

THE MASS SPECTRUM OF CH₃CDO

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A mixture of deuterated acetaldehydes containing CH₃CDO in a high percentage was prepared and the mass spectrum of the sample was investigated. After correcting for the contributions of the various isotopic impurities, the spectrum of CH₃CDO was obtained, and on this basis important fragmentation processes are discussed.

Introduction

The use of isotopes may supply valuable information in the solution of various chemical problems. Methods like isotope labelling, the kinetic isotope method [1], the isotope dilution method, etc., prove to be especially useful in the elucidation of the mechanisms of complex chemical reactions and in the determination of important kinetic data.

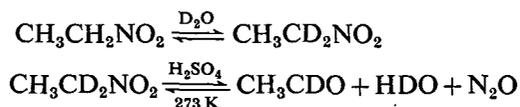
The investigation of the kinetics of the acetaldehyde pyrolysis [2] drew our attention to certain problems of the mechanism which could be studied by the deuterium labelling technique. These experiments required the preparation of CH₃CDO, determination of the isotopic composition of the labelled sample and detailed knowledge of the mass spectrum of CH₃CDO.

The mass spectrum of CH₃CDO had been studied previously [3] using a sample which consisted of various deuterated and undeuterated aldehyde species. The reinvestigation of the spectrum with aldehyde of better isotopic purity seemed to be desirable in order to minimize the corrections permitting to take into account the contributions from aldehyde species of different deuterium content.

In this paper the mass spectrometric study of a mixture of deuterated acetaldehydes containing CH₃CDO in a high percentage is described, and the spectrum of CH₃CDO obtained from the analysis of the experimental data is given.

Experimental

The labelled acetaldehyde sample was prepared by the method of LEITCH [4], *i.e.*



Some modification of the original procedure was found to improve the isotopic purity of the CH_3CDO prepared. This is described below.

The nitroethane (FLUKA, $\cong 95\%$) was distilled prior to use. The main fraction (b.p. 385.5—386.5 °K) was only used. Equal amounts of $\text{CH}_3\text{CH}_2\text{NO}_2$ and D_2O (FLUKA, p.a., $\cong 99.8\%$) with some sodium acetate added were placed in a three-necked flask equipped with a stirrer and a reflux condenser. The system was carefully protected from moisture. H—D exchange was carried out at 363 °K under vigorous stirring. The extent of the exchange was checked from time to time by mass spectrometric analysis. The heavy water sample was replaced by a fresh one when the process seemed to approach equilibrium. This was done three times during the procedure which lasted altogether about 250 hours. Thereafter the organic phase was dried over sodium sulfate and distilled. The labelled aldehyde was obtained from $\text{CH}_3\text{CD}_2\text{NO}_2$ in the same way as described in LEITCH's paper. After drying over sodium sulfate, the sample was purified by bulb-to-bulb vacuum distillation. No chemical impurities could be detected by gas chromatography.

Acetaldehyde (FLUKA, p.a., $\cong 99.8\%$) was purified by bulb-to-bulb distillation.

Mass spectra were obtained on a FINNIGAN 1015 S/L quadrupole instrument. All spectra were taken at an ionizing voltage of 70 eV, the electron current was 250 μA . The instrument was equipped with an electron multiplier detector. Spectra were recorded in the mass range of 1—55 by a three-channel light beam oscillograph (relative sensitivities being 1:10:100), with a scanning-time of 10 s per mass range.

The spectra of labelled and normal acetaldehyde were taken shortly one after the other in order to obtain well comparable results.

Results and discussion

Corrections and pressure dependence. The recorded spectra were corrected for (i) the background, (ii) the natural abundances of isotopes, and (iii) for the pressure-dependent character of certain ions.

The background was negligible, except for measurements made at low aldehyde pressures in the ion-source. In these cases the spectra had to be corrected for the presence of traces of air and water. All spectra were corrected for the natural abundances of ^{13}C and ^{18}O .

The results given below were obtained under conditions where the pressure in the ion-source was fixed at a value of $6 \cdot 10^{-6}$ torr. In a few measurements, however, the pressure was varied between $7 \cdot 10^{-7}$ and $1 \cdot 10^{-5}$ torr. It was found that the relative intensities (compared to the intensity of the parent ion) of ions at m/e 48 and 47 in the spectra of the labelled aldehyde sample and those at m/e 45 in the spectra of normal acetaldehyde increased with increasing pressure. It is to be noted that the parent or molecular ions (designated as p^+) of acetaldehyde- d_2 , acetaldehyde- d_1 and acetaldehyde- d_0 give peaks at m/e 46, 45, and 44, respectively, while the pressure-dependent ions were observed at masses $(p+D)^+$ and $(p+H)^+$ in the spectra of the labelled and the normal aldehyde, resp., *i.e.* at m/e 48, 47, and 45. Therefore it was concluded that the ions showing pressure-dependence are formed in ion-molecule reactions. The intensities measured for these ions at $6 \cdot 10^{-6}$ torr were corrected by multiplying with the ratio (I_{p+D}/I_p) and (I_{p+H}/I_p) , respectively, obtained at the lowest pressures studied.

Isotopic composition of the labelled acetaldehyde sample. Determination of the isotopic composition of the labelled acetaldehyde sample was based on the assumption that the specific intensity (the intensity observed at a fixed pressure in the ion-source) of the molecular ion is the same for CH₃CHO and different deuterated acetaldehyde species. This assumption was shown by BRINTON and BLACET [3] to be applicable in case of various acetaldehyde species.

In the spectrum of the labelled acetaldehyde sample, contributions to ion intensities at *m/e* 48 to 44 are expected from the parent ions of normal and deuterated acetaldehyde species as well as from fragment ions of the deuterated aldehydes. In order to obtain the relative abundance of the various acetaldehyde species, the measured intensities have to be corrected by subtracting the contributions of the fragment ions. However, the spectra of the deuterated aldehydes are not readily available, therefore assumed relative abundances for compounds of higher deuterium content were used (Table I). While this approximation is accurate enough for acetaldehyde-*d*₂, acetaldehyde-*d*₃ and acetaldehyde-*d*₄ present in small quantities in the labelled sample, a different treatment is required for acetaldehyde-*d*₁ which is the major component (see below).

In the second column of Table II intensities of ions measured at *m/e* 48 to 44 of the labelled acetaldehyde spectrum are given. After correction for fragment ion contributions originating from the acetaldehyde-*d*₂, acetaldehyde-*d*₃ and acetaldehyde-*d*₄ present in the sample, the data given in column 3 are obtained. The figure given for *m/e* 44 still contains the contribution of the fragment peak of acetaldehyde-*d*₁, which can be calculated on the basis of the assumption that the specific intensities of the parent ions of the various acetaldehyde species are the same.

The sum of the peak heights¹ given in column 3 is 272.2 which compared with the peak height of 256 measured at mass 44 in the spectrum of CH₃CHO yields 16.2 for the required fragment ion intensity of acetaldehyde-*d*₁. Hence, the parent ion intensities (peak heights) given in the last column of Table II are derived.

Table I

*Assumed^a relative intensities for acetaldehyde-*d*₂, acetaldehyde-*d*₃ and acetaldehyde-*d*₄ in the *m/e* range 48—44*

<i>m/e</i>	aldehyde- <i>d</i> ₂	aldehyde- <i>d</i> ₃	aldehyde- <i>d</i> ₄
48			1000
47		1000	—
46	1000	34	400
45	68	400	—
44	400	36	100

^a Obtained by extrapolation from known spectra of CH₃CHO and the labelled aldehyde sample

Table II

Peak heights at masses 48—44 in the spectrum of the labelled acetaldehyde sample

<i>m/e</i>	Corrected for background and natural abundances of ¹³ C and ¹⁸ O	Corrected for fragments of aldehyde- <i>d</i> ₂ , - <i>d</i> ₃ and - <i>d</i> ₄	Peak heights of parent ions
48	~0.1	~0.1	~0.1
47	0.7	0.7	0.7
46	4.1	4.0	4.0
45	245	244	244
44	25	23.4	7.2

¹ Peak heights were obtained from spectra taken at identical ion-source pressures of 6 · 10⁻⁶ torr.

It has been shown by BRINTON and BLACET [3] that the parent peak intensities can be used as a measure of the relative abundance of the various acetaldehyde species present in the sample. With this postulate on the basis of results given in the last column of Table II the isotopic composition of the labelled aldehyde sample was obtained:

2.8% acetaldehyde- d_0	0.3% acetaldehyde- d_3
95.3% acetaldehyde- d_1	<0.1% acetaldehyde- d_4
1.6% acetaldehyde- d_2	

Regarding the position of the deuterium atom (or atoms) in the aldehyde molecule, a comparison of the heavy and light formyl ion intensities may supply information. At the electron bombardment of the labelled aldehyde sample, ions at m/e 30 are formed from formyl deuterated species by simple fission of the C—C bond. However, the situation is more involved regarding the formation of ions at mass 29. The presence of a peak at m/e 29 in the spectrum of CH_3CDO (see below) indicates that H—D exchange occurs before or simultaneously with fragmentation. Thus, ions of mass 29 are formed in case of the labelled aldehyde sample in two ways: by simple C—C splitting from aldehydes containing a CHO group, and by a process involving H—D exchange from aldehydes having a CDO functional group.

The ratio of the number of molecules with CHO and CDO groups can be estimated from the intensities (I) measured at m/e 29 and 30: (number of CHO groups)/(number of CDO groups) = $(I_{29} - 0.072I_{30})/I_{30}$, where 0.072 is the intensity ratio at m/e 29 and 30 in the spectrum of pure CH_3CDO .

Using intensities obtained at m/e 29 and 30 with the labelled aldehyde sample, the value 0.027 for the ratio (number of CHO groups)/(number of CDO groups) can be calculated, which means that 2.6 per cent of the molecules contain undeuterated formyl groups. This value is equal, within the limits of experimental error, with the value found for the CH_3CHO content of the sample studied. Hence we conclude that the formyl group in heavy aldehyde molecules is virtually fully deuterated. Thus the composition of the labelled aldehyde sample may be given as

2.8% CH_3CHO	1.6% CH_2DCDO	<0.1% CD_3CDO
95.3% CH_3CDO	0.3% CHD_2CDO	

Mass spectrum of CH_3CDO . The spectra of the labelled acetaldehyde sample and of CH_3CHO are shown in columns 3 and 2, resp., of Table III. The peak heights given are corrected for the background and for the natural abundances of ^{13}C and ^{18}O isotopes.

In order to derive the spectrum of CH_3CDO from that of the labelled aldehyde sample, the contributions from isotopic species other than CH_3CDO have to be subtracted. Since the amount of CD_3CDO and CHD_2CDO was found to be small, only the contributions of their parent ions (at mass 48 and 47) were taken into account. Correction for the presence of 1.6% CH_2DCDO was made on the basis of an assumed spectrum (relative intensities): 1000(m/e 46), 400(m/e 44), 1350(m/e 30), 300(m/e 17), and 400(m/e 16). Contributions from the 2.8 per cent of CH_3CHO were calculated by means of the measured spectrum of acetaldehyde. In this way the spectrum for pure CH_3CDO , given in columns 4 and 5 was obtained. For comparison, the last column of Table III contains the spectrum of CH_3CHO .

Table III
The mass spectrum of CH₃CDO

m/e	CH ₃ CHO (peak heights)	Labelled sample (peak heights)	CH ₃ CDO (peak heights) ^a	CH ₃ CDO (relative intensities)	CH ₃ CHO (relative intensities)
48		~0.1			
47		0.7			
46		4.1			
45		245	244	1000	
44	256	25	16	66	1000
43	138	99	95	389	539
42	34	27	26	107	133
41	14	10	9	37	55
30		333	328	1343	
29	330	33	24	97	1289
28	11	21	21	86	43
27	14	21	21	86	55
26	26	13	12	49	102
25	11	6	6	25	43
17	2	18	17	70	8
16	22	69	67	275	86
15	171	101	96	393	668
14	59	27	25	103	230
13	20	12	11	45	78
12	8	7	7	29	31

^a For derivation see text.

A detailed study of the spectrum of CH₃CDO has been published by BRINTON and BLACET [3]. The spectra obtained by these authors and in the present work agree in the main features but some differences are to be pointed out. There are differences in two mass ranges of the spectra; these are the m/e range 30—27 and 17—13. In both ranges we find lower intensities relative to the parent ion intensity. Similar differences occur at m/e 29—28 and 16—13 in the spectrum of CH₃CHO reported by BRINTON and BLACET [3] and that obtained in the present work. It seems that the cause for this is related to the different experimental conditions rather than to the dissimilar isotopic purity of the samples investigated.

Fragmentation processes. The main fragmentation processes for both CH₃CDO and CH₃CHO are the formation of formyl-type ions by the simple split of the C—C bond of the molecules. However, these processes were found to be somewhat less important than suggested by BRINTON and BLACET [3]. The appearance of the CHO⁺ ion in the spectrum of CH₃CDO clearly indicates that H—D exchange occurs between the methyl and formyl groups before or simultaneously with fragmentation. The ratio of probability of the C—C fission accompanied by H—D exchange to that of simple C—C fission was found to be 0.072 in good agreement with the value of 0.079 derived from the spectrum of BRINTON and BLACET.

Another question of importance is the formation of methane and methyl ions from CH₃CDO. Assuming that the contribution of OH⁺ is the same in the case of CH₃CDO and CH₃CHO, a value of about 62 for the relative intensity of the CH₃D⁺ ion can be estimated. High intensity is found at mass 16 in the spectrum

of CH₃CDO, which is not fully explained by the formation of O⁺. Taking O⁺ < 86 (from the spectrum of CH₃CHO) is obtained CH₂D⁺ > 189, *i.e.* CH₂D⁺ ions are formed from CH₃CDO with considerable probability. The deuterated methyl ion may be formed provided H—D exchange occurs before or simultaneously with the split of the C—C bond. (Note that H—D exchange also accompanies the C—C split yielding a formyl-type ion). Ions of mass 15 might be CH₃⁺ and CHD⁺, the

relative probabilities of which are difficult to estimate. Thus we can give only the upper limit CH₃⁺ < 393. Hence, CH₂D⁺/CH₃⁺ > 0.5, *i.e.* a considerable portion of the methyl radicals are formed in a process involving H—D exchange between the methyl and formyl groups.

Table IV
Relative probabilities for parent-, formyl-, and methyl-type ion formation

	Parent ion	Formyl-type ion	Methyl-type ion
CH ₃ CHO	1000	1289	668
CH ₃ CDO	1000	1440	580

Finally, in Table IV the probabilities of formation of formyl-type (CHO⁺ and CDO⁺) and methyl type (CH₃⁺ and CH₂D⁺) ions are given relative to that of the corresponding parent ions. Formyl formation is more probable from CH₃CDO than from CH₃CHO, while for the methyl formation the opposite seems to be true.

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МАСС-СПЕКТРЫ CH₃CDO

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Синтезирована смесь дейтерированных ацетальдегидов с высоким содержанием CH₃CDO и проведено ее масс-спектрографическое изучение. С учетом необходимых поправок на вклады различных изотопных загрязнений, определен спектр чистого CH₃CDO и обсуждены наблюдавшиеся основные фрагментационные процессы.