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Mass Spectrometric Study of a Mixture of Deuterated Acetaldehydes

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An investigation of the composition of samples of deuterium containing acetaldehyde was made by mass spectrometric methods. The complete determination of the relative abundance of all possible heavy acetaldehyde species was accomplished by combining data from the direct mass spectrometric analysis with information on the relative amounts of heavy methyl iodides produced when the gaseous heavy acetaldehyde mixture was photolyzed with ultraviolet light in the presence of iodine vapor. The distribution of the various acetaldehydes in the mixture was about 80 percent CH_3CDO and 17 percent CH_2CDO with small amounts of acetaldehydes of higher deuterium content. The mass spectrum of the acetaldehyde mixture was corrected to give the spectrum of the single species, CH_3CDO . Inspection of the corrected spectrum indicated that on impact by 60 electron-volt electrons the split of the C—H bond of CH_3CHO is more probable than the corresponding split of C—D bond in CH_3CDO in agreement with the findings of Delfosse and Hipple who first reported this difference in the behavior of C—H and C—D bonds for *cis* and *trans* ethene-1,2 d_2 . The formation of formyl positive ion in the case of CH_3CDO is evidently by a clean split of the C—C bond with little exchange of hydrogen and deuterium between carbon atoms at the time of electron impact. The formation of methyl positive ion, on the other hand, is accompanied by a large interchange of hydrogen and deuterium between carbon atoms.

INTRODUCTION

THE mass spectrometric study of *cis* and *trans* ethene-1,2 d_2 by Delfosse and Hipple,¹ methane- d by Evans, Bauer, and Beach,² acetylene- d and acetylene- d_2 by Mohler and Dibeler,³ and ethane- d , propane-1 d , and propane-2 d by Turkevich, Friedman, Soloman, and Wrightson⁴ has clearly indicated that a splitting of the C—H bond is more probable than a corresponding C—D rupture on dissociation by electron impact. Additional data substantiating these studies have been obtained in this laboratory in the study of acetaldehyde- d (CH_3CDO) which was prepared⁵ for photochemical studies. The compound as prepared was unfortunately not a single isomer but contained normal acetaldehyde, acetaldehyde- d , and small amounts of acetaldehyde of higher deuterium content. The relative proportions of molecules in the heavy acetaldehyde mixture containing one, two, three and four deuterium atoms could be determined rather simply by making use of the observation of these same workers¹⁻⁴ that the specific intensities (intensity per unit pressure against the spectrometer leak) of the parent mass ions of a corresponding protium and deuterium compound were equal. However, such a determination does not uniquely fix the position of a deuterium atom on the two available carbon atoms in the molecule. In addition, the relative intensities of the fragmentation ions obtained in the mass spectrum of acetaldehyde- d were contradictory in the sense that certain ion intensities seemed to indicate a large amount of deuterium on the methyl

carbon atom while certain other ion intensities indicated the deuterium to be present substantially only on the carbonyl carbon atom.

In order to obtain a complete analysis of the heavy acetaldehyde mixture use was made of the observation of Gorin⁶ and Blacet and co-workers⁷ that methyl radicals formed on the irradiation of acetaldehyde vapor could be effectively trapped by iodine vapor to yield methyl iodide. Combination of the data from the analysis of the original heavy acetaldehyde mixture with the mass spectrometric determination of the relative abundance of normal and heavy methyl iodides present in the products of the photolysis would allow a calculation of the amounts of all types of acetaldehyde present. The spectrum of CH_3CDO could be obtained by correcting the spectrum of the heavy acetaldehyde mixture for contributions of all other acetaldehyde species present. A study of the CH_3CDO spectrum should give some evidence as to possible mechanisms of electron impact dissociation.

EXPERIMENTAL

The mass spectrometric analyses were carried out in the Westinghouse Type LV instrument described by Hipple and coworkers.⁸ The operating conditions which were maintained constant in all trials were: Ion source temperature, 200°C; electron energy, 60 ev; electron current, 10 μa ; and ion draw out voltage, 3v. The magnet flux was adjusted so that m/e peaks (mass to charge ratios) from 13 to 55 could be covered by scanning electrically from 1300 to 300 volts. It was found that the cracking pattern of both the heavy acetaldehyde mixture

¹ J. Delfosse and J. A. Hipple, Phys. Rev. **54**, 1060 (1938).

² M. W. Evans, N. Bauer, and J. Y. Beach, J. Chem. Phys. **14**, 701 (1946).

³ F. L. Mohler and V. Dibeler, Phys. Rev. **72**, 158 (1947).

⁴ J. Turkevich, L. Friedman, E. Soloman, and F. M. Wrightson, J. Am. Chem. Soc. **70**, 2638 (1948).

⁵ The method of preparation to be submitted for publication elsewhere.

⁶ E. Gorin, Acta. Physicochimica **9**, 681 (1938).

⁷ (a) F. E. Blacet and J. D. Heldman, J. Am. Chem. Soc. **64**, 889 (1942). (b) F. E. Blacet and D. E. Loeffler, *ibid.* **64**, 893 (1942).

⁸ J. A. Hipple, D. J. Grove, and W. M. Hickam, Rev. Sci. Inst. **16**, 69 (1945); J. A. Hipple, Electronics **16**, 120 (1943).

and normal acetaldehyde changed somewhat over a period of time apparently as a result of small differences in operating conditions. For this reason the mass spectra of both products were run one following the other in as short a period of time as possible.

A check on the accuracy of using the parent peak intensities as a measure of the relative abundance of the various acetaldehyde species was made by an independent method. The heavy acetaldehyde mixture was ignited in a stream of oxygen and the heavy water purified after the method described by Keston, Ritten-

TABLE I. Relative intensities of ions produced by 60-volt electrons on normal and heavy acetaldehydes.

Ion mass <i>m/e</i>	Heavy acetaldehyde mixture	CH ₃ CHO	Calculated CH ₃ CDO
48	4		
47	9		
46	24		
45	1000		1000
44	288	1000	67
43	409	530	310
42	135	147	105
41	55	63	39
40	13	14	10
30	1820		1770
29	493	1620	140
28	279	196	242
27	113	53	102
26	75	98	53
25	33	42	22
24	11	9	9
19	7		5
18	31	35	17
17	100	7	86
16	371	107	336
15	664	800	490
14	183	274	123
13	79	88	60

berg, and Schoenheimer.⁹ The composition of the water was determined by the falling drop method¹⁰ of density measurement. The water composition of 79.1 percent H₂O—20.9 D₂O (ignoring for simplicity the existence of HDO) calculated from this method agreed within experimental error (0.5 percent) with a hypothetical water composition of 78.7 percent H₂O—21.3 percent D₂O which would have been obtained on basis of the mass spectrometric analysis.

The apparatus used in the photolysis of the heavy acetaldehyde mixture was identical to that described by Blacet and Heldman.^{7a} Radiation from the 2537Å and 2654Å lines of an atmospheric pressure mercury arc used in conjunction with a crystal quartz monochromator was used to photolyze a gaseous mixture of the acetaldehydes at about 300 mm pressure and iodine maintained at a pressure greater than 2 mm. The

products of the photolysis which were condensable at -190°C were collected when the decomposition of the acetaldehydes was about 2 percent completed and analyzed by the mass spectrometer. In one determination the large excess of aldehyde was removed previous to the analysis by polymerization over solid potassium hydroxide. Other determinations were made directly on the photolysis products since the aldehyde did not interfere in the high *m/e* region of the parent peaks of the methyl iodides.

RESULTS

The mass spectra of the heavy acetaldehyde mixture and fractionated Eastman "White Label" acetaldehyde are shown in columns two and three of Table I. The intensities of mass peaks 39 to 36 were very small and are not shown. In all cases the spectra are corrected for the naturally occurring amounts of C¹³, O¹⁷, and O¹⁸ isotopes. The absolute accuracy in the intensity range 0 to 100 is about ±2, in the 100 to 500 range about ±4, and ±8 above intensity 500.

The calculation of the relative amounts of the various heavy acetaldehydes present was made on the basis of the specific intensities of the 48, 47, 46, and 45 peaks of the heavy acetaldehyde mixture in relation to the specific intensity of the 44 peak of normal acetaldehyde (CH₃CHO). It was necessary to make small corrections in the 46 and 45 peaks for aldehydes of higher deuterium content. This was done by making reasonable assumptions as to the spectra of these aldehydes. The corrections were small in all cases and only the percentage of the acetaldehyde with two deuterium atoms per molecule could be in error by an appreciable amount. Table II shows the composition of the heavy acetaldehyde mixture obtained by this analysis. The percentage of normal acetaldehyde present is by difference.

Two separate samples of the heavy acetaldehyde mixture whose composition is given in Table II were photolyzed in the presence of iodine vapor. The methyl iodide from these photolyses was analyzed by the mass spectrometer and the relative amounts of the various methyl iodide species found are shown in Table III.

The data of Tables II and III allow the calculation of the amounts of all different acetaldehyde species in the heavy acetaldehyde mixture. The method is apparent from the following schematic representations where the percentages shown on the left are from the direct spectrometric analysis

0.4%	CD ₃ CDO	0.4%
0.7%	CD ₂ CHO	
	CD ₂ HCDO	
1.8%	CD ₂ HCHO	1.1%
	CDH ₂ CDO	
	CDH ₂ CHO	3.2%
80.0%	CH ₃ CDO	
17.1%	CH ₃ CHO	95.3%

and those on the right from the methyl iodide composition. Table IV indicates the percentages of each species

⁹ A. S. Keston, D. Rittenberg, and H. Shoenheimer, *J. Biol. Chem.* **122**, 227 (1937).

¹⁰ K. Fenger-Ericksen, A. Krough, and H. Ussing, *Biochem. J.* **30**, 1264 (1936).

of acetaldehyde present in the mixture as calculated from these data.

The mass spectrum of CH_3CDO shown in column 4 of Table I was obtained by correcting the spectrum of the heavy acetaldehyde mixture in column 2 for contributions of CH_3CHO (17.1 percent) and the additional deuterium containing acetaldehydes (1) through (6) by the amounts shown in Table IV. The corrections were made by an estimation of the most probable individual spectra of these individual compounds. In no case was the correction of large magnitude, so possible errors made in the correction were not of significant importance.

DISCUSSION

A comparison of the spectra of CH_3CHO and CH_3CDO reveals several interesting aspects on the mechanism of the dissociation by electron impact.

1. The loss of a single hydrogen atom by acetaldehyde on electron impact occurs mainly by a C—H bond rupture on the functional group. The low intensity of peak 44 in the CH_3CDO spectrum seems to indicate that approximately 85 percent of the acetyl type positive ion is formed by such a process. In addition the split of the C—H bond of the functional group in CH_3CHO is considerably more likely than the corresponding split of the C—D bond in CH_3CDO as shown by the smaller peak 43 intensity for CH_3CDO than for CH_3CHO . A quantitative evaluation of the relative probability of these two processes is not possible since the 43 peak from CH_3CDO is made up of both CHCDO^+ and CH_3CO^+ ions while the 43 peak from CH_3CHO has contribution from CH_2CHO^+ and CH_3CO^+ ions. If the probability of the loss of a single hydrogen atom from the methyl group accompanied by formation of a positive ion of the remaining fragment is assumed equal for the two aldehydes, then CH_3CO^+ ion from CH_3CHO would be $530-67=463$. The intensity of CH_3CO^+ from CH_3CDO is less than 310 depending on the abundance of CHCDO^+ ion, which is probably small. It would appear that the rupture of the C—D bond of the functional group of CH_3CDO is about 0.6 as probable as the corresponding C—H bond split of CH_3CHO .

2. The formation of the formyl type positive ion seems to occur mainly (more than 90 percent) by a simple fission of the C—C bond of the molecule. However, the existence of a relative intensity for peak 29 of 140 for CH_3CDO may indicate that the process is more complicated for the remaining 10 percent of formyl positive ions formed. A protium-deuterium rearrangement after electron impact and before fragmentation would be necessary to account for this intensity. The probability of formation of the formyl positive ion is somewhat greater for CH_3CDO than CH_3CHO since the relative intensity of CHO^+ ion of CH_3CHO is about 85 percent of the combined CDO^+ and CHO^+ intensities of CH_3CDO . The proportion of the 29 peak of CH_3CDO due to the CH_3CD^+ ion is in

doubt, but comparison of the two spectra seems to indicate that this type ion is of small abundance.

3. The process taking place for the formation of the methyl type positive ion is not a simple split of the C—C bond of the molecule. In order to inspect this process more thoroughly it is first necessary to make more specific assignment to individual ions in this region of the spectra. From the CH_3CDO spectrum the intensity at $m/e=17$

$$\text{OH}^+ + \text{CH}_3\text{D}^+ = 86$$

but OH^+ must be less than 7 since the OH^+ intensity would not be as great for CH_3CDO as for CH_3CHO . Then

$$\text{CH}_3\text{D}^+ \approx 80.$$

If an equal probability of methane type ion and O^+ ion is assumed for both aldehydes,

$$\text{CH}_4^+ \approx 80$$

in the CH_3CHO spectrum. Since $\text{CH}_4^+ + \text{O}^+ = 107$ (CH_3CHO spectrum)

$$\text{O}^+ \approx 27$$

for both aldehydes. Correction of mass peaks 16 and 17

TABLE II. The composition of the heavy acetaldehyde mixture.

Deuterium atoms per molecule	Percentage composition
4	0.4%
3	0.7
2	1.8
1	80.0
0	17.1

TABLE III. The composition of methyl iodides from photolysis of the heavy acetaldehyde mixture in presence of iodine vapor.

	Trial 1	Trial 2	Average
CD_3I	0.4%	0.4%	0.4%
CD_2HI	1.2	1.0	1.1
CDH_2I	3.5	3.0	3.2
CH_3I	94.9	95.6	95.3

TABLE IV. Acetaldehydes present in heavy acetaldehyde mixture.

(1)	CD_3CDO	0.4%
(2)	CD_3CHO	Trace
(3)	CD_2HCDO	0.7
(4)	CD_2HCHO	0.4
(5)	CDH_2CDO	1.4
(6)	CDH_2CHO	1.8
(7)	CH_3CDO	78.2
(8)	CH_3CHO	17.1

for contributions of OH^+ and O^+ leads to the ion intensities shown in Table V.

The ion intensities shown in parentheses in Table V arise by adding the further assumption that intensities of ions of CH^+ and CH_2^+ types are identical whether

TABLE V. Relative intensities of individual ions of acetaldehyde and acetaldehyde-*d*.

<i>m/e</i>	CH ₃ CHO	CH ₃ CDO
17		CH ₃ D ⁺ =80
16	CH ₃ ⁺ =80	CH ₂ D ⁺ =309
15	CH ₃ ⁺ =800	CH ₃ ⁺ (311)+CHD ⁺ (179)=490
14	CH ₂ ⁺ =274	CH ₂ ⁺ (95)+CD ⁺ (28)=123
13	CH ⁺ =88	CH ⁺ =60

deuterium or protium is present in them. CH⁺=88 from the CH₃CHO spectrum and CH⁺+CD⁺=88 by this assumption.

Thus

$$CD^+ = 88 - 60 = 28$$

and

$$CH_2^+ = 123 - 28 = 95, \text{ from } CH_3CDO.$$

CH₂⁺=274 from the CH₃CHO spectrum and CH₂⁺+CHD⁺=274 by a similar assumption as to the equality of CH₂⁺ type ion formation.

$$CHD^+ = 274 - 95 = 179$$

$$CH_3^+ = 490 - 179 = 311, \text{ from } CH_3CDO.$$

Although the imposition of the restrictive of equal CH⁺ and CH₂⁺ ion probabilities from the two aldehydes is not completely valid, the magnitude of the CH₃⁺, CHD⁺, CH₂⁺, and CD⁺ ion intensities is at least close to the values shown in Table V. It is interesting to note that the formation of CH₃⁺ and CH₂D⁺, methyl type ions from CH₃CDO, is almost equally probable. In

the formation of the methyl type radical by electron impact on acetaldehyde, the over-all mechanism must accommodate a rapid exchange of hydrogen atoms between the two carbon atoms. The final methyl ion must contain hydrogen atoms originally present on the functional carbon atom as well as on the methyl carbon atom. It is perhaps possible to postulate more exact mechanisms for this ionization process but little justification is forthcoming from the experimental evidence. Evidence for a similar mobility of hydrogen atoms during an electron impact may be found in the mass spectra of various hydrocarbon compounds. The existence of considerable ethyl positive ion from the fragmentation of isobutane as reported by Stevenson and Hipple¹¹ is an example of this type of exchange.

The result of C-C bond splitting in the two type acetaldehydes is somewhat different. The ratio of methyl type ion/formyl type ion is about 0.49 for CH₃CHO and 0.33 for CH₃CDO.

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¹¹ D. P. Stevenson and J. A. Hipple, J. Am. Chem. Soc. **64**, 1588 (1942).