

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Thermodynamics and Vibrational Spectrum of Acetaldehyde

BY KENNETH S. PITZER AND WILLIAM WELTNER, JR.

In the preceding paper DeVries and Coleman¹ present data for the heat capacity of acetaldehyde in the gas state which are in marked disagreement with the values calculated by Smith.² The calculations of Smith are based on a vibrational assignment by Morris³ who measured the infrared spectra of both acetaldehyde and acetaldehyde-*d*₄. The Raman spectra of both had been observed previously and are cited and discussed by Morris.

At the suggestion of Professor DeVries, we have attempted to resolve the disagreement by reassigning the vibration frequencies of acetaldehyde in such a manner as to give agreement with the heat capacity of the gas in addition to the experimental spectra. In addition, we have considered the heat and equilibrium constant data for the reaction with hydrogen to give ethyl alcohol. All these data suffice to give a reasonably definite, though not too precise, picture of the thermodynamic properties of acetaldehyde. A value is obtained for the potential barrier to internal rotation.

Vibration Spectrum.—The spectral data employed are those measured or cited by Morris. Thompson and Harris⁴ had previously studied acetaldehyde in detail and had offered a vibrational assignment. Their assignment gives better but still unsatisfactory agreement with the calorimetric heat capacities. Furthermore, Morris failed to find the band at 625 cm.⁻¹ taken as a fundamental by Thompson and Harris. Thus revision at this point would be necessary.

Table I gives the previous vibrational assignments together with the one which we are proposing. The corresponding frequencies from propylene⁵ are also listed.

TABLE I
VIBRATION FREQUENCIES OF ACETALDEHYDE

Sym.	Motion	Morris	T. and P. and H.	W.	Propylene
	C-O-O bending	426	525	525	417
	CH ₃ rocking	890	883	918	1042
	C-C stretching	917	918	1114	920
	C-H wagging	1121	1114	1350	1297
A'	CH ₃ <i>sym.</i> bending	1370	1355	1370	1370
	CH ₃ <i>unsym.</i> bending	1414	1405	1414	1444
	C=O stretching	1740	1720	1740	..
	CH ₃ <i>sym.</i> stretching	2710	2732	2710	..
	CH ₃ <i>unsym.</i> stretching	2915	2844	2915	..
	CH stretching	2788	3004	3004	..
	C-H rocking	515	625	764	(580, 990)
A"	CH ₃ rocking	760	764	883	1050
	CH ₃ <i>unsym.</i> bending	1445	1440	1440	1444
	CH ₃ <i>unsym.</i> stretching	2964	2976	2976	..

(1) Coleman and DeVries, *THIS JOURNAL*, **71**, 2839 (1949).

(2) J. M. Smith, *Trans. Am. Inst. Chem. Engrs.*, **42**, 983 (1946).

(3) J. C. Morris, *J. Chem. Phys.*, **11**, 230 (1943).

(4) H. W. Thompson and G. P. Harris, *Trans. Faraday Soc.*, **38**, 37 (1942).

(5) J. E. Kilpatrick and K. S. Pitzer, *J. Research, Natl. Bur. Sids.*, **38**, 191 (1947), R.P. 1768.

The changes which we have made are not very numerous. The reason for discarding the 625 cm.⁻¹ band of Thompson and Harris has been mentioned. The 426 cm.⁻¹ band of Morris was discarded because its experimental behavior was peculiar⁶ and because some shift to higher frequencies is necessary to fit the heat capacity.

Various intermediate frequencies are then assigned the next higher experimental value. The discarded low frequency is replaced by the band at 1350 cm.⁻¹ for the C-H wagging motion. This value is higher than that expected from propylene but is much closer than the 1120 value previously assigned to this motion. The C-C stretching frequency, 1114 cm.⁻¹, higher than that in propylene (920 cm.⁻¹), is consistent with the shorter C-C distance, 1.50 Å., in acetaldehyde as compared with 1.53 Å. in propylene.

In Table II our revised assignment for acetaldehyde-*d*₄ is given and compared with that for light acetaldehyde. Also given are the Teller-Redlich product rule comparisons. For the moments of inertia, the bond distances⁷ were taken as C-H, 1.09 Å.; C-C, 1.50 Å.; C=O, 1.22 Å.; angles at CH₃ tetrahedral and at CHO, 120°. The internal rotation comes in the A" class. On the assumption of equal potential barriers for the light and heavy molecule and of negligible interaction of torsional oscillation with other vibrations, it is possible to insert the ratio of the reduced moments of inertia for internal rotation along with those

TABLE II
VIBRATION FREQUENCIES OF ACETALDEHYDE-*d*₄

Sym.	Motion	Acetaldehyde- <i>d</i> ₄	Acetaldehyde	Product rule ratios
	C-C-O bending	419	525	
	CH ₃ rocking	763	918	
	C-C stretching	944	1114	
	C-H wagging	1036	1350	
	CH ₃ <i>sym.</i> bending	1048	1370	Theory 0.106
A'	CH ₃ <i>unsym.</i> bending	1130	1414	Obs. 0.111
	C=O stretching	1730	1740	
	CH ₃ <i>sym.</i> stretching	2033	2710	
	CH ₃ <i>unsym.</i> stretching	2128	2915	
	C-H stretching	2235	3004	
	C-H rocking	570	764	
A"	CH ₃ rocking	730	883	Theory 0.335
	CH ₃ <i>unsym.</i> bending	1155	1440	Obs. 0.348
	CH ₃ <i>unsym.</i> stretching	2089	2976	

(6) One of the referees of this paper is a member of the staff of Shell Development Co. Consequently, the absorption in this region (410-800 cm.⁻¹) was quickly checked by their Spectroscopic Department and they report that while 500 mm. Hg acetaldehyde in a 15-cm. cell is totally absorbing at 515 cm.⁻¹, no absorption was detected at 426 cm.⁻¹.

(7) D. P. Stevenson, H. D. Burnham and V. Schomaker, *THIS JOURNAL*, **61**, 2922 (1939).

for over-all rotation. One obtains then, the theoretical ratio for the ordinary vibration frequencies, excluding internal rotation.

It is apparent that our assignment checks the product rule satisfactorily. Furthermore, the small deviations of observed from calculated ratios are in the direction to be expected from the neglect of anharmonicities. Apparently Morris failed to employ the product rule since he makes no mention of it and his assignment does not yield the theoretical ratios.

Our assignment appears to fit the observed spectra and the guiding data from propylene and the product rule at least as well as other assignments in addition to giving agreement with thermal data.

Thermodynamic Data.—Using the molecular data given above, thermodynamic properties were calculated for comparison with the heat capacity of the gas and the equilibrium with hydrogen and ethyl alcohol. In treating the latter, the heat of hydrogenation of acetaldehyde to ethanol was taken as $\Delta H = -16.750$ kcal./mole at 355°K . as given by Dolliver, Gresham, Kistiakowsky, Smith and Vaughan⁸ and the free energy function of hydrogen⁹ and of ethanol¹⁰ from the literature. The barrier to internal rotation is also needed to complete these calculations.¹¹ Various values from 0 to 3000 cal./mole were tried and 1000 cal./mole was selected as the best compromise which gives agreement within experimental error at all points. While this value of 1000 cal./mole is rather lower than expected, it is still of a reasonable magnitude.

Figure 1 compares the experimental gas heat capacity values which are for the real gas at one atm. with the calculated values for the ideal gas. An approximate correction for gas imperfection was obtained from the second virial coefficient, B , measured by Alexander and Lambert.¹² The theoretical treatment which they presented was fitted to experimental data only over the short range 15 to 40° . We have preferred to fit an empirical equation (of form suggested by their association equilibrium) to their data over the full temperature range 15 to 300° . We obtained for the second virial coefficient, $B = 100 - 49.1 \exp(1942/RT)$ cc./mole, where the covolume term was estimated to be approximately 100 cc. from the liquid volume. Since $(\partial C_p/\partial P)_T = -T(\partial^2 B/\partial T^2)$, considerable uncertainty is involved in the correction to be applied to the C_p values. The arrows in Fig. 1 indicate the change

(8) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, *THIS JOURNAL*, **60**, 440 (1938).

(9) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Stds.*, **34**, 143 (1945), R. P. 1634.

(10) J. G. Aston, *Ind. Eng. Chem.*, **34**, 514 (1942).

(11) See K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942), for calculation of contribution of internal rotation to thermodynamic functions.

(12) E. A. Alexander and J. D. Lambert, *Trans. Faraday Soc.*, **37**, 421 (1941).

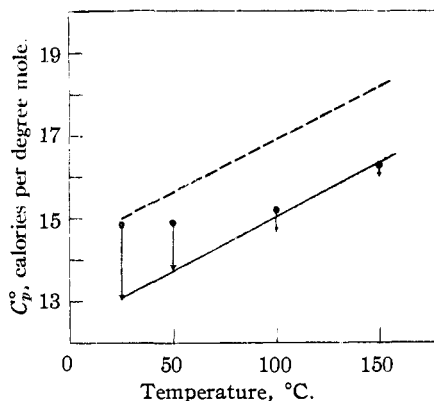


Fig. 1.—The heat capacity of acetaldehyde: ●, experimental points for the real gas at 1 atm. pressure; ---, calculation of Smith for ideal gas; —, calculation of this paper for ideal gas. Arrows indicate approximate corrections for gas imperfection obtained from the second virial coefficient.

in the C_p of the real gas when corrected by the above equation to the ideal gas state. The relatively exact agreement at 25 and 50° is fortuitous, but the result clearly indicates that the correction for gas imperfection is of this general magnitude.

Figure 2 shows the observed equilibrium constants of Rideal¹³ in relation to our calculated curve. Since Rideal followed the reaction only by the change of total pressure and there was evidence of some side reactions, his results are subject to considerable uncertainty. Thus the agreement may be considered satisfactory.

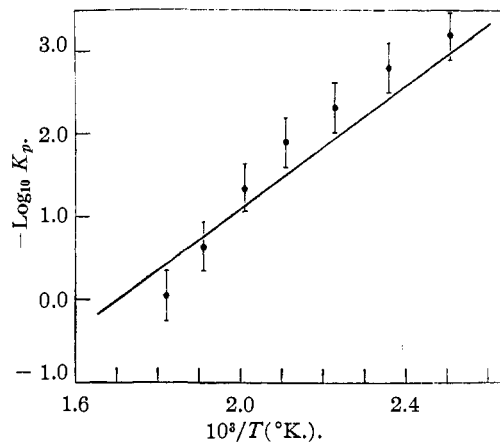


Fig. 2.—The $\log_{10} K_p$ versus $1/T$ plot for the equilibrium $\text{C}_2\text{H}_5\text{OH}(\text{g}) = \text{H}_2(\text{g}) + \text{CH}_3\text{CHO}(\text{g})$. Circles indicate experimental points, lines through circles indicate estimated error, solid line indicates the calculation of this paper.

Table III gives a summary of the thermodynamic properties of acetaldehyde. While they should not be regarded as highly accurate we believe they are reasonably reliable. The values for the heat and free energy of formation from the

(13) Rideal, *Proc. Roy. Soc. (London)*, **99A**, 153 (1921).

elements (ΔH_f° and ΔF_f°) were calculated from the heat of combustion of ethanol,¹⁴ the heat of formation of carbon dioxide⁹ and water,⁹ and the heat of hydrogenation of acetaldehyde,⁸ together

with the other data in Table III. The absolute uncertainty in the heat and free energy of formation values is about 0.2 kcal./mole. The second decimal place is retained because of the higher relative accuracy of values at different temperatures.

TABLE III

THERMODYNAMIC PROPERTIES OF ACETALDEHYDE

T (°K.)	C_p	S°	$-\frac{(F^\circ - H^\circ_0)}{T}$	$H^\circ - H^\circ_0$	$-\Delta H_f^\circ$	$-\Delta F_f^\circ$
0	0	0	0	0	37.15	37.15
298.16	13.06	63.15	52.85	3.070	39.67	31.77
400	15.73	67.37	56.03	4.535	40.48	28.95
500	18.27	71.14	58.67	6.24	41.18	25.97
600	20.52	74.68	61.05	8.18	41.77	22.87
700	22.50	78.00	63.24	10.34	42.25	19.69
800	24.20	81.12	65.28	12.68	42.64	16.44
900	25.68	84.06	67.20	15.17	42.95	13.14
1000	26.96	86.84	69.03	17.81	43.16	9.81

(14) F. D. Rossini, *J. Research, Natl. Bur. Stds.*, **13**, 189 (1934).

Summary

The assignments of vibrational frequencies for acetaldehyde and acetaldehyde- d_4 are revised so as to agree with the heat capacity of gaseous acetaldehyde in addition to the observed spectra and the product rule. A potential barrier to internal rotation of 1000 cal./mole is found to give best agreement with thermodynamic data which include the equilibrium with hydrogen and ethanol in addition to the heat capacity of gaseous acetaldehyde. A tabular summary of thermodynamic properties is given.

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Metal-Nicotine Double Sulfates

By CLAUDE R. SMITH

The inorganic double sulfates represented by the formula $R_2M(SO_4)_2 \cdot 6H_2O$, where R is an alkali metal, thallium or ammonium, and M is Cu, Mg, Zn, Fe, Co, Ni, Mn or Cd constitute an important isomorphous group of compounds. Although slight variations in crystal measurements and other physical properties occur, they appear to be largely determined by some property of the univalent R-metal or radical rather than the specific M-metal.

The metal-nicotine double sulfates described here contain the bivalent cations of the M-metals and also the trivalent cations of Fe, Cr and Al. No similar group of double sulfates containing nicotine or other organic base has been reported previously. This study forms part of an extensive investigation in this Laboratory on the coordination of nicotine in forming nicotineamine and double salt compounds.

Experimental

Compounds 1 to 7, inclusive, in Table I represent the addition of "neutral" nicotine sulfate ($2C_{10}H_{14}N_2 \cdot H_2SO_4$) to the metal sulfate. The nicotine sulfate was prepared by dissolving weighed amounts of base and acid in absolute ethanol, but adjustment was made until a drop of the solution, after dilution with water, gave an intermediate tint with methyl red indicator. Number 7, however, crystallized better if nicotine was used in sufficient excess to give a yellow tint with the indicator. "Acid" nicotine sulfate ($C_{10}H_{14}N_2 \cdot H_2SO_4$), prepared by dissolving weighed amounts of base and acid in absolute ethanol, reacted directly with the normal sulfates of nos. 8, 10 and 11, but a better procedure for no. 10 was to form the sulfato-

acid $Cr_2(SO_4)_3 \cdot 3H_2SO_4$ in ethanol-water and then add the nicotine in ethanol slowly with stirring. Number 9 also was better prepared through the sulfate-acid $Fe_2(SO_4)_3 \cdot H_2SO_4$ in ethanol-water by the addition of nicotine in ethanol.

Number 1 (representative of nos. 1 to 6, inclusive) was prepared as follows: 7.5 g. (0.03 mole) of cupric sulfate was dissolved in 20 ml. of water in a 250-ml. Erlenmeyer flask, and mixed with 100 ml. of absolute ethanol containing 0.04 mole of neutral nicotine sulfate (one-third excess). Absolute ethanol was then added in 10-ml. portions until complete precipitation of the double salt occurred. After standing for several hours (or overnight), the crystals were filtered off and washed with 95% ethanol. It was dried in air but bottled as soon as dry, for it lost hydrate water under low-humidity conditions.

For no. 7, 13.4 g. (0.06 mole) of manganous sulfate tetrahydrate was used with 0.04 mole of nicotine sulfate (prepared as indicated above).

Number 8 was prepared by dissolving 0.03 mole of magnesium sulfate heptahydrate in 12 ml. of water (with gentle warming), and adding 0.04 mole of acid nicotine sulfate in 100 ml. of absolute ethanol. Absolute ethanol was then added in 10-ml. portions until a suspension of the crystals was formed. After standing, the crystals were filtered off and washed with absolute ethanol. It was dried to constant weight in a desiccator with renewed amounts (a few grams) of calcium chloride. If properly prepared, it was not appreciably hygroscopic.

Number 9 was prepared from Monsel's salt, $Fe_4(SO_4)_3 \cdot (OH)_2 \cdot 10H_2O$, following the equation $Fe_4(SO_4)_3 \cdot (OH)_2 + 3H_2SO_4 + 4C_{10}H_{14}N_2 \rightarrow 2[Fe_2(SO_4)_3 \cdot 2C_{10}H_{14}N_2 \cdot H_2SO_4 \cdot 6H_2O] + xH_2O$, except that $4H_2SO_4 + 6C_{10}H_{14}N_2$ was used to provide an excess of neutral nicotine sulfate. Probably a better procedure is to dissolve 9.2 g. of Monsel's salt (mol. wt., 917.8) in a 100-ml. solution composed of 80 ml. of ethanol and 20 ml. of water containing sulfuric acid (0.04 mole) and then add 0.06 mole of nicotine in 100 ml. of ethanol. If required for a good crystal suspension, more ethanol is added.

It was dried in the same way as No. 8. It was kept in a closed container in a desiccator containing calcium chloride because it was deliquescent.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.