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THE INFRARED SPECTRA OF PROPIONALDEHYDE
AND PROPIONALDEHYDE- d_1 *

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January 18, 1962

ABSTRACT

The infrared spectra of C_2H_5CHO and C_2H_5CDO from 4000 to 450 cm^{-1} have been observed and a tentative assignment of the observed bands has been made.

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INTRODUCTION

A sample of C₂H₅CDO was prepared and the vapor phase infrared spectra of C₂H₅CHO and the C₂H₅CDO were observed to determine the specificity of the deuteration. The vapor phase spectra of these compounds were not found in a search of the literature. Only the liquid phase Raman [1] and infrared [2,3] spectra of C₂H₅CHO have been reported.

The present investigation covers the infrared region from 450 to 4000 cm⁻¹. A tentative assignment of the observed bands has been made on the basis of isotope shifts and assignments in similar molecules.

EXPERIMENTAL AND RESULTS

Technical grade propionaldehyde was fractionally distilled in nitrogen atmosphere and the center fraction was transferred to a vacuum line where it was dried over anhydrous copper sulfate and further purified by trap-to-trap distillations in vacuum.

[1] K. W. F. Kohlrausch and E. Koppl, Z. physik chem. B24, 370 (1934).

[2] American Petroleum Institute Project 44, Carnegie Institute of Technology. S. N. 1223.

[3] S. Pinchas, Anal. Chem. 27, 2 (1955).

The propionaldehyde- d_1 was synthesized using the reactions

where R is C_2H_5 and R' is C_5H_{11} . The deuterio acetic acid was prepared from 99.5 per cent D_2O and freshly distilled acetic anhydride.

The procedure for reaction (1) given by Hill et al [4] was followed. The propanol- d_3 from Reaction (1) was separated from the reaction products by distillation and converted to the aldehyde by Reaction (2) using the procedure given by Blatt [5]. The propionaldehyde- d_1 obtained from the reaction was purified by gas chromatography, transferred to a vacuum line, dried over anhydrous copper sulfate and stored at dry ice temperature.

A sample of normal propionaldehyde was prepared by the same procedures. The infrared spectrum of this sample was identical with that of the sample of purified commercial propionaldehyde.

The spectra were recorded with a Perkin-Elmer Model 21 Infrared Spectrometer provided with NaCl and CaF_2 optics and with a Perkin-Elmer Model 12C Spectrometer provided with KBr optics. The spectral range from 450 to 4000 cm^{-1} was covered with these two instruments. A 10 cm cell with KBr windows and an 11 cm cell with NaCl windows were employed. All spectra were of vapors at pressures between 10 and 235 mm Hg.

[4] D. G. Hill, W. A. Judge, P. S. Shell, S. W. Kanter and C. R. Hauser, J. Am. Chem. Soc. 74, 5599 (1952).

[5] A. H. Blatt, Organic Synthesis Vol. II (Wiley, New York, N. Y., 1943) p. 541.

Reproductions of the spectra are shown in Figs. 1 and 2. The conditions of observation are given in the figure captions. The frequencies and assignment of all the observed bands are given in Table 1.

DISCUSSION

Propionaldehyde and propionaldehyde- d_1 have, at most, C_s symmetry since the only element of symmetry possible is a single plane. The molecules have 15 a' and 9 a'' modes of motion and all the modes are infrared-active and Raman-active. An assignment of the fundamental modes for the two molecules is given in Table 2. The Raman frequencies in the table are from Kohlrausch and Koppl [1].

The C_2H_5 hydrogen stretch and hydrogen deformation motions were assigned with reference to the corresponding assignments by Nolin and Jones [6] for 3-pentanone. The CH_2 twist and rock motions were assigned in accordance with assignments in paraffins [7]. The assignment of the motions involving the $CCHO$ ($CCDO$) group followed directly from the observed frequency shifts on deuteration and from the corresponding assignments in the acetaldehydes [8].

The CH in-plane bend is set at 1395 cm^{-1} although a band was not observed in the infrared spectrum. The Raman frequency 1392 cm^{-1} can be assigned as this motion since this frequency is not found in the Raman spectrum of propionyl chloride [9]. No band was observed which could be assigned as the a'' CD wag, but the band should be found in the region 720 to 660 cm^{-1} . The band is expected to be very weak since, by analogy with the findings in the acetaldehydes [8], the band should

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- [6] B. Nolin and R. N. Jones, J. Am. Chem. Soc. 75, 5626 (1951).
[7] J. K. Brown, N. Sheppard and D. M. Simpson, Phil. Trans Roy Soc. (London) A247, 35 (1954).
[8] J. C. Evans and H. L. Bernstein, Can. J. Chem. 34, 1083 (1956).
[9] K. W. Fritz Kohlrausch, Ramanspektren (J. W. Edwards, Ann Arbor, Mich., 1945), p. 282-5.

Figure 1. Spectrum of propionaldehyde, $\text{CH}_3\text{CH}_2\text{CHO}$.

Optics (pressure in mm Hg): a, CaF_2 (10); b, CaF_2 (20);

c, NaCl (235); d, CaF_2 (40); e, NaCl (54); f, KBr (101).

Figure 2. Spectrum of propionaldehyde- d_1 , CH_3CH_2CDO .

Optics (pressure in mm Hg): a, CaF_2 (10); b, CaF_2 (22); c, $NaCl$ (235); d, CaF_2 (43); e, $NaCl$ (34); f, KBr (101).

Table 1. Infrared frequencies (in cm^{-1})
of the propionaldehydes

<u>CH₃CH₂CHO</u>			<u>CH₃CH₂CDO</u>		
<u>$\nu \text{ cm}^{-1}$</u>	<u>Intensity</u>	<u>Assignment</u>	<u>$\nu \text{ cm}^{-1}$</u>	<u>Intensity</u>	<u>Assignment</u>
3840	w	2721 + 1105; 2993 + 850	3820	wsh	2993 + 856
3612	vw	2721 + 895	3780	w	2066 + 1730
3490	m	2 x 1750	3453	m	2 x 1730
3220	vw	2720 + 507	3170	vw	1730 + 1465
3154	w	1750 + 1423	3040	vwsh	2066 + 2 x 507
2993	vs	ν_2 ; ν_{16}	2993	vs	ν_2 ; ν_{16}
2943 (?)	vw	$\nu_{17}(\text{?})$	2946(?)	vw	$\nu_{17}(\text{?})$
2919	vs	$\nu_{1,3}$	2917	vs	$\nu_{1,3}$
2813	vs	Fermi doublet of 1400 overtones and ν_4	2815	w	1400 overtones
2721	vs		2719	w	1350 overtones; Residual CH ₃ CH ₂ CHO
2504	vw	1423 + 1094	2539	vw	1465 + 1092
2402	w	1750 + 664	2427	vw	1334 + 1092
2331	vw	1468 + 848	2356	vw	1251 + 1099
2251	vw	1146 + 1105	2316	vw	1465 + 856
2181	w	2 x 1094	2195	w	2 x 1092
2101	vw	1465 + 664	2180	w	
2026	vw	1384 + 664	2066	vs	ν_4
1960	vw	1105 + 858	2050	vs	
1930	vw	1094 + 848	1887	w	1092 + 794; 1384 + 496
1850	vw	1340 + 507	1746	vs	ν_5
1763	vs	ν_5	1729		
1744			1478		
1480			1465	s	ν_9
1468	s	ν_9	1455		
1456			1430		
1434			1419	s	ν_{10}
1423	s	ν_{10}	1410		
1410			1383	m	ν_8
1384	m	ν_8			

Table 1. (continued)

<u>CH₃CH₂CHO</u>			<u>CH₃CH₂CDO</u>		
<u>ν cm⁻¹</u>	<u>Intensity</u>	<u>Assignment</u>	<u>ν cm⁻¹</u>	<u>Intensity</u>	<u>Assignment</u>
1349		ν_{12}	1344		ν_{12}
1340	m		1334	m	
1332			1324		
1261		ν_{19}	1257		ν_{19}
1254	w		1251	w	
1247			1241		
1146	m	ν_6	1194	w	$\nu_6(?)$ or combination
1129			1134	wsh	ν_6
			1119?	vwsh	
1105			1099		
1094	s	ν_7	1092	s	ν_{13}, ν_7 Overlapped
			1080		
1020			995		
1003	m	2 x 507	984	m	2 x 496
			978		
907		ν_{11}	863		ν_{11}
895	s		856	s	
883			849		
858		ν_{20}	804		ν_{20}
848	s		794	s	
836			783		
791	vw	ν_{22}			
768		ν_{21}	753		ν_{21}
760	vw		747	vw	
745			740		
672		ν_{14}	660		ν_{14}
664	s		653	s	
652			644		
519		ν_{15}	509		ν_{15}
507	s		496	s	

be weaker than the CH band in propionaldehyde which is a very weak band. The presence of a strong broad band at 653 cm^{-1} in propional- d_1 may make detection of the band difficult even with long path lengths. The Raman spectrum or the infrared spectrum of the solid may reveal the frequency of this mode.

The a' and a'' CH_3 rock motions were assigned to bands which behave in an analogous manner to bands observed in the corresponding acetaldehydes in this frequency region and assigned to these modes of motion. The frequency shifts observed upon deuteration are quite large for a group which is isolated from the site of deuteration, but the shifts undoubtedly result from interactions of the same nature as those proposed to explain the findings in the acetaldehydes [8].

Table 2. Assignments for
the propionaldehydes^a

Symmetry	Designation	Motion	<u>CH₃CH₂CHO</u>		<u>CH₃CH₂CDO</u>
			Infrared (cm ⁻¹)	Raman (cm ⁻¹)	Infrared (cm ⁻¹)
a'	ν_1	CH ₃ sym. str.	2919	2939) Fermi 2883) doublet	2919
	ν_2	CH ₃ asym. str.	2993	2978	2993
	ν_3	CH ₂ sym. str.	2919	2939	2919
	ν_4	CH str.	2813) 2721)	2823) Fermi 2724) doublet	2050
	ν_5	CO str.	1744	1722	1729
	ν_6	CC str.	1129	1089	1134
	ν_7	CC str.	1094		1080
	ν_8	CH ₃ sym. def.	1384		1383
	ν_9	CH ₃ asym. def.	1468	1454	1465
	ν_{10}	CH ₂ sym. def.	1423	1416	1419
	ν_{11}	CH ₃ rock	895	893	856
	ν_{12}	CH ₂ wag	1340	-	1334
	ν_{13}	CH wag	~1395	1392	1094
	ν_{14}	CCC def.	664	666	653
	ν_{15}	CCO def.	509	512	496
a''	ν_{16}	CH ₃ asym. str.	2993	2978	2993
	ν_{17}	CH ₂ asym. str.	2943	2939	2946
	ν_{18}	CH ₃ asym. def.	1468	1454	1465
	ν_{19}	CH ₂ twist	1254	1246	1251
	ν_{20}	CH ₃ rock	848	846	794
	ν_{21}	CH ₂ rock	760	-	747
	ν_{22}	CH wag	791	-	>660
	ν_{23}	CH ₃ torsion	-	-	-
	ν_{24}	CHO torsion	-	-	-

^aThe Raman frequencies used in this assignment are from Kohlrausch. [9]

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- [1] K. W. F. Kohlrausch and FKoppl, Z. physik chem. B24, 370 (1934).
- [2] American Petroleum Institute Project 44, Carnegie Institute of Technology. S. N. 1223.
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- [7] J. K. Brown, N. Sheppard and D. M. Simpson, Phil. Trans. Roy Soc. (London) A247, 35 (1954).
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