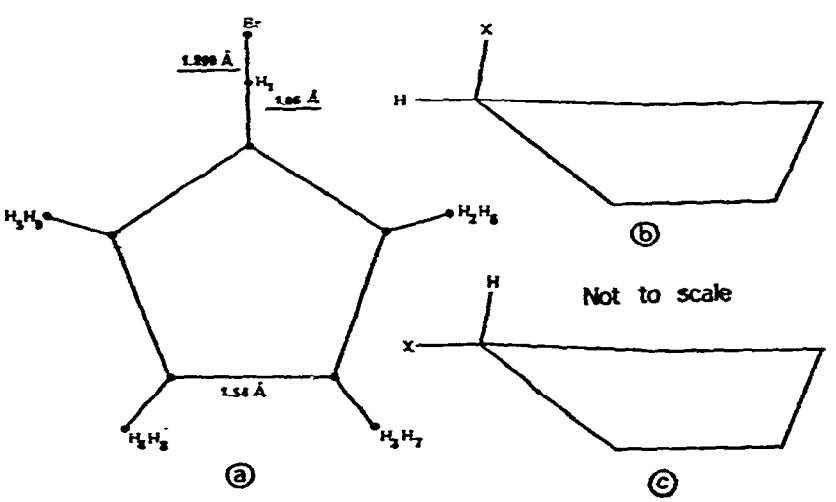

Fig. 6. Structure of bromocyclopentane with possible conformers. (a) Bromocyclopentane structure used to calculate the moment of inertia product; (b) Possible axial conformer; (c) Possible equatorial conformer.

TABLE 2

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

	a	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]
Bromocyclopropane				
C_p°	−1.7891	7.35	−3.386	0.2266
S°	50.8437	7.37	−1.721	0.0249
$-(F^\circ - H_0^\circ)/T$	47.8081	4.22	−0.8661	0.0501
$(H^\circ - H_0^\circ)/T$	3.0357	3.15	−0.8550	0.0686
Bromocyclobutane				
C_p°	−2.7016	8.93	−3.817	0.2465
S°	52.2396	8.63	−1.806	0.0370
$-(F^\circ - H_0^\circ)/T$	49.3369	4.82	−0.8789	0.0462
$(H^\circ - H_0^\circ)/T$	2.9026	3.80	−0.9274	0.0799
Chlorocyclobutane				
C_p°	−4.102	9.06	−3.832	0.2235
S°	47.8924	8.16	−1.534	0.1055
$-(F^\circ - H_0^\circ)/T$	45.1685	4.56	−0.7680	0.0425
$(H^\circ - H_0^\circ)/T$	2.7239	3.60	−0.7658	0.1287
Fluorocyclobutane				
C_p°	−5.7489	9.22	−3.86	0.1967
S°	48.2992	7.79	−1.358	0.0858
$-(F^\circ - H_0^\circ)/T$	46.1452	4.27	−0.6492	0.0372
$(H^\circ - H_0^\circ)/T$	2.1539	3.53	−0.7091	0.1227
Iodocyclobutane (estimated)				
C_p°	−1.93	8.85	−3.75	—
S°	59.0	8.80	−1.90	—
$-(F^\circ - H_0^\circ)/T$	56.5	4.83	−0.905	—
$(H^\circ - H_0^\circ)/T$	3.00	4.00	−0.175	—
Bromocyclopentane				
C_p°	−1.7571	10.86	−4.521	0.2570
S°	56.4023	10.90	−2.300	0.0265
$-(F^\circ - H_0^\circ)/T$	52.9403	6.06	−1.099	0.0572
$(H^\circ - H_0^\circ)/T$	3.4621	4.84	−1.201	0.0766

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

Bromocyclopentane

The thermodynamic functions (Table 1) for bromocyclopentane were calculated using the fundamental frequencies assigned by Durig et al.[10]. The belief advanced by Durig et al.[10] that the chloro- and bromocyclopentane rings may not undergo pseudo-rotation (form conformers) is indirectly supported by Vovelle et al.[11] through their observations that the position of the bromine atom (axial or equatorial, Fig. 6) does not affect the fundamental frequencies. These considerations have permitted to calculate the thermodynamic functions for bromocyclopentane as a planar ring mole-

TABLE 3

MOLECULAR PARAMETERS OF HALOGENATED MONOCYCLOALKANES

Bromocyclopropane			*Bromocyclobutane*			*Chlorocyclobutane*			*Fluorocyclobutane*			*Bromocyclopentane*		
Fundamental frequencies [V, cm^{-1}]														
3078[a]	3015	2957	3020[b]	3005	2977	3015[b]	3005	2967	3006[b]	2992	2912	2994[c]	2976	2924
1448	1423	1264	2962	2868	1459	2923	2854	1480	2861	2950	1472	2875	2852	1473
1238	1200	1165	1451	1262	1197	1455	1288	1207	1453	1361	1242	1449	1315	1208
1089	1051	1030	1092	486	1015	1103	1024	851	1140	1098	1079	1219	1209	1178
927	887	862	808	785	699	848	781	717	959	783	750	1003	2976	2924
810	760	545	633	302	143	530	365	159	599	456	166	2875	2852	1477
493	309	273	2992	2977	1440	2989	2979	1430	2988	2966	1441	1403	1282	1237
			1227	1181	1159	1266	1242	1172	1263	1221	1161	1134	1066	1028
			1025	963	938	1123	971	940	1049	1057	921	1003	935	803
			896	824	247	910	815	286	899	835	371	742	584	305
												231	903	886
												742	716	515
												452	289	150[d]
Principal moments[e] of inertia, $g\,cm^2 \times 10^{39}$														
$I_A = 34.304$			$I_A = 8.356$			$I_A = 8.320$			$I_A = 19.887$			$I_A = 15.661$		
$I_B = 5.105$			$I_B = 51.501$			$I_B = 33.439$			$I_B = 24.878$			$I_B = 63.729$		
$I_C = 32.695$			$I_C = 56.377$			$I_C = 38.349$			$I_C = 8.241$			$I_C = 71.473$		
Molecular shape factor, σ														
$\sigma = 1$			$\sigma = 1$			$\sigma = 1$			$\sigma = 1$			$\sigma = 1$		
Molecular weight														
120.97			135.012			90.544			74.094			149.02		

[a] All frequencies from ref. 1. [b] All frequencies from ref. 8. [c] All frequencies, except 150 cm^{-1}, from ref. 10. [d] Estimated, this work, see Fig. 7. [e] Calculated, this work.

cule[3] existing structurally in state as shown by Fig. 6a. This point is strengthened through the observation that 10% error in the $I_{(ABC-planar)}$ value would yield an inaccuracy for entropy and free energy function values of $[\ln I_{(ABC-planar)} - \ln I_{(ABC-bent)}]$, about 0.105 cal mol^{-1} K^{-1}.

The missing fundamental ring puckering frequency for bromocyclopentane[10] was estimated to be 150 ± 8 cm^{-1} (Table 3) by comparing (see Fig. 7) the frequencies of bromocyclopentane to those of chlorocyclopentane[10] for which all of the fundamental frequency values were available.

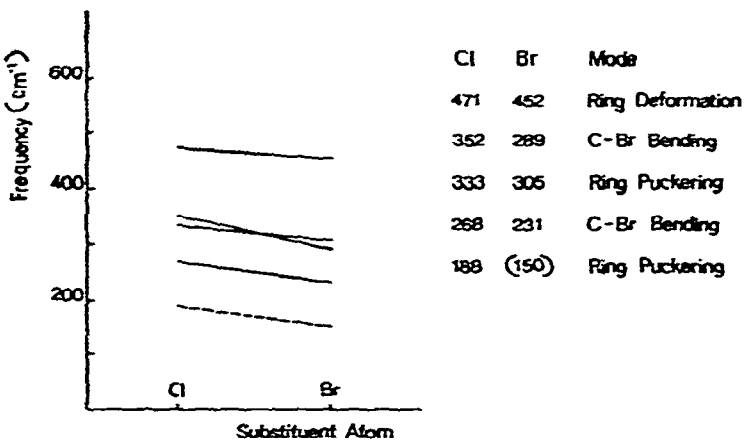

Fig. 7. Estimation of the missing fundamental ring puckering frequency for bromocyclopentane.

ACCURACY

Since there was no available experimental evidence, it was not possible to compare the calculated thermodynamic function values with the experimental data. However, indirectly a measure of the accuracy of the presented thermodynamic function values (Table 1) may be obtained, as the structural and spectroscopic data used (Table 3) are highly accurate and none of the listed compounds may undergo pseudorotation. In view of this, it is expected that the calculated classical thermodynamic function values will be within the possible measurement error range.

ACKNOWLEDGEMENT

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