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THERMODYNAMIC PROPERTIES OF OXYGEN COMPOUNDS

I. VINYL ACETATE

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ABSTRACT

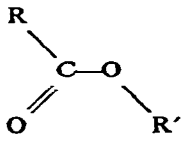
A complete vibrational assignment is made and ideal gas thermodynamic properties of vinyl acetate have been reported from 100–1500 K. Internal rotational contributions have been calculated using Pitzer and Gwinn's tables.

INTRODUCTION

In the course of our process engineering studies of vinyl acetate from acetylene and acetic acid, we found that no ideal gas thermodynamic properties for vinyl acetate have been published so far. Therefore, we decided to collect the literature information on molecular parameters and fundamental frequencies so as to enable us to calculate the ideal gas thermal functions for this molecule.

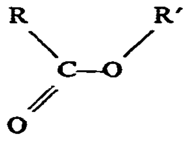
MOLECULAR STRUCTURE

Two planar conformations are possible for vinyl acetate:



Cis

and



Trans

where R and R′ are methyl and vinyl groups, respectively. As no microwave studies have been carried out for vinyl acetate, the molecular conformation is not known. However, from infrared studies[1,2] it is found that no rotational isomers are present. Rao and Curl[3] have established *cis* conformation for vinyl formate from their microwave spectral studies. Crowder[4] interpreted the infrared and Raman data for vinyl trifluoroacetate in terms of one conformer of C_s symmetry. The review article by Jones and Owen[5] makes it very clear that vinyl acetate exists as *cis* conformer with C_s symmetry as shown in Fig. 1. Here the carbon oxygen skeleton has a planar structure and one hydrogen of the methyl group is in plane while the other two are symmetrically arranged with respect to it. The values of the structural parameters adopted in this work are given in Fig. 1. These are taken from the parameters of similar molecules, namely vinyl formate[1], divinyl ether[6], methyl acetate[6,7] and acetic acid[8].

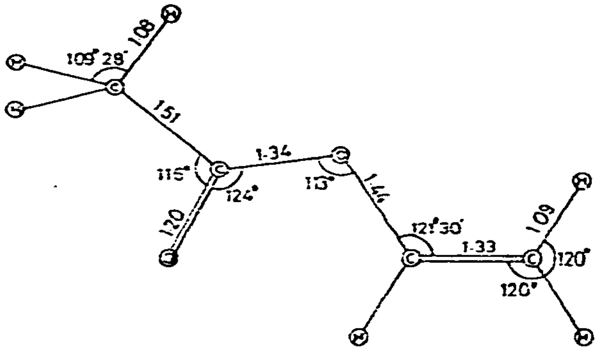


Fig. 1. Molecular structure of vinyl acetate.

VIBRATIONAL ASSIGNMENTS

Kotorlenko et al.[2] reported assignments for this molecule only from infrared measurements. Feairheller and Katon[1] thoroughly studied the infrared and Raman spectra and reported 19 in-plane and 9 out-of-plane fundamental frequencies. The missing in-plane frequency is $\delta_{C=C-O}$ and the one out of plane is the torsional frequency due to methyl group.

McManis[9] studied the infrared spectra of series of vinyl esters and assigned 464 cm^{-1} to the $\delta_{C=C-O}$ mode. Crowder[4] reported a similar value (465 cm^{-1}) for this mode in the case of vinyl trifluoroacetate. Assignments of the three lowest in-plane frequencies of similar molecules are given in Table 1. We felt that we should reassign the two lowest in-plane frequencies reported by Feairheller and Katon[1]. We have assigned 462 cm^{-1} to the $\delta_{C=C-O}$ mode and 406 cm^{-1} to the $\delta_{C-C=O}$ mode. This means that δ_{C-O-C} has not been observed by Feairheller and Katon. The missing δ_{C-O-C}

TABLE I

COMPARISON OF SOME IN-PLANE FREQUENCIES

Mode	*Methyl acetate*[11]	*Vinyl trifluoroacetate*[4]	*Vinyl acetate*	
			Ref. 1	*This work*
$\delta_{C=C-O}$	—	464	—	462
$\delta_{C-C=O}$	429	356[a]	462	406
δ_{C-O-C}	303	295	406	299

[a] Low value because of mass effect of CF_3 group.

frequency is found to be 306–323 cm^{-1} in aliphatic esters[10], 303 cm^{-1} in methyl acetate[11] and 295 cm^{-1} in vinyl trifluoroacetate[4]. We have adopted the average value 299 cm^{-1} in our calculations.

The out-of-plane missing torsional frequency adopted in this work is 100 cm^{-1} which is transferred from methyl acetate[12]. In acetic acid this value is reported to be 93 cm^{-1} by Haurie and Novak[13] and 101 cm^{-1} by Fukushima and Zwolinski[14]. The fundamental frequencies adopted in this work are given in Table 2.

TABLE 2

ADOPTED FUNDAMENTAL FREQUENCIES OF VINYL ACETATE (cm^{-1})

In-plane frequencies (a')					
1	3120	$\nu_a(CH_2)$	11	1353	$\delta(CH)$
2	3090	$\nu(CH)$	12	1291	$\nu(C–C)$
3	3040	$\nu_s(CH_2)$	13	1217	$\nu_a(COC)$
4	2996	$\nu_a(CH_3)$	14	1018	$\delta(CH_2)$ rock
5	2940	$\nu_s(CH_3)$	15	972	$\delta(CH_3)$ rock
6	1760	$\nu(C=O)$	16	847	$\nu_s(COC)$
7	1644	$\nu(C=C)$	17	637	$\delta(CO_2)$
8	1428	$\delta(CH_2)$	18	462	$\delta(C=C–O)$
9	1382	$\delta_a(CH_3)$	19	406	$\delta(C–C=O)$
10	1370	$\delta_s(CH_3)$	20	299	$\delta(C–O–C)$
Out-of-plane frequencies (a'')					
21	3020	$\nu_a(CH_3)$	26	712	$\gamma(CH_2)$ twist
22	1428	$\delta_a(CH_3)$	27	583	$\gamma(CH_3CO_2)$
23	1134	$\delta(CH_3)$ rock	28	238	Skeletal def.
24	948	$\gamma(CH_2)$ wag	29	160	Skeletal def.
25	874	$\gamma(CH)$	30	100	Torsion (C–CH$_3$)

THERMODYNAMIC FUNCTIONS

The ideal gas thermal functions C_p°, $(H^\circ - H_0^\circ)/T$, S°, $-(G^\circ - H_0^\circ)/T$ have been calculated using the moments of inertia obtained from the molecular parameters given in Fig. 1 and the vibrational frequencies given in Table 2. The internal rotational contributions of the methyl group to the thermodynamic functions have been obtained using Pitzer and Gwinn's tables[15]. For this purpose the potential barrier height[16] was obtained from eqn (1)

$$V^\circ = \frac{v_{\mathrm{tors}}^2}{F} + \frac{v_{\mathrm{tors}}}{2} + \frac{9F}{4} \tag{1}$$

where $F = h/8\pi^2 c I_r$

h = Planck's constant

c = velocity of light

I_r = reduced moment of inertia

TABLE 3

IDEAL GAS THERMODYNAMIC PROPERTIES OF VINYL ACETATE[a]

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	12.641	59.632	50.936	0.979	−72.903	−66.429	145.17950
200.00	17.912	70.176	57.643	2.507	−74.191	−61.279	66.96290
273.15	22.168	76.377	61.844	3.970	−75.154	−56.411	45.13482
298.15	23.662	78.386	63.146	4.544	−75.460	−54.672	40.07530
300.00	23.773	78.533	63.241	4.588	−75.482	−54.540	39.73194
400.00	29.567	86.181	68.034	7.258	−76.503	−47.383	25.88859
500.00	34.648	93.340	72.388	10.476	−77.479	−39.980	17.47523
600.00	38.900	100.044	76.441	14.161	−78.157	−32.411	11.80567
700.00	42.441	106.314	80.264	18.235	−78.663	−24.740	7.72403
800.00	45.418	112.182	83.889	22.633	−79.018	−17.007	4.64606
900.00	47.946	117.681	87.340	27.306	−79.241	−9.241	2.24396
1000.00	50.104	122.847	90.634	32.211	−79.337	−1.436	0.31374
1100.00	51.955	127.711	93.786	37.316	−79.334	6.303	−1.25223
1200.00	53.547	132.302	96.807	42.592	−79.261	14.123	−2.57219
1300.00	54.919	136.643	99.707	48.016	−79.131	21.891	−3.68020
1400.00	56.107	140.758	102.495	53.567	−78.952	29.701	−4.63647
1500.00	57.138	144.665	105.178	59.230	−78.733	37.434	−5.45408

[a] $I_a = 47.230$ amu Å^2; $I_b = 235.820$ amu Å^2; $I_c = 279.921$ amu Å^2; $I_r = 2.294$ amu Å^2; $V_0 = 622.8$ cal mol^{-1}.

As there is some uncertainty in the torsional frequency the internal rotational contributions were calculated by varying the torsional frequency by ±10 cm^{-1}. The calculated potential barrier heights are 526, 623 and 728 cal mol^{-1} corresponding to the torsional frequencies 90, 100 and 110 cm^{-1}, respectively. The maximum deviations due to the uncertainty in torsional frequency are at lower temperatures and they are ±0.08, ±0.04, ±0.05 and ±0.09 cal deg^{-1} mol^{-1} for C_p°, $(H^\circ - H_0^\circ)/T$, S° and $-(G^\circ - H_0^\circ)/T$, respectively. This shows that the errors in the thermal functions are very low owing to the uncertainty in the torsional frequency. The enthalpy of formation, Gibbs energy of formation and logarithm of equilibrium constant of formation as a function of temperature were calculated by the usual procedure. The enthalpy of formation[17] at 298.15 K was taken as -75.46 ± 0.18 kcal mol^{-1}. The values of thermal functions of C[18,19], H_2[20], and O_2[21] in their reference states are used. The calculated thermodynamic properties are given in Table 3.

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