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Note

THERMODYNAMIC PROPERTIES OF TETRACHLOROCYCLOPROPENE

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As part of our continuing interest in the spectroscopic [1,2] and thermodynamic [3,4] properties of three-membered ring compounds, the present communication reports the results from a calculation of statistical thermodynamic properties for tetrachlorocyclopropene (TCCP).

Electron diffraction studies by Mair and Bauer [5], and Barzdain et al. [6] confirmed that TCCP possesses C_{2v} symmetry. The 15 fundamental vibrations of this molecule may thus be classified according to the symmetry species C_{2v}, namely A_1, A_2, B_1, and B_2. There are six A_1, two A_2, four B_1, and three B_2 vibrations. With the exception of the A_2 block, whose transitions are forbidden in the IR, all fundamental vibrations are IR and Raman active. The symmetry number is $\sigma = 2$.

The molecular vibrations of TCCP have been investigated by Tobey and West [7] and by Ito [8] using IR absorption and Raman scattering techniques. However, four of the bending modes were not reported at that time. This precluded the reliable calculation of the thermodynamic properties of TCCP since these modes usually have low wave members and, thus, when entering the vibrational partition function, generate the most important Boltzmann factors, and, consequently, the greatest effect on the calculated values. Recently, we have made complete assignments of the vibrational fundamentals of this molecule and have verified them by means of a normal coordinate analysis [2]. The absorbed frequencies (cm^{-1}) were found to be 1809, 1149, 616, 521, 414, and 272 for the A_1 block; 348 and 113 for the A_2 block; 1057, 689, 298, and 137 for the B_1 block; and, finally, 751, 535, and 147 for the B_2 block. The principal moments of inertia, 1a = 447.505, 1b = 559.287, and 1c = 712.726 amu Å^2, have been determined from the

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TABLE 1

Thermodynamic properties of tetrachlorocyclopropene

Temp. (K)	C_p^0 (cal K^{-1} mol^{-1})	S^0 (cal K^{-1} mol^{-1})	$-(G^0 - H_0^0)/T$ (cal K^{-1} mol^{-1})	$H^0 - H_0^0$ (kcal mol^{-1})
100	14.21	65.32	54.98	1.034
200	21.04	77.38	63.31	2.814
273.15	24.67	84.51	68.06	4.492
298.15	25.67	86.71	69.53	5.122
300	25.74	86.87	69.64	5.169
400	28.85	94.73	74.96	7.910
500	30.96	101.41	79.60	10.907
600	32.44	107.19	83.73	14.081
700	33.52	112.28	87.45	17.382
800	34.31	116.81	90.84	20.775
900	34.91	120.89	93.96	24.237
1000	35.37	124.59	96.84	27.752
1100	35.74	127.98	99.52	31.308
1200	36.02	131.10	102.02	34.897
1300	36.26	133.99	104.37	38.511
1400	36.44	136.67	106.58	42.146
1500	36.60	139.21	108.67	45.799
1600	36.73	141.58	110.66	49.466
1700	36.84	143.80	112.54	53.145
1800	36.94	145.91	114.34	56.834
1900	37.02	147.91	116.05	60.531
2000	37.08	149.81	117.70	64.237

molecular geometry reported by Mair and Bauer [5].

With the availability of a complete set of vibrational and structural parameters, it is now possible to evaluate the heat capacity, entropy, Gibbs free energy, and enthalpy for the temperature range 100–2000 K. An ideal gas at 1 atm pressure, composed of rigid rotors capable of vibrating as independent harmonic oscillators, has been used as the model for TCCP. The calculations have been performed using the well-known methods of statistical mechanics. The results are listed in Table 1.

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