Mass-spectrometric Study on Ionization and Dissociation of Formaldehyde, Acetaldehyde, Acetone and Ethyl Methyl Ketone by Electron Impact

By Ichiro KANOMATA

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The ionization and dissociation of ethyl alcohol[1,2] and diethyl ether[3] molecules caused by electron impact have previously been studied by the present author. It has been concluded that the ionization takes place by the removal of one of the lone pair electrons of the oxygen atom and that the bond energy additivity can be applied to the ionized dissociation of these molecules by considering the trivalent character of the O^+.

In this report, the ionization and dissociation of formaldehyde, acetaldehyde, acetone and ethyl methyl ketone molecules, each of which has an oxygen atom as in the case of alcohols and ethers, are discussed in relation to the determination of appearance potentials of the ions produced by electron impact. In the case of formaldehyde and acetaldehyde, Reed[4,5] previously carried out an appearance potential study for the purpose of determining the dissociation energies of D(H–CHO), D(H–CO) and D(CH_3–CHO) and the ionization potential of CHO radical. Further, Morrison et al.[6] reported the determination of the ionization potentials of these two molecules. A similar study was also made by Kambara[7] with acetone.

Experimental

The mass-spectrometer[8] used for this study is of a 90° sector type (r=12 cm.). The appearance potentials (AP) of ions were determined by the retarding potential difference method[9] (RPD). The apparatus[10] is nearly identical with Fox's[11], and its details have been described[12]. The ionization potentials and uppor break points on the ionization efficiency curves of N_2, CO and Kr obtained in the present study agree well with Fox's results.

The ionization potential of argon (15.77 eV.) was used as a standard for parent ions, although, owing to the RPD method, such a standard was not necessary in as much as the ion source was clean. Appearance potentials of fragment ions were determined by referring to the appearance potentials of parent ions.

The samples were chemically pure. Formaldehyde was prepared through the thermal decomposition of the polymer, and other sample gases were used after dehydration by calcium chloride.

Results

The appearance ratios of the ions produced by 75 eV. electron impact and their appearance potentials are shown in Tables I and II respectively. Some ionization efficiency curves are illustrated in Fig. 1. Owing to the RPD method, characterized by a narrow distribution (0.2 eV.) of electron energy, fine structures appear in the ionization efficiency curves.

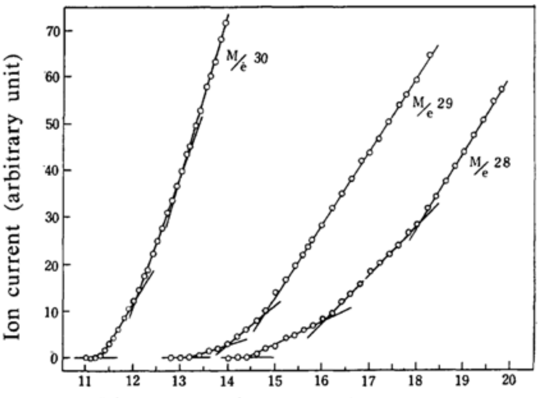

Fig. 1. Ionization efficiency curves of $HCHO^+$, CHO^+ and CO^+.

Discussion

The production processes of ions are as follows:

1) Formaldehyde

M/e=30 $HCHO^+$

The ion is a parent ion. Two distinct breaks exist in the ionization efficiency curve; the

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[1] T. Kambara and I. Kanomata, *Butsuri*, **4**, 71 (1949).

[2] T. Kambara and I. Kanomata, *Hitachi Hyoron Rombun-shu*, No.7, 15 (1949).

[3] I. Kanomata, This Bulletin, **34**, 1596 (1961).

[4] R. E. Reed, *Trans. Faraday Soc.*, **53**, 1195 (1957).

[5] R. E. Reed, ibid., **54**, 949 (1958).

[6] H. Hurzeler, M. G. Inghram and J. D. Morrison, *J. Chem. Phys.*, **28**, 76 (1958).

[7] T. Kambara, *J. Phys. Soc. Japan*, **5**, 84 (1950).

[8] I. Kanomata, Y. Kaneko and T. Oguri, *Mass Spectroscopy*, No. **3**, 12 (1954).

[9] R. E. Fox, W. M. Hickam, T. Kjeldaas and D. J. Grove, *Phys. Rev.*, **84**, 859 (1951).

[10] I. Kanomata, Y. Kaneko and T. Oguri, *Mass Spectroscopy*, No. **6**, 46 (1956).

[11] R. E. Fox et al., *Rev. Sci. Instr.*, **26**, 1101 (1955).

[12] I. Kanomata, Y. Kaneko and T. Oguri, *J. Appl. Phys. Japan*, **30**, 502 (1961).

TABLE I. APPEARANCE RATIO

M/e	Ion	Appearance ratio			
		$(CH_3)(C_2H_5)CO$	$(CH_3)_2CO$	CH_3CHO	$HCHO$
72	$C_4H_8O^+$	53.0			
58	$C_3H_6O^+$		37.4		
57	$C_3H_5O^+$	22.4	1.3		
45	$C_2H_5O^+$	0.5			
44	$C_2H_4O^+$	2.4	2.3	64.5	
43	$C_2H_3O^+$	**100.0**	**100.0**	37.8	
42	$C_2H_2O^+$, $C_3H_6^+$	6.5	4.8	10.7	
41	C_2HO^+, $C_3H_5^+$	2.4	2.4	4.8	
40	C_2O^+, $C_3H_4^+$	1.2	1.3		
39	$C_3H_3^+$	4.3	3.7		
38	$C_3H_2^+$	2.4	1.8		
37	C_3H^+	2.3	1.4		
30	CH_2O^+	4.5			90
29	CHO^+, $C_2H_5^+$	20.2	3.3	**100.0**	**100**
28	CO^+, $C_2H_2^+$	7.4	14.6	13.4	29.8
27	$C_2H_3^+$	5.4	4.8		
26	$C_2H_2^+$	1.3	3.1	7.1	
25	C_2H^+		7.7		
16	CH_4^+, O^+			7.0	
15	CH_3^+	23.7	19.6	44.5	
14	CH_2^+	5.1	2.7	16.0	5
13	CH^+	1.6		5.0	4
12	C^+	1.7			3

TABLE II. APPEARANCE POTENTIAL (eV.)

M/e	Ion	Appearance potential			
		$(CH_3)(C_2H_5)CO$	$(CH_3)_2CO$	CH_3CHO	$HCHO$
72	$(CH_3)(C_2H_5)CO^+$	9.88 ± 0.03, 10.5_3			
58	$(CH_3)_2CO^+$		9.84 ± 0.04 $10.6_7\pm0.1$ $11.5_4\pm0.1$		
57	$C_2H_5CO^+$	10.81 ± 0.04, 12.0			
44	CH_3CHO^+			10.31 ± 0.04 $11.2_4\pm0.1$ 12.2	
43	CH_3CO^+, CH_2CHO^+	11.10 ± 0.03, 12.4	10.94 ± 0.04 $11.9_4\pm0.1$ $12.9_4\pm0.1$	11.38 ± 0.04 $12.0_5\pm0.1$ 12.7 ± 0.1 13.7 ± 0.1	
30					10.86 ± 0.02 $11.6_6\pm0.1$ $12.6_3\pm0.15$
29	$C_2H_5^+$, CHO^+	12.71 ± 0.03, 15.2		12.53 ± 0.04 13.8 ± 0.15 14.8 ± 0.2 16.9 ± 0.2	12.90 ± 0.07 13.6 ± 0.1 $14.2_5\pm0.1$
28	CO^+, $C_2H_4^+$	14.4 ± 0.2, 15.6 17.4	14.6 ± 0.2 15.4 16.8	$14.5_4\pm0.1$ 15.3～15.6 17.4 ± 0.2	14.1 ± 0.05 15.5～15.9 18.3 ± 0.3
27	$C_2H_3^+$		16.9		
15	CH_3^+	15.4 ± 0.2	15.53 ± 0.08 17.3 ± 0.15	$14.8_2\pm0.05$	

energy values corresponding to the threshold and the breaks are 10.86 ± 0.02, $11.6_6 \pm 0.1$ and $12.6_3 \pm 0.15$ eV. respectively. Sugden and Price[13] determined the first, second and third ionization potentials of HCHO as 10.8 ± 0.1, 11.8 ± 0.2 and 13.1 ± 0.2 eV. respectively through the measurement of the total ion current produced by the impact of accelerated photo-electrons. The three values obtained by the present author may be expected to correspond to these ionization potentials.

The first ionization potential of 10.86 eV. agrees well with Reed's result of 10.85 eV. obtained by electron impact[4], with Watanabe's of 10.87 eV. by photon impact[14], and with the spectroscopic value of 10.88 eV.[15] It was pointed out by McMurry[16] in his report on absorption spectra that lone pair electrons of the oxygen atom in the molecule are at the highest occupied orbital. Therefore, the first ionization potential corresponds to the energy necessary for the removal of one of the lone pair electrons.

The second ionization potential of 11.6_6 eV., on which there are very few data[13], may relate to the ionization caused by the removal of the π-electron of the C–O bond, as has been theoretically pointed out by Foster and Boys[17] and by Sugden.

The third ionization potential of 12.6_3 eV. is thought to correspond to the removal of a σ-electron from the C–O bond, as has also been pointed out by Foster and Boys.

The values of the first ionization potentials of parent molecules of aldehyde and ketone obtained by the present author are listed in Table III with their dipole moments. It is shown that the ionization potentials decrease by 0.5 eV. in the order of HCHO, CH_3CHO and $(CH_3)_2CO$, but that the ionization potential of $(CH_3)(C_2H_5)CO$ is a little larger than that of $(CH_3)_2CO$.

TABLE III. IONIZATION POTENTIAL AND DIPOLE MOMENT

Molecule	Ionization potential, eV.	Dipole moment* (D)
HCHO	10.86	2.27
CH_3CHO	10.31	2.72
C_2H_5CHO	—	2.73
$(CH_3)_2CO$	9.84	2.85
$(CH_3)(C_2H_5)CO$	9.88	2.79

* Dipole moment : Compiled by L. G. Wesson, a publication of the Technology press. M.I.T.

The fact that ionization potentials decrease with the increase of the number of CH_3 group may be due to the effect of hyper-conjugation on the ionization of the oxygen atom. That is, it is considered, in general, that the hyperconjugation effect is predominant when the carbon atom bound with the CH_3 group is in an sp^2 configuration. The fact that the ionization potential of ethyl methyl ketone is somewhat larger than that of acetone seems to indicate that the hyper-conjugation plays an important role in the present case.

These results closely relate to the change of the dipole moments of the molecules which can be explained by the hyper-conjugation. The ionization potential decreases with the increment of dipole moment.

M/e=29 $H{-}C{\equiv}O^+$

Two breaks exist in the ionization efficiency curve of this ion. The values of the threshold and the breaks are 12.90, 13.6 and 14.2_5 eV. respectively.

The appearace potential of the R_1^+ ion produced from the R_1R_2 molecule is expressed as follows when excess energy (excitation and kinetic energy of R_1^+ and/or R_2) is disregarded.

$$A(R_1^+) = I(R_1) + D(R_1 - R_2)$$

If the ionization takes place by the removal of one of the lone pair electrons belonging to the oxygen atom in the molecule, the energy necessary for this reaction is 10.86 eV. By inserting the value of D(H–CHO) (79.3 kcal./mol. or 3.45 eV.) in the above equation, the ionization potential of R_{29} is obtained as 9.45 eV. (12.9 eV.$-$3.45 eV.). This value is 1.4 eV. lower than the ionization potential of the formaldehyde molecule. This may be explained by the fact that the triple bond formation can be expected between C and O^+ in the ionized state of CHO, while, for the ionized state of formaldehyde, only the double bond can exist. That is, the formation of the triple bond brings the stabilization of 1.4 eV. on the CHO^+. The value of 1.4 eV. is considerably smaller than the stabilization energy of 2.35 eV. in the case of $H_2C{=}O^+{-}C_2H_5$ produced from diethyl ether[3].

The bond energy between C and O in formaldehyde is 144 kcal./mol.[18] If it is assumed that this bond energy is not affected by the ionization of the lone pair electron of the oxygen atom in the molecule, the total bond energy of O^+ in the CHO^+ is calculated as 176.2 kcal./mol. (144 kcal./mol.$+23.06 \times 1.4$ kcal./mol.).

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[13] T. M. Sugden and W. C. Price, *Trans. Faraday Soc.*, **44**, 116 (1948).

[14] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[15] W. C. Price, ibid., **3**, 256 (1935).

[16] H. L. McMurry, ibid., **9**, 231 (1941).

[17] J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960).

[18] Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond", Interscience Publishers, New York.

The author has previously pointed out in his discussion of the ionized decomposition of diethyl ether³⁾ that the total bond energies of O^+ in $H_2C{=}O^+{-}C_2H_5$ and in $H{-}C{\equiv}O^+$ are 204 kcal./mol. and 183 kcal./mol. respectively. The present datum (176 kcal./mol.) agrees with the previous result (183 kcal./mol.) on the whole.

The reason why the energy of trivalence in the $H{-}C{\equiv}O^+$ is smaller than that in the $H_2C{=}O^+{-}C_2H_5$ is thought to be due to the fact that the former has a smaller number of resonance structures.

M/e=28 CO^+

The observed appearance potentials of this ion are 14.1±0.05, 15.5~15.9 and 18.3±0.3 eV. respectively.

The following two processes may be considered for the creation of CO^+ from formaldehyde:

$$HCHO+e \rightarrow CO^{+\ 19)}+H_2+2e$$

$$HCHO+e \rightarrow CO^+ +2H+2e$$

The heat of reaction, or the appearance potential of CO^+, is calculated as 14.1 eV. for the former reaction and as 18.5 eV. for the latter. These values agree well with the appearance potentials obtained in the present work.

The break between 15.5~15.9 eV. in the ionization efficiency curve is vague; it sometimes appears, and sometimes it dose not. The value is close to the ionization potential of the nitrogen molecule, so it is thought that the break is due to the ionization of N_2, which exists as a background in the mass-spectrometer.

On the other hand, from the thermal decomposition experiments previously made by the present author, it has been found that HCHO is thermally unstable, that it decomposes easily to the CO molecule, and that the CHO radical can not be expected through the thermal decomposition. Therefore, it is also reasonable to consider that a part of formaldehyde gas thermally decomposes into CO gas on the tungsten filament of the ion source and that the CO molecule is ionized when it enters again into ionization chamber. According to this assumption, the first appearance potential of M/e=28 corresponds to the ionization potential of the CO molecule; the experimental result does not disagree with the above conclusion. In this case, the second breaks at 18.3 eV. may correspond to the excited state of the CO^+ ion.

2) Acetaldehyde

M/e=44 CH_3CHO^+

The observed value of 10.31 eV. is the first ionization potential of the acetaldehyde molecule. Two breaks exist, at 11.2_4 and 12.2 eV. on the ionization efficiency curve.

Sugden and Price¹³⁾ have previously obtained observed values of 10.4±0.1, 11.3±0.1, 12.3±0.1 and 13.5±0.2 eV. through measurement of the total ionization current. The first three values agree well with the values of the present author. At the electron energy as large as 13.5 eV., the dissociation of molecular ion certainly takes place. So Sugden's method, which dealt with only the total ionization current, is unsuitable for the determination of the higher ionization potentials of the parent molecule.

As regards the classification of the ionization potentials of CH_3CHO, it is reasonable to consider, as in the case of $HCHO^+$, that 10.31 eV. corresponds to the energy necessary for the removal of one of the lone pair electrons of the oxygen atom in the molecule, that 11.2_4 eV. is the energy needed for the removal of a π-electron in the C–O bond, and that 12.3 eV. is the energy needed for the removal of an σ-electron in the C–O bond in the molecule.

M/e=43 CH_3CO^+ or CH_2CHO^+

The appearance potential of this ion is 11.38 eV., and breaks exist at 12.1, 12.7 and 13.7 eV. The M/e=43 ion is produced by subtracting a hydrogen atom from the parent molecular ion. The bond dissociation energy of C–H in the aldehyde radical is thought to be smaller than that in the methyl radical; moreover, if a hydrogen atom is removed from the aldehyde radical, the stabilization of energy due to the formation of a triple bond of O^+ may take place. Accordingly it is reasonable to conclude that the hydrogen atom is removed from the aldehyde radical in the molecule. Thus, when relation $A(R43^+)=I(R43)+D(CH_3CO{-}H)$ and $D(CH_3CO{-}H)=3.48$ eV.²⁰⁾ are used, $I(CH_3CO)$ is obtained as 7.90 eV.

This value is 2.41 eV. (55 kcal./mol.) smaller than the ionization potential of the parent molecule. It can be considered that the stabilization by 2.41 eV. takes place with the formation of a triple bond of O^+ in this ion. If it is assumed that the bond energy between C and O atoms in acetaldehyde is not affected by the ionization of one of the lone pair electrons of oxygen atom and that the bond energy additivity is applicable to such an ionic state, the total bond energy of O^+ in $CH_3C{\equiv}O^+$ is

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19) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions", Academic Press Inc. Publishers, New York (1957).

20) J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

obtained as 204.5 kcal./mol. (149.5+55 kcal.) by considering that the bond energy between C and O in acetaldehyde is 149.5 kcal.[18]

On the other hand, the total bond energy of O^+ in CHO^+ was calculated as 176 and 183 kcal. by the author, as has been described above. The increase of the stabilization in the CH_3CO^+ ion seems to be due to the resonance between different structures, for example, $H_3{\equiv}C{-}C{\equiv}O^+$ and $H^+H_2{=}C{=}O$.

As for the second and the third ionization potentials, no information has been obtained to interpret them.

M/e=29 CHO^+

As $D(CH_3{-}CHO)$[20] is 71.5 kcal./mol. (3.10 eV.), $I(CHO)$ is calculated as 9.43 eV. from the observed appearance potential of the ion. This value agrees well with the value of $I(CHO)$ obtained from HCHO in this report, and it is only a little smaller than Reed's value of 9.87 eV.[4] In this case the stabilization energy is obtained as follows:

$I(CH_3CHO) - I(CHO) = 0.88$ eV. (20.4 kcal./mol.). Therefore, the total bond energy of O^+ in $H{-}C{\equiv}O^+$, calculated under the assumptions described above, is 170 kcal./mol. (149.5+20.4 kcal./mol.). This value should more closely agree with the 183 kcal./mol. obtained from diethyl ether and with the 176 kcal./mol. from formaldehyde. However, such a discrepancy among these values is unavoidable under these loose assumptions.

M/e=28 CO^+ or $C_2H_4^+$

The ionization efficiency curve of M/e=28 has an uncertain break between 15.3∼15.6 eV. and a rather distinct break at 17.4 eV. The heat of reactions, or the appearance potentials of CO^+ from CH_3CHO, are obtained, by considering the heat of the formation of CO^+ and of the other related molecules and radicals, as follows:

$CH_3CHO+e \rightarrow CO^+ + CH_4 + 2e$ 13.8 eV.

$CH_3CHO+e \rightarrow CO^+ + CH_2 + H_2 + 2e$ 15.8 eV.

$CH_3CHO+e \rightarrow CO^+ + H + CH_3 + 2e$ 18.2 eV.

The calculated values do not agree with the observed appearance potentials of the M/e=28 ion. However, as the appearance ratio of this ion is very small the influence of N_2^+ from the background in the mass-spectrometer could be expected to be greater, and so the apparent appearance potentials should also be greater than expected. By considering such a bad observing condition, the observed values may be said to correspond closely enough to the above-estimated reactions.

On the other hand, if the reaction is assumed as $CH_3CHO \rightarrow C_2H_4^+ + O$, the heat of reaction would be 15.3 eV.

M/e=15 CH_3^+

The reaction to produce CH_3^+ is supposed as

$CH_3CHO+e \rightarrow CH_3^+$[19]$+CHO+2e$

or $CH_3CHO+e \rightarrow CH_3^+ + CO + H + 2e$

The ionization potential of CH_3 radical can be estimated from various data. The mean value of the data given from various ionized decompositions of organic compounds is 10.0 eV. Moreover, the energy for direct ionization of CH_3 radical is also 10.0 eV. If $I(CH_3) = 10.0$ eV., $D(CH_3-CHO) = 3.10$ eV.[20] and $D(H-CO) = 1.13$ eV.[20], the heat of reaction for these processes is calculated as 13.10 eV. and 14.23 eV. respectively. The observed value agrees with the latter calculated value by assuming that the reaction has an excess energy of 0.6 eV.

3) *Acetone*

M/e=58 $(CH_3)_2CO^+$

Two break points exist in the ionization efficiency curve. The values of the threshold and the break points are 9.84±0.04, 10.6_7±0.1 and 11.5_4±0.1 eV. respectively. It is thought that these values must be compared with Sugden and Price's values, 10.2±0.1, 11.3±0.1, 12.2±0.1 and 13.6±0.2 eV., which were obtained by the measurement of the total ionization current produced by the impact of accelerated photo-electrons. The discrepancy is large. Sugden's method seems, however, to be unsuitable for the determination of the higher ionization potentials of the parent molecule because of the formation of fragment ions. The first ionization potential of the molecule was determined as 9.92 and 9.89 eV. mass-spectrometrically, by Morrison et al.[21] and Omura et al.[22] respectively, as 9.69 eV. from the measurement of the total ionization current produced by photon impact by Watanabe[23], and as 9.705 eV. spectrometrically. It is reasonable that the first, second and third ionization potentials obtained are correlated, as in the case of formaldehyde, to the ionization of the lone pair electron of the oxygen atom, of the π-electron and of the σ-electron in the C-O bond respectively.

M/e=43 CH_3CO^+

There are two breaks in the ionization efficiency curve. By considering that $D(CH_3-COCH_3)$ is 3.15 eV.[20], $I(CH_3CO)$ is obtained as

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[21] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

[22] I. Omura, K. Higasi and H. Baba, This Bulletin, **29**, 504 (1956).

[23] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

7.79 eV. from the relation of $I(CH_3CO)=A(CH_3CO^+)-D(CH_3-COCH_3)$. The value is 2.05 eV. smaller than the ionization potential of acetone. By assuming the structure of this ion as $CH_3C\equiv O^+$, in which the trivalency is satisfied, the value of 2.05 eV. is thought to be the stabilization energy through the formation of the triple bond.

The total bond energy of O^+ in the ion is calculated as 202 kcal./mol. by adopting 155 kcal./mol.[18] as the bond energy between C and O in acetone. The value 202 kcal./mol. agrees well with that calculated in the case of acetaldehyde.

M/e=28 CO^+ or $C_2H_4^+$

The appearance ratio of this ion is small, and the influence of N_2^+ in background seems to be large, so the accuracy is not great. The heat of reaction for seven processes, which are all expected to produce M/e=28, is calculated as follows:

$(CH_3)_2CO+e \rightarrow CO^{+\,19)}+C_2H_6+2e$ 14.3 eV.

$(CH_3)_2CO+e$
$\rightarrow CO^++H_2+C_2H_4+2e$ 15.7 eV.

$(CH_3)_2CO+e \rightarrow CO^++2(CH_3)+2e$ 17.9 eV.

$(CH_3)_2CO+e$
$\rightarrow C_2H_4^{+\,19)}+CO+H_2+2e$ 12.2 eV.

$(CH_3)_2CO+e$
$\rightarrow C_2H_4^++HCHO+2e$ 12.1 eV.

$(CH_3)_2CO+e$
$\rightarrow C_2H_4^++CHO^{20)}+H+2e$ 15.5 eV.

$(CH_3)_2CO+e$
$\rightarrow C_2H_4^++CO+2H+2e$ 16.6 eV.

However, a conclusion as to a process suitable for the production of the M/e 28 ion could not be obtained.

M/e=27 $C_2H_3^+$

This ion must be $C_2H_3^+$. The calculated appearance potentials for this ion are as follows:

$(CH_3)_2CO+e$
$\rightarrow C_2H_3^{+\,19)}+H_2+CHO+2e$ 14.3 eV.

$(CH_3)_2CO+e$
$\rightarrow C_2H_3^++H+H_2+CO+2e$ 15.5 eV.

$(CH_3)_2CO+e$
$\rightarrow C_2H_3^++3H+CO+2e$ 19.8 eV.

These values do not agree with the observed value. Therefore, the mechanism of the production of this ion can not be found.

M/e=15 CH_3^+

The calculated appearance potentials of this ion are as follows:

$(CH_3)_2CO+e$
$\rightarrow CH_3^{+\,19)}+CH_3CO^{20)}+2e$ 13.1 eV.

$(CH_3)_2CO+e$
$\rightarrow CH_3^++CH_3+CO+2e$ 13.9 eV.

$(CH_3)_2CO+e$
$\rightarrow CH_3^++CH+H_2+CO+2e$ 16.3 eV.

Accordingly, the second and the third reactions would be possible if the reactions take place with excess energies (kinetic and/or excitational energies) of 1.6 and 1.0 eV. respectively. In order to know the possible reactions conclusively, however, the kinetic energies of produced ions must be measured more precisely.

4) Ethyl Methyl Ketone

M/e=72 $CH_3COC_2H_5^+$

There is a break in the ionization efficiency curve of this ion, and there seem to exist something like breaks above the first break point.

The first ionization potential is thought to be the energy by which the removal of one of the lone pair electrons of the O atom in the molecule takes place, as in the previous discussion of this report. The value obtained by the present author is a little larger than that of acetone. The fact is reasonably explained by assuming that hyper-conjugation is a little smaller in ethyl methyl ketone. This tendency was recognized also in a comparison of dipole moments.

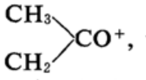
M/e=57 $C_2H_5CO^+$ or $CH_2CO^+CH_3$

If this ion is assumed to be $C_2H_5CO^+$, the corresponding reaction is as follows:

$$CH_3COC_2H_5+e \rightarrow C_2H_5CO^++CH_3+2e$$

Moreover, the structure of the ion produced should be $C_2H_5\text{-}C\equiv O^+$, which satisfies the trivalency as in the case of HCO^+ from formaldehyde and of CH_3CO^+ from acetaldehyde as well as acetone. $I(C_2H_5CO)$ is obtained as 7.66 eV. by use of the relations, $A(C_2H_5CO^+)=I(C_2H_5CO)+D(CH_3-COC_2H_5)$ and $D(CH_3-COC_2H_5)=3.15\ eV$[20]. This value is a little smaller than the value of $I(CH_3CO)$ obtained previously in this report.

From the value of $I(C_2H_5CO)$, the stabilization energy by the formation of triple bond of O^+ in this ion is calculated as 2.22 eV. (9.88 eV.−7.66 eV.). Hence, the total binding energy of O^+ in this ion is obtained as 206 kcal./mol. (157 kcal./mol.[18]$+23.06\times2.22$ kcal./mol.). This value agrees quite well with the values for $CH_3C{\equiv}O^+$ obtained in the case of acetaldehyde and acetone.

On the other hand, if this ion is assumed to be  $\begin{matrix}CH_3\\ CH_2\end{matrix}\rangle CO^+$, the ionization potential of this ion is obtained as 7.20 eV., provided that the dissociation energy between C atoms in the ethyl radical in the molecule is assumed as 3.60 eV., which is the dissociation energy of ethane. However, in this case the stabilization due to the formation of the triple bond of O^+ in the ion can not take place. The value of 7.20 eV. is therefore thought to be as abnormally small as the ionization of the oxygen atom in the radical.

M/e=43 CH_3CO^+

The assumed reaction for the production of this ion is as follows:

$$CH_3COC_2H_5+e \rightarrow CH_3CO^+ + C_2H_5 + 2e$$

$I(CH_3CO)$ is calculated as 7.97 eV. by the use of $D(CH_3CO-C_2H_5)=3.13$ eV.[20] This value of $I(CH_3CO)$ must, of course, agree with the values of $I(CH_3CO)$ in the cases of acetaldehyde and acetone. In this case also, by assuming 1.91 eV., which is the difference between this value and the ionization potential of the parent molecule, as the stabilization energy due to the formation of the triple bond of O^+ in the ion, 202 kcal. is obtained as total bond energy of the O^+ in the $CH_3{-}C{\equiv}O^+$ ion (157 kcal. + 23.06 × 1.91 kcal.). This also agrees quite well with the values previously described in this report. Furthermore, the heat of the formation of CH_3CO^+ is calculated, by using the value obtained above, as 174 kcal./mol. The value agrees well with the value cited above (cf. Ref. 19).

M/e=29 $C_2H_5^+$ or CHO^+

If this ion is assumed to be $C_2H_5^+$, the heat of reaction, or the appearance potentials, are calculated as follows:

$$CH_3COC_2H_5+e \rightarrow C_2H_5^+ + CH_3CO + 2e \qquad 11.8\ \text{eV.}$$

$$CH_3COC_2H_5+e \rightarrow C_2H_5^+ + CH_3 + CO + 2e \qquad 12.55\ \text{eV.}$$

The second process seems to take place. In this case, the reaction by which the CH_3CO radical is produced is impossible, as in the case of acetone.

On the other hand, if the ion is assumed to be CHO^+, energetically there is some possibility as follows:

$$CH_3COC_2H_5+e \rightarrow CHO^+ + C_3H_7 + 2e \qquad 12.1\ \text{eV.}$$

$$CH_3COC_2H_5+e \rightarrow CHO^+ + C_2H_4 + CH_3 + 2e \qquad 13.2\ \text{eV.}$$

M/e=28 CO^+ or $C_2H_4^+$

As the appearance ratio of this ion is very small, a high degree of accuracy in measurement can not be expected. The heat of reaction for the following processes is calculated:

$$MeEtCO+e \rightarrow CO^+ + C_3H_8 + 2e \qquad 14.3\ \text{eV.}$$

$$MeEtCO+e \rightarrow CO^+ + CH_4 + C_2H_4 + 2e \qquad 16.35\ \text{eV.}$$

$$MeEtCO+e \rightarrow CO^+ + Me + Et + 2e \qquad 17.9\ \text{eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_4 + CO + 2e \qquad 11.65\ \text{eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_3CHO + 2e \qquad 11.8\ \text{eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_3 + CHO + 2e \qquad 14.9\ \text{eV.}$$

$$MeEtCO+e \rightarrow C_2H_4^+ + CH_2 + H_2 + CO + 2e \qquad 11.6\ \text{eV.}$$

If the second appearance potential of 15.6 eV. is rejected for the reason described previously in the discussion on the M/e=28 ion produced from formaldehyde, the first and the third processes will probably be possible.

M/e=15 CH_3^+

The heat of the reaction of the following process is calculated as 15.05 eV.

$$CH_3COC_2H_5+e \rightarrow CH_3^+ + C_2H_5 + CO + 2e$$

The appearance potential of the CH_3^+ agrees with the above-calculated heat of reaction if the excess energy of 0.3 eV. is permitted in the above process.

On the other hand, if the reaction is assumed to be $CH_3COC_2H_5+e \rightarrow CH_3^+ + CH_3COCH_2 + 2e$, and the values of $I(CH_3)$ and $D(C{-}C)$ to be 10.0 eV. and 3.6 eV. respectively, the heat of the reaction of this process is obtained as 13.6 eV. This does not agree with the appearance potential.

The reason why the process through which CH_3^+ is produced from acetone has a relatively large excess energy, while the process through which CH_3^+ is produced from ethyl methyl ketone has a small excess energy, is not obvious.

5) Heat of Formation of CHO^+, CH_3CO^+ and $C_2H_5CO^+$

The appearance potential of an ion is the heat of the reaction by which the ion is formed if no excess energy is involved, and the process may be treated by the usual methods

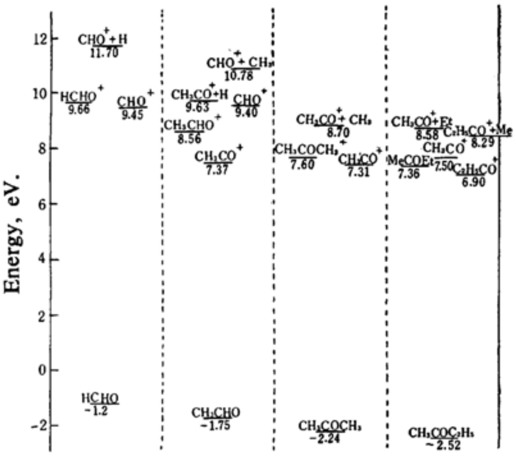


Fig. 2. Heat of formation of ions determined.

of thermochemistry. Thus, for the reaction $R_1R_2 \rightarrow R_1^+ + R_2$, the relation

$$A(R_1^+) = \Delta H_f(R_1^+) + \Delta H_f(R_2) - \Delta H_f(R_1R_2)$$

is given, provided that the reaction involves no excess energy.

By introducing the measured appearance potentials and the heat of formation of related molecules as well as radicals into the above relation, heats of formation of CHO^+, CH_3CO^+ and $C_2H_5CO^+$ are obtained, as shown in Fig. 2. The agreement between the heats of formation for the same ion produced from different molecules is very good, considering that the values are obtained through the appearance potential study.

Summary

A study of the ionization and dissociation of formaldehyde, acetaldehyde, acetone and ethyl methyl ketone, all of which have an oxygen atom, was carried out through the appearance potential method. As appearance potentials were obtained by the retarding potential difference method, break points, which correspond to successively occurring ionization, appeared in the ionization efficiency curves of molecules and fragments. By considering the relation of energy, it is concluded that the ionization of the molecule takes place at first by the removal of one of the lone pair electrons of oxygen atom in the molecule, and that, in the formation of a fragment ion including an oxygen atom, dissociation takes place to create a triple bond, satisfying the trivalency of O^+ in the fragment ions.

The total bond energy of O^+ in $CH_3C{\equiv}O^+$ and $C_2H_5C{\equiv}O^+$ are calculated as about 200 kcal./mol., while in $HC{\equiv}O^+$ it is 170∼180 kcal./mol. as in the case of diethyl ether reported previously. This fact may be explained by the number of resonance structures related.

The second and the third ionization potentials are thought to correspond to the removal of the π-electron and σ-electron in C–O bond respectively. The heat of formation of CHO^+, CH_3CO^+ and $C_2H_5CO^+$ are obtained from various reactions.

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Department of Physics
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo