Thermochimica Acta, 12 (1975) 11–17

THERMODYNAMIC PROPERTIES OF OXYGEN COMPOUNDS
II. β-PROPIOLACTONE, γ-BUTYROLACTONE, AND γ-BUTYROLACTAM (2-PYRROLIDONE)

SHANTI A. KUDCHADKER AND ARVIND P. KUDCHADKER
Kanpur Critical Data Center, Department of Chemical Engineering,
Indian Institute of Technology, Kanpur-208016 (India)

(Received 13 December 1974)

ABSTRACT

A complete vibrational assignment is made and ideal gas thermodynamic properties are reported for β-propiolactone, γ-butyrolactone and γ-butyrolactam over the range 100–1500 K.

INTRODUCTION

The thermodynamic properties of γ-butyrolactone and γ-butyrolactam were required for our process engineering studies of Nylon-4 from tetrahydrofuran. These data are not available in the literature and hence we decided to calculate them from the available information on structural parameters and vibrational frequencies. β-Propiolactone was included as a part of this series. No data are available for β-propiolactam as it is very unstable.

In this study, we have attempted to complete the vibrational frequency assignments for the three molecules and to calculate the thermodynamic properties from 100 to 1500 K.

EXPERIMENTAL

β-Propiolactone

Bregman and Bauer[1] reported the molecular parameters from their electron diffraction studies. Kwak et al.[2] studied the microwave spectrum and reported the moments of inertia for this molecule which are adopted in this work (Table 1).

Durig[3] studied the infrared (vapor, liquid) and Raman (liquid) spectra and reported the complete vibrational analysis. He reported the ring puckering mode as 113 cm^{-1} from combination bands in the infrared studies of vapor state. Later Durig et al.[4] reinvestigated the Raman low region and far infrared region for the liquid state and reported the ring puckering mode to be 200 cm^{-1} in the far infrared region and 204 cm^{-1} in the Raman region. These are much higher than those obtained from the microwave measurements[2,5]. It is a well known fact that the lower-membered ring compounds are more strained than the higher ones. β-Propiolactone is more strained than γ-butyrolactone and one would expect a higher value for the ring puckering mode in the former than in the latter[6] for which it is 148 cm^{-1}. Hence, we have adopted the ring puckering mode as 200 cm^{-1}. The adopted values are given in Table 2.

TABLE 1

MOMENTS OF INERTIA (Amu Å^2) OF β-PROPIOLACTONE, γ-BUTYROLACTONE, AND γ-BUTYROLACTAM

Compound	I_a	I_b	I_c
β-Propiolactone	40.74	96.39	130.66
γ-Butyrolactone	69.4193	140.9553	197.2172
γ-Butyrolactam	71.0586	149.0469	210.3117

TABLE 2

FUNDAMENTAL FREQUENCIES (cm^{-1}) OF β-PROPIOLACTONE, γ-BUTYROLACTONE AND γ-BUTYROLACTAM

β-Propiolactone		*γ-Butyrolactone*		*γ-Butyrolactam*	
3028	$\nu_{(CH)}$	2965(3)	$\nu_{(CH)}$	3474	$\nu_{(NH)}$
3001	$\nu_{(CH)}$	2885(3)	$\nu_{(CH)}$	2965(3)	$\nu_{(CH)}$
3000	$\nu_{(CH)}$	1770	$\nu_{(CO)}$	2885(3)	$\nu_{(CH)}$
2935	$\nu_{(CH)}$	1490	$\nu_{(CH_2)}$	1692	$\nu_{(C=O)}$
1882	$\nu_{(C=O)}$	1466	$\nu_{(CH_2)}$	1490	$\delta_{(CH_2)}$
1475	$\delta_{(CH_2)}$	1426	$\nu_{(CH_2)}$	1460	$\delta_{(CH_2)}$
1427	$\delta_{(CH_2)}$	1390*	$\omega_{(CH_2)}$	1439	$\delta_{(CH_2)}$
1319	$\omega_{(CH_2)}$	1379	$\omega_{(CH_2)}$	1422	$\delta_{(NH)}$
1199	$\omega_{(CH_2)}$	1284	$\omega_{(CH_2)}$	1390	$\omega_{(CH_2)}$
1184	$t_{(CH_2)}$	1242	$t_{(CH_2)}$	1375	$\omega_{(CH_2)}$
1139	$t_{(CH_2)}$	1192	$t_{(CH_2)}$	1284	ring
1093	ring	1190*	$t_{(CH_2)}$	1266	$\omega_{(CH_2)}$
1046	$\gamma_{(CH_2)}$	1166	ring	1225	$t_{(CH_2)}$
1005	ring	1082*	$\gamma_{(CH_2)}$	1190	$t_{(CH_2)}$
924	ring	1037	ring	1166	$t_{(CH_2)}$
891	ring	990	ring	1082	$\gamma_{(CH_2)}$
790	$\gamma_{(CH_2)}$	929	ring	1068	ring
746	ring def.	898*	$\gamma_{(CH_2)}$	993	ring
513	ring def.	890	ring	916	ring
490	$\gamma_{(C=O)}$	800	$\gamma_{(CH_2)}$	898	$\gamma_{(CH_2)}$
200	ring puckering	674	ring def.	886	ring
		637	ring def.	810	$\gamma_{(CH_2)}$
		536	ring def.	745	$\gamma_{(NH)}$
		491	$\gamma_{(C=O)}$	685	ring def.
		225	ring twisting	630	ring def.
		148	ring puckering	539	ring def.
				491	$\gamma_{(C=O)}$
				316	ring twisting
				225	ring puckering

γ-Butyrolactone

Durig et al.[6] reported the moments of inertia for this molecule from microwave measurements which are adopted in this work (Table 1).

Very scanty data on the vibrational frequencies are available. Mecke et al.[7] studied the infrared and Raman spectra from 400 to 2000 cm^{-1} and reported partial assignments. Durig et al.[8] reported the six lowest frequencies from their studies in the far infrared region. Their further studies of the Raman measurements in the gaseous state resulted in the reassignment of the ring twisting and ring puckering modes[6]. This molecule has thirty vibrational frequencies. Mecke et al. have reported eighteen of them, out of which the lowest four overlap with Durig et al.'s data and are in excellent agreement with them. The ring twist and the ring puckering modes are reported by Durig et al. This means ten frequencies are missing. These are six C–H stretch, one CH_2 twist, one CH_2 wag, and two CH_2 out of plane bend. Comparing the rest of the frequencies with γ-butyrolactam (given in Table 2) one notices that the frequencies due to the CH_2 group are almost identical. Hence, we feel that the transfer of missing frequencies due to this group from γ-butyrolactam is justifiable. The adopted frequencies are given in Table 2.

γ-Butyrolactam

No experimental molecular parameters or moments of inertia are available. Mecke et al.[7] studied the infrared and Raman spectra in the region 400–2000 cm^{-1} and reported partial assignments. Parsons[9] studied the infrared of vapor and liquid states from 400 to 4000 cm^{-1}. Rey-Lafon et al.[10] studied the infrared spectra in different physical states from 250 to 3500 cm^{-1} and the Raman spectra below 1800 cm^{-1}. Warshel et al.[11] confirmed Rey-Lafon et al.'s assignments from their calculations using consistent force field. They also estimated the molecular structure which slightly deviates from the planar model. These parameters are adopted in this work. The calculated moments of inertia are given in Table 1.

The two lowest frequencies, the ring twisting (220 cm^{-1}) and the ring puckering (36 cm^{-1}) modes, calculated by Warshel et al. do not agree with those observed by Rey-Lafon et al. (316 cm^{-1} for ring twisting and 225 cm^{-1} for ring puckering). Comparing these two frequencies in various similar molecules, as can be seen from Table 3, we feel that the two lowest frequencies assigned by Rey-Lafon et al. seem to

TABLE 3

COMPARISON BETWEEN RING TWISTING AND RING PUCKERING FREQUENCIES (cm^{-1}) IN SOME SMALL RING COMPOUNDS

Mode	*β-Propiolactone*[4]	*γ-Butyrolactone*[6]	*γ-Butyrolactam*[10]	*Pyrrolidine*[12]	*Tetrahydrofuran*[3]	*Cyclopentanone*[8]	*δ-Valerolactam*[14]
Ring twisting	—	225	316(220)[11]	300	278	236	323
Ring puckering	200	148	225(36)[11]	—	—	95	188

be the correct ones. Furthermore, the five-membered ring should be more strained, and hence have a higher frequency for the ring puckering motion than the six-membered ring. If this is so, one would expect γ-butyrolactam to have a higher value for this mode than δ-valerolactam[14] for which the ring puckering mode is observed at 188 cm^{-1}.

γ-Butyrolactam and γ-butyrolactone are isoelectronic molecules. Similarly pyrrolidine and tetrahydrofuran are isoelectronic. We have the potential barrier heights for these two molecules as 300 and 143 (50 cm^{-1}) cal mol^{-1}, respectively, due to hindered free rotation[15,16]. These can be converted to the ring puckering frequencies using the formula

$$\nu_t = \frac{n}{2\pi}\left(\frac{V_0}{2I_r}\right)^{\frac{1}{2}}$$

where n = symmetry number;

V_0 = potential barrier height;

I_r = reduced moment of inertia.

Here the ring puckering motion is assumed to be similar to hindered rotation. We find that the ratio of these frequencies in tetrahydrofuran and pyrrolidine is

$$\frac{\nu_{\text{tetrahydrofuran}}}{\nu_{\text{pyrrolidine}}} = \left(\frac{V_{0_t}}{V_{0_p}}\right)^{\frac{1}{2}} \approx \left(\frac{143}{300}\right)^{\frac{1}{2}} \approx 0.69$$

as the symmetry number and the reduced moments of inertia are the same in these two molecules ($I_r = 8.56 \times 10^{-40}$ and 8.57×10^{-40} g cm^2, respectively)[17,15].

The ratio of this frequency for γ-butyrolactone and γ-butyrolactam is

$$\frac{\nu_{\gamma\text{-butyrolactone}}}{\nu_{\gamma\text{-butyrolactam}}} = \frac{148}{225} = 0.67$$

This shows that the lowest two frequencies for γ-butyrolactam could be 316 and 225 cm^{-1}. The adopted frequencies are reported in Table 2.

Thermodynamic properties

All three molecules have ring puckering motion. But as pointed out by Durig et al.[8] the barrier heights to pseudorotation are high enough and the ring puckering motion can be treated as an ordinary vibration in which puckering oscillates about a most stable configuration.

The ideal gas thermodynamic properties C_p°, $H^\circ - H_0^\circ$, S°, $(G^\circ - H_0^\circ)/T$ were calculated using the rigid rotor, harmonic oscillator assumption. The moments of inertia and the vibrational frequencies were used from Tables 1 and 2, respectively. The enthalpy, the Gibbs energy, and the equilibrium constant of formation from 100 to 1500 K were calculated for β-propiolactone using the computed thermal functions

TABLE 4

IDEAL GAS THERMODYNAMIC PROPERTIES OF β-PROPIOLACTONE

Temp. (K)	C_p° (cal deg^{-1} mol^{-1})	S° (cal deg^{-1} mol^{-1})	$-(G^\circ-H_0^\circ)/T$ (cal deg^{-1} mol^{-1})	$H^\circ-H_0^\circ$ (kcal mol^{-1})	ΔH_f° (kcal mol^{-1})	ΔG_f° (kcal mol^{-1})	log K_f
100.00	9.281	55.231	46.894	0.834	−68.901	−65.339	142.79775
150.00	10.716	59.254	50.373	1.332	−69.411	−63.450	92.44573
200.00	12.529	62.576	53.017	1.912	−69.958	−61.378	67.07101
273.15	15.811	66.951	56.171	2.945	−70.749	−58.117	46.49996
298.15	17.026	68.388	57.135	3.355	−71.000	−56.944	41.74100
300.00	17.117	68.494	57.205	3.387	−71.018	−56.855	41.41843
400.00	21.885	74.080	60.730	5.340	−71.815	−51.991	28.40654
500.00	26.018	79.422	63.939	7.742	−72.588	−46.934	20.51494
600.00	29.402	84.475	66.945	10.518	−73.099	−41.753	15.20850
700.00	32.165	89.222	69.792	13.601	−73.469	−36.495	11.39428
800.00	34.448	93.671	72.502	16.936	−73.724	−31.193	8.52144
900.00	36.355	97.842	75.088	20.478	−73.878	−25.867	6.28135
1000.00	37.962	101.758	77.561	24.197	−73.939	−20.513	4.48301
1100.00	39.325	105.441	79.930	28.063	−73.927	−15.210	3.02186
1200.00	40.487	108.914	82.202	32.055	−73.865	− 9.845	1.79295
1300.00	41.482	112.195	84.384	36.155	−73.763	− 4.519	0.75977
1400.00	42.337	115.302	86.483	40.347	−73.628	0.837	−0.13065
1500.00	43.076	118.248	88.503	44.618	−73.465	6.136	−0.89403

TABLE 5

IDEAL GAS THERMODYNAMIC PROPERTIES OF γ-BUTYROLACTONE

Temp. (*K*)	C_p° (*cal deg*$^{-1}$ *mol*$^{-1}$)	S° (*cal deg*$^{-1}$ *mol*$^{-1}$)	$-(G^\circ - H_0^\circ)/T$ (*cal deg*$^{-1}$ *mol*$^{-1}$)	$H^\circ - H_0^\circ$ (*kcal mol*$^{-1}$)
100.00	10.387	57.757	48.952	0.881
150.00	12.186	62.295	52.674	1.443
200.00	14.537	66.108	55.565	2.109
273.15	18.928	71.265	59.084	3.327
298.15	20.578	72.993	60.178	3.821
300.00	20.702	73.121	60.257	3.859
400.00	27.305	79.989	64.333	6.263
500.00	33.166	86.730	68.142	9.294
600.00	38.045	93.223	71.785	12.863
700.00	42.067	99.399	75.293	16.875
800.00	45.407	105.241	78.674	21.253
900.00	48.204	110.756	81.936	25.938
1000.00	50.561	115.960	85.080	30.880
1100.00	52.559	120.875	88.113	36.038
1200.00	54.260	125.523	91.039	41.382
1300.00	55.713	129.925	93.862	46.882
1400.00	56.961	134.101	96.589	52.517
1500.00	58.036	138.068	99.223	58.268

TABLE 6

IDEAL GAS THERMODYNAMIC PROPERTIES OF γ-BUTYROLACTAM

Temp. (*K*)	C_p° (*cal deg*$^{-1}$ *mol*$^{-1}$)	S° (*cal deg*$^{-1}$ *mol*$^{-1}$)	$-(G^\circ - H_0^\circ)/T$ (*cal deg*$^{-1}$ *mol*$^{-1}$)	$H_T^\circ - H_0^\circ$ (*kcal mol*$^{-1}$)
100.00	9.455	57.161	48.830	0.833
150.00	11.543	61.368	52.332	1.355
200.00	14.291	65.049	55.056	1.999
273.15	19.256	70.215	58.426	3.220
298.15	21.093	71.981	59.488	3.725
300.00	21.231	72.112	59.566	3.764
400.00	28.521	79.229	63.591	6.255
500.00	34.962	86.305	67.428	9.439
600.00	40.315	93.168	71.150	13.211
700.00	44.729	99.725	74.768	17.470
800.00	48.400	105.945	78.280	22.132
900.00	51.484	111.829	81.684	27.139
1000.00	54.096	117.392	84.979	32.413
1100.00	56.320	122.655	88.167	37.937
1200.00	58.223	127.639	91.250	43.666
1300.00	59.857	132.366	94.233	49.572
1400.00	61.265	136.854	97.118	55.630
1500.00	62.484	141.124	99.911	61.819

and the literature enthalpy of formation[18,19], ΔH_f° (gas) at 298.15 K of -67.60 ± 0.21 kcal mol^{-1}. No gaseous enthalpies of formation are available for the other two compounds. The calculated thermodynamic properties are reported in Tables 4–6.

ACKNOWLEDGEMENTS

The authors thank the IIT/K Computer Center for providing the computer facilities and the National Standard Reference Data Program of the U.S. National Bureau of Standards for financial support.

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