Thermodynamic Functions of
1, 2, 3, 4-tetrahydro-2, 6-dioxopyrimidine-4-carboxylic Acid

Sushil Kumar[1,*] and Dr. S.D. Sharma[2]
[1,*]Assistant Professor, SRM University, NCR campus Modinagar, India.
[2]Retd. Reader/Principal, D.N.P.G College, Meerut, India.

The statistical computation of an ideal gas state thermodynamic functions namely enthalpy, entropy, free energy, heat capacity of 1,2,3,4-Tetrahydro-2,6-dioxopyrimidine-4-carboxylic acid have been performed. These calculations have been made at a pressure of 1 atmosphere in the temperature range 100 °K to 1500 °K under rigid rotor harmonic oscillator approximation for 1 mole of perfect gas and on the basis of vibrational frequencies obtained from FTIR & Raman spectra and also with the help of moment of inertia.

1. INTRODUCTION

In addition to the application of the study of infrared and Raman spectra of polyatomic molecules to the determination of the structure of the molecules, there are a number of other important applications. The calculation of thermodynamic quantities appears to be most important application. On the basis of the molecular data obtained from the spectra as was first suggested by Urey [1] and Tolman and Badger [2], it is possible to predict with great precision the values of thermodynamic quantities, such as the heat capacity of the particular gases. This possibility is of great practical importance, particularly since the direct experimental measurement of these quantities is usually difficult and tedious and sometimes impossible. Frequently the values calculated from the spectroscopic data are more accurate than those determined by direct thermal measurements. These calculations are carried out at different temperatures from 100°K to 1500°K in the rigid rotor harmonic oscillator approximation for 1 mole of the perfect gas at 1 atmosphere. These thermo dynamical parameters can be calculated by using the standard expression given by Colthup [3], Herzberg [4] and other project reports given by Pitzer [5-7], Viney [7], Pitzer & Scott [8] and others [9-11] refined on time to time. We can also determine the rotational contribution by knowing the structural parameters of the molecule. The principal moment of inertia along the three axes (x, y, z) of the molecule can also be calculated by knowing the Cartesian coordinates of each atoms attached to the molecule. Therefore this paper has been devoted to calculate the principal moment of inertia, rotational constants and thermodynamic functions of 1,2,3,4-Tetrahydro-2,6-dioxopyrimidine-4-carboxylic acid.

2. METHOD

The principal moment of inertia and the thermodynamic functions viz. entropy, enthalpy, heat capacity and free energy can be calculated by adopting the following procedure of formulae by using spectroscopic data & structural parameters.

$$Q = Q_{tr}.\ Q_{rot}.\ Q_{vib} \tag{1}$$

Energy:
$$E^0 - E_0^{\ 0} = RT^2\ \frac{d\ I_n\ Q}{dT} \tag{2}$$

Enthalpy Function:
$$\frac{H^0 - E_0^0}{T} = RT^2 \frac{d\ I_n\ Q}{dT} + R \tag{3}$$

Heat Capacity:
$$C_P = R + \frac{d}{dT}\ [RT^2\Big(\frac{d\ I_n\ Q}{dT}\Big)] \tag{4}$$

Entropy:
$$S^0 = RT\ \frac{d\ I_n\ Q}{dT} + RI_{nQ} - RI_nN + R \tag{5}$$

Free Energy Function:
$$\frac{G^0 - E_0^0}{T} = -\ RI_n\ \frac{Q}{N} \tag{6}$$

Where, the Q is the Partition function, E_0^0 is the energy at absolute zero, E^0 is the total internal Energy, T is absolute temperature, I_n is the principal moment of Inertia.

3. RESULTS

For determining the rotational contribution the structural parameters viz. bond length, bond angle etc are taken from the literature [11,12] and described here for the above said molecule.

$N_1 - C_2$ = 1.34 Å, $C_2 - N_2$ = 1.40 Å

$N_2 - C_4$ = 1.42 Å, $C_4 - C_5$ = 1.42 Å

$C_5 - C_6$ = 1.45 Å, $C_6 - N_1$ = 1.33 Å

$C_2 - H_2$ = 1.084 Å, $C_4 - H_4$ = 1.085 Å

$C_5 - H_5$ = 1.084 Å, $C_6 - H_6$ = 1.084 Å

< $C_2\ N_2\ C_4$ = 121°, < $N_2\ C_4\ C_5$ = 120.5°

< $C_4\ C_5\ C_6$ = 1170°, < $C_5\ C_6\ N_1$ = 122.5°

< $C_6\ N_1\ C_2$ = 122°, < $N_1\ C_2\ N_2$ = 120°

All other angles are taken as 120°

—NH group: C-N = 1.65 Å, < NCN = 122°

—CH_3 group: C-C = 1.53 Å, C — H = 1.091 Å,

<HCH = 109.5°, <CCH = 109.5°

OH group: O – H = 0.97 Å, C – O = 1.35 Å,

< COH = 107°, <CCO = 120°

C-Br = 1.9025 Å, <CC Br = 120.530°

The symmetry number for overall rotation is taken as 1 for C_{2v} symmetry and internal rotation is taken as 2 for all compounds. The vibrational frequencies (3n-6) of these compounds are taken from the literature. The molecules which are studied contain single top group –CH_3, NH, N-O, NH_2 respectively. The x,y plane are taken for molecules and z axis to pass through the para position of the ring. The principle moment of inertia about x, y and z axis are calculated by the procedure given in the literature [3,4,10] and the calculated moment of inertia for all molecules is given in Table 1. The rotational constants for the molecule is calculated by the method of Herzberg [4] and given in Table 1.

Table 1: Principal moment of inertia of present molecule with x, y, z and rotational constants.

Molecules	Principal Moment of inertia (X 10^{-40} gm-cm^2)			Rotational Constants		
	IA	IB	IC	A	B	C
TDPCA	90.28	115.22	28.29	0.310	0.243	0.989

The calculations of total contribution of thermodynamic functions using (3n-6) fundamental frequencies at various temperatures viz. 100 °K to 1500 °K are carried out on the rigid rotor harmonic oscillator approximation and these are related to one mole of perfect gas at one atmospheric pressure. The thermodynamic functions calculated for above said molecule is presented in Table 2.

The values of thermodynamic quantities viz. entropy, enthalpy, free energy, and heat capacity at constant pressure calculated for title molecules show good relationship to the values calculated by various investigators [13].

The enthalpy function represents the total energy stored in a system. When a system changes from solid to liquid and then to gaseous state, the enthalpy of the system increases. Similar trend is reflected from the enthalpy values for present molecules as we increase the temperature in the range 100° - 1500 °K.

The entropy is regarded as the measure of randomness in a system. As the temperature increases, entropy also increases as shown in the Table 2. Similar trend will be followed for the values of free energy and heat capacity for title molecules under investigations. It was also found that the thermodynamic functions rise more rapidly in the low

temperature range and less rapidly in the high temperature range. The variation of these thermodynamic functions (cal/mole-^{0}K) with temperature as given in Table 2 are in good agreement with the trend reported in the literature [12-18].

Table 2: Thermodynamic functions of TDPCA.

Temperature (^{0}K)	Enthalpy	Free Energy(-)	Entropy	Heat Capacity
100	8.02	51.15	59.51	10.93
200	9.65	52.22	60.21	11.14
273	10.39	54.49	62.53	12.33
298	12.59	55.47	63.11	13.26
300	12.95	55.93	63.79	14.01
400	13.72	57.16	67.16	18.11
500	14.32	58.26	70.25	20.39
600	15.16	60.37	73.39	22.26
700	16.77	62.25	77.65	24.61
800	20.67	63.75	80.77	26.71
900	22.85	64.21	82.88	30.85
1000	26.67	66.33	88.94	32.92
1100	28.88	67.55	90.23	34.33
1200	30.79	68.03	92.65	36.11
1300	31.17	68.81	96.78	40.22
1400	33.15	69.31	98.81	44.65
1500	34.83	70.11	102.31	46.14

REFERENCES

[1] Robert C. Glen; "A fast empirical method for the calculation of molecular polarizability", Journal of Computer-Aided Molecular Design, Vol. 8(4), pp. 457-466, 1994.

[2] R.C. Tolman and R.M. Badger; "The entropy of diatomic gases and rotational specific heat, J. Am. Chem. Soc., Vol. 45910), pp. 2277-2285, 1923.

[3] N.B. Colthup, L.H. Daly and S.E. Wiberley; "Introduction of I.R. & Raman spectroscopy", Academic press, New York, 1975.

[4] G. Herzberg; "Molecular spectra and molcular structure-I & II", D. Van Nostrand Co. Princeton, New York, 1945.

[5] K.S. Pitzer and S. Kenneth; "Energy levels and thermodynamic functions for molecules with internal rotation: II. Unsymmetrical tops attached to a rigid frame", J. Chem. Phys. 14, pp. 239-243, 1946.

[6] K.S. Pitzer; "Internal rotation in molecules with two or more methyl groups", J. Chem. Phys., Vol. 10, pp. 605-606, 1942.

[7] K.S. Pitzer; "The molecular structure and thermodynamics of propane. The vibration frequencies, barrier to internal rotation, entropy, and heat capacity", J. Chem. Phys., Vol. 12(7), pp. 310-314, 1944.

[8] B.J. Mcclelland; "Statistical thermodynamics", Chapman & hall & science paperback pub. Co. London, 1973.

[9] S.M. Maron and J.B. Lande, "Fundamentals of physical chemistry", Macmillan, New York.

[10] K.K. Innes, H.D. McSwinay Jr., J.D. Simmons and S.G. Tilford; "Analysis of the $\tilde{A}^L B_L - \tilde{X}^L A_L$ electronic transitions of pyrimidine-d_0 and d_4 vapors", J. Mole. Spectroc., Vol. 31(1-13), pp. 76-94, 1969.

[11] H Landolt, R Börnstein, O Madelung, K H Hellwege, A M Hellwege, Wolfgang Pies, and Alarich Weiss; "Landolt-Börnstein numerical data and functional relationships in science and technology. Group 3, Crystal and solid state physics. Vol.7, Crystal structure data of inorganic compounds", Springer Berlin, 1976 and 1987.

[12] Praveen Kumar; "Electronic and vibrational spectral studies of some substituted Pyridines", Ph.D. Thesis, C.C.S. University, Meerut, 1998.

[13] Yogesh Kumar Gupta; "Electronic and vibrational spectral studies of some substituted Pyrimidines", Ph.D. thesis, Meerut University, Meerut, 1993.

[14] V.K. Rastogi, M. Palafox, B. Lal and Vaibhav Jain; "Vibrational spectra and thermodynamics of anthranilonitrile molecule", IJPAP, Vol. 38, pp. 564-569, 2000.

[15] V. Krishna Kumar and R.K. Xavier; "Normal co-ordinate analysis of 2-mercapto and 4,6-dihydroxy-2-mercapto pyrimidines", Indian journal of pure and applied physics, Vol. 41, pp. 597-601, 2003.

[16] Atul Kumar; "Electronic and vibrational spectral studies of some substituted n-heterocyclic compounds", Ph.D. Thesis, C.C.S. University, Meerut, 2008.

[17] M. Thomas and K.C. George; "Infrared and magnetic study of nanophase zinc ferrite", IJPAP, Vol. 47(2), pp. 81-86, 2009.

[18] Gagan Deep, Vipin Kumar and U.K. Jetly; "The Study on Thermodynamic Parameters and Fungiudal Activity of 3,4,5-Trimethoxybenzaldehyde Thiosemicarbazone", International Journal of advance research in Science and Engineering (IJARSE), Vol. 1(1), December 2012.