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Thermodynamic Functions of 2, 5 Dicloro Pyridine

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Abstract:

The Experimental observed fundamental frequencies of 2,5 dichloro pyridine, are used to calculate the thermodynamic functions, namely the entropy, enthalpy, heat capacity and the free energy in the temperature range 200-1500 K using the rigid rotator harmonic approximation.

Keywords: 2, 5 dichloro pyridine, thermodynamic functions, enthalpy, heat capacity, free energy function, entropy.

I. Introduction

Aromatic compounds like benzene, pyridine, cytosine, uracil and their derivatives are of great biological importance but due to their high complexity and low symmetry very few workers have studied these compound [1-2]. The computation in thermodynamic functions appear to be one of most important application of vibrational spectra of the complex molecules. From the vibrational data obtained from the spectra, Urey [3], Tolman and Badger [4] first suggested that it is quite possible to calculate the accuracy, the values of various thermodynamic functions. This is of great practical importance particularly since the direct experimental measurements of these quantities are quite difficult. The values of thermodynamic functions calculated from spectroscopic data are more accurate than the values obtained from the thermal measurements. The thermodynamic functions of the molecule 2,5 dichloropyridine have not been reported so far. With this end in view, the decision to compute the thermodynamic functions namely, the enthalpy function $\left(H^{o}-E_{o}^{o}\right)/T$, the heat capacity $\left(C_{p}^{o}\right)$. The free energy function $\left[-\left(F^{o}-E_{o}^{o}\right)/T\right]$ and the entropy $\left(S^{o}\right)$ were taken for the said compound at a pressure of atmosphere in the temperature range 200-1500 K under rigid rotator-harmonic oscillator approximation. The frequencies of the different modes of vibrations are used for the calculation of the various thermodynamic functions

The total energy (E) of a system of molecules is given as

$$E=\varepsilon_{trans}+\varepsilon_{rot}+\varepsilon_{vib}+\varepsilon_{elec} \quad \ldots (1)$$

And total partition (Ω) can be expressed as the product of the individual partition function.

Hence,

$$Q=Q_{trans}\times Q_{rot}\times Q_{elec} \quad \ldots (2)$$

Where the subscripts trans, rot, vib and elec stands for translation, rotational, vibrational and electronic respectively. Also

$$Q=\sum g_{i}\exp\left(-\varepsilon_{i}/\ kT\right) \quad \ldots (3)$$

Where g_i the statistical weight of the ith energy level [5] is k is the Boltzman constant and T is the absolute temperature. Contribution of each partition function may be evaluated separately and then added to the corresponding thermodynamic functions to obtain the total values. The electronic contribution is small and hence ignored. This is because ε_{elec} is large in comparison to kT at ordinary temperature. The various equations used in computation of various partition functions and their contribution to different thermodynamic functions are given by Herzberg [6]. The entropy function represents the total energy stored in a system and the entropy is regarded as a measure of randomness a system.

II. Experiment

The spec-pure compounds 2,5 dichloro pyridine was obtained from M/s Aldrich Chemie, West Germany and used as such. The purity of the compound was confirmed by elementary analysis and melting point determination. The infrared absorption spectrum of the compound was recorded on Perkin Elmer Spectrophotometer model FT/IR-4100 type A in the region 400-4000 cm^{-1} using KBr pellet method.

III. Result and Discussion

The Structural diagram of the compound is shown in Fig.-1

Thermodynamic functions viz. enthalpy, heat capacity, free energy and entropy of the said compound have been computed using the standard expression [6-7] by y-axis perpendicular to the molecular plane and z-axis to pass through the para position .For determining the rotational contribution the following structural parameters are given in Table-1 were used [8-9] Where N_1 is nitrogen atom along with C_2 to C_5 carbon atoms of pyridine ring and Cl_7 and Cl_8 group in the molecule 2,5 dichloro pyridine. The thermodynamic functions have been calculated at different temperature 200-1500 K Using 3n-6(n=14) fundamental frequencies and assuming the rigid rotor–harmonic oscillator approximation. The symmetry number for overall rotation is three and internal rotation has taken as one. The principal moments of inertia are found to be 535.6×10^{-39}, 108.07×10^{-39}, 700.84×10^{-39} gm/cm^2 respectively.

The various thermodynamic functions computed for 2,5 dichloro pyridine have been given in Table 2. The calculations of the thermodynamic functions at various temperatures (200-1500 K) were carried out for one mole of ideal gas at one atmospheric pressure. The variation of enthalpy function the enthalpy function $\left(H^o - E_o^o\right)/T$ and heat capacity $\left(C_p^o\right)$ with absolute temperature have been shown in Fig.-2 while the variation of free energy function $\left[-\left(F^o - E_o^o\right)/T\right]$ and the entropy $\left(S^o\right)$ with absolute temperature have been shown in Fig.-3 respectively.

As the temperature increases, entropy increases shown in Table- 2. Similar trend is followed for free energy and heat capacity for the molecule. When a system changes from solid to liquid to gaseous state, the enthalpy of system increases. Similar trend is reflected for the enthalpy for 2,5 dichloro pyridine as we increase the temperature in the range 200 – 1500 K. It is also found that the thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range. The variations of these thermodynamic functions with temperature are in good agreement with the trend reported in the literature [10-15].

The study has become more relevant in view of its great biological importance because the thermodynamic will be used as important tools for the field of research.

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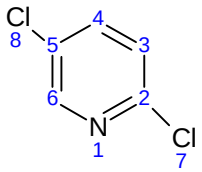

Fig.1

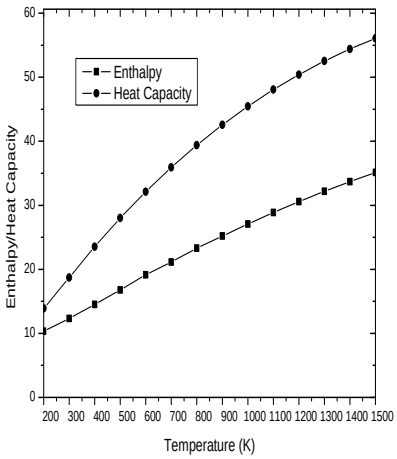

Fig.2. Temperature vs enthalpy and heat capacity for 2.5 dicloro pyridine

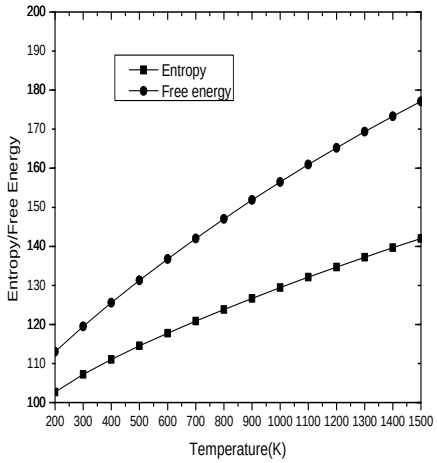

Fig.3 Temperature vs entropy and free energy for 2,5 dichloro pyridine

Table 1. Structural parameters

Bond lengths	**(A°)**	**Bond angles (in degree)**	
N_1C_2	1.3387	$\angle N_1C_2C_3$	122
C_2C_3	1.3387	$\angle C_2C_3C_4$	122
C_3C_4	1.3974	$\angle C_3C_4C_5$	119
C_4C_5	1.3900	$\angle C_4C_5C_6$	118
C_5C_6	1.3974	$\angle C_5C_6N_1$	122
C_6N_1	1.3387	$\angle C_6N_1C_2$	117
C_2Cl_7	1.7299	$\angle N_1C_2Cl_7$	119
C_5Cl_8	1.7299	$\angle Cl_7C_2C_3$	119
		$\angle C_4C_5Cl_8$	121
		$\angle Cl_8C_5C_6$	121

Table - 2: Thermodynamic functions of 2,5 dichloro pyridine (in Cal/mol–K)

Temperature(K)	$\left(H^o - E_o^o\right)/T$	$\left(C_p^o\right)$	$\left[-\left(F^o - E_o^o\right)/T\right]$	$\left(S^o\right)$
200	10.326	13.878	102.698	112.975
300	12.309	18.716	107.198	119.507
400	14.516	23.519	111.039	125.555
500	16.771	28.006	114.52	131.292
600	19.142	32.128	117.775	136.768
700	21.143	35.911	120.866	142.009

800	23.309	39.383	123.825	147.034
900	25.185	42.56	126.673	151.859
1000	27.07	45.45	129.425	156.496
1100	28.861	48.068	132.09	160.952
1200	30.561	50.415	134.675	165.237
1300	32.171	52.521	137.185	169.357
1400	33.693	54.403	139.626	173.319
1500	35.131	56.081	142	177.131