Mass-spectrometric Study on Ionization and Dissociation of Diethyl Ether by Electron Impact

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Since 1930 many studies on ionization and dissociation of organic molecules by electron impact have been made by means of a mass-spectrometer. The reason for using a mass-spectrometer for these kinds of studies is to obtain the information on the decomposition processes through determination of M/e values and of the appearance potentials of ions formed by electron impact.

The study on the processes of ionized decomposition by electron impact is not only fundamental for the radiation chemistry of organic compounds but also helpful for the researches on molecular structures and chemical reactions.

The author previously reported the mass-spectrometric study on ionization and dissociation of the ethyl alcohol molecule by electron impact[1,2]. The present report relates to the decomposition of the diethyl ether molecule which has one oxygen atom, and the ionization of the molecule is thought to "cause the removal" of one of the lone pair 2 p electrons of this oxygen atom as well as in the case of ethyl alcohol in the previous study.

Experimental

The mass spectrometer[3] used for this study was a 90° sector type (R=12 cm.), and the appearance potentials (AP) of ions were determined by the extrapolated difference method[4]. The ionization potential of the molecule was calibrated with the ionization potential of argon (15.76 eV.) and the appearance potentials of fragment ions were determined by referring to the ionization potential of the molecule. The sample was chemically pure and was not particularly refined.

Results

The appearance ratios of ions produced from the molecule by 75 eV. electron impact are shown in Table I. From the table it is obviously recognized that the M/e=31 ion (CH_2OH^+ or CH_3O^+) is the most abundant, and the M/e=29, 59, 45 and 74 ions are also abundant. The appearance potentials of these five species of ions obtained are tabulated in Table II.

TABLE I. APPEARANCE RATIOS

M/e	Ion	Appearance ratio
75	Isotope peak	0.3
74	$(C_2H_5)_2O^+$	25.7
60	$(CH_3)(C_2H_5)O^+$, isotope peak	2.1
59	$(CH_2)(C_2H_5)O^+$	46.0
46	$C_2H_5OH^+$, isotope	0.4
45	$(C_2H_5)O^+$	31.3
44	$C_2H_4O^+$	3.1_5
43	$C_2H_3O^+$	12.7_5
42	$C_2H_2O^+$	3.0
41	C_2HO^+	6.0
31	CH_2OH^+ or CH_3O^+	100.0
30	CH_2O^+	3.1_5
29	CHO^+ or $C_2H_5^+$	63.5
28	CO^+ or $C_2H_4^+$	10.2
27	$C_2H_3^+$	37.1
26	$C_2H_2^+$	8.0
15	CH_3^+	14.3
14	CH_2^+	2.7

TABLE II. APPEARANCE POTENTIALS (eV.)

M/e	Ion	Appearance potential
74	$(CH_3CH_2)O^+(CH_2CH_3)$	9.55 ± 0.02
59	$CH_2O^+CH_2CH_3$	10.80 ± 0.08
45	$CH_3CH_2O^+$	13.23 ± 0.04
31	CH_2O^+H or CH_3O^+	$12.3_5\pm0.1$
29	$C_2H_5^+$ or CHO^+	14.0 ± 0.2

Discussion

When a molecule R_1R_2 is composed of R_1 and R_2 atoms (or radicals), the appearance potential of R_1^+ ions is given by

$$A(R_1^+)=I(R_1R_2)+D(R_1^+-R_2) \tag{1}$$

$$=I(R_1)+D(R_1-R_2) \tag{2}$$

Here, $I(R)$ is the ionization potential of atom (radical) R, and $D(R_1-R_2)$ is the bond dissociation energy between R_1 and R_2. Of course, radicals or atoms produced may generally have some excitational or kinetic energy. In case the molecule consists of many atoms as organic compounds, however, the potential

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

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

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

[4] J. W. Warren, *Nature*, **165**, 811 (1950).

surfaces that give the binding energies between atoms approach each other, and therefore the excess energy may be small as reported by some authors[5,6]. From this point of view the neglect of this excess energy will not be serious in the course of this discussion.

The processes of production of ions are as follows:

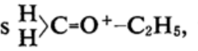
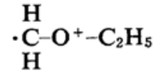
$$M/e=74\ \ (C_2H_5)_2O^+,\ \ \text{AP}\ 9.55\ \text{eV}.$$

This ion is the parent ion and the appearance potential is the ionization potential of diethyl ether molecule. This value was obtained by Morrison[7] as 9.72 eV. by critical slope method and by Price[8] spectroscopically as 10.2 eV. These results are largely different from each other beyond their errors of measurement, though the reason can not be explained.

It must be considered what kind of electron in the molecule is concerned with its ionization. Mulliken[9] reported that the lone pair electrons of the oxygen atom in the molecules, such as water and alcohol, have the lowest ionization potential by charge transfer effect. Hence the ionization occurs at first by the removal of one of these electrons. The fact that the ionization potentials decrease in the order of H–O–H (12.76 eV.), CH_3–O–H (10.95 eV.), CH_3–O–CH_3 (10.5 eV.) and C_2H_5–O–C_2H_5 (9.55 eV.) can be explained by this charge transfer effect. This postulate was also used when the present author and Kambara studied the ionization and dissociation of ethyl alcohol[1,2], propyl alcohol[10,11], acetone and acetic acid[12] molecules by electron impact, and will be required to discuss the dissociation process for the production of M/e=59 ion from diethyl ether. From these facts, the ionization potential 9.55 eV. is thought to be that of the oxygen atom in the molecule.

$$M/e=59\ \ (CH_2\text{–}O\text{–}C_2H_5)^+,\ \ \text{AP}\ 10.80\ \text{eV}.$$

Equation 1, in this case, leads to $A(R_{59}{}^+)=I(R_{74})+D(R_{59}{}^+-R_{15})$. Inserting the observed values, $D(R_{59}{}^+-R_{15})=10.80-9.55=1.25$ eV. is obtained. This dissociation energy of the ionic state should correspond to the dissociation energy of the C–C bond of the neutral molecule. The reason why the dissociation energy for such an ionized molecule is apparently low may be elucidated as follows.

If one of the lone pair electrons of the oxygen atom in the molecule is removed by ionization in accordance with Mulliken's postulate, the other electron left in the atom may have new binding activity, that is, the trivalency of the O^+ ion. Therefore, when the structure of M/e=59 ion is assumed as  $\overset{H}{\underset{H}{}}\!\!>C{=}O^+\text{–}C_2H_5$, this ion should be more stabilized, by the energy of formation of trivalent structure, than the structure of  $\cdot\overset{H}{\underset{H}{C}}\text{–}O^+\text{–}C_2H_5$ which is yielded by only removing a CH_3 radical from the parent ion.

In order to estimate this stabilization energy of formation of trivalent bond, it is assumed that the dissociation energy of the C–C bond of the diethyl ether molecule is equal to that of ethane.

$$\begin{aligned} D(R_{59}-R_{15}) = D(CH_3-CH_3) &= 80\pm6\ \text{kcal.}^{13)} \\ &= 83.3\pm1\ \text{kcal.}^{14)} \\ &= 3.6\ \text{eV.} \end{aligned}$$

Then the stabilization energy becomes $3.6-1.25=2.35$ eV.=54 kcal./mol. Consequently, under the assumption of the additivity of bond energy, the total binding energy of trivalent bond of O^+ in this case is obtained as (3.26 eV. $\times 2+2.35$ eV.=8.87 eV.=)204 kcal./mol., where 3.26 eV. is the value of D(C–O).

It may be recognized that in this ion resonance occurs as in carbon monoxide molecule, causing the stabilization near 58 kcal. of resonance energy of carbon monoxide[15].

$$M/e=45(C_2H_5-O)^+,\ \ \text{AP}\ 13.23\ \text{eV}.$$

This ion is thought to be produced by the removal of a C_2H_5 radical from the parent ion. Therefore the relation $A(C_2H_5-O\cdot^+)=I(C_2H_5-O\cdot)+D(R_{45}-R_{29})$ exists. According to Syrkin and Dyatkina's data[16] on heat of dissociation, D(C–O) for diethyl ether is 75 kcal./mol. (3.26 eV.), hence from the above equation $I(C_2H_5-O^+\cdot)=10.0$ eV. is obtained. This value is somewhat greater than the ionization potential of the parent molecule (9.55 eV.). This seems to be due to the charge transfer effect which is adopted to explain the low value of the ionization potential of the parent molecule. As regards this ion, of course, the stabilization due to trivalency of O^+ can not take place.

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[5] F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Academic Press Inc. Publishers, New York (1957).

[6] C. E. Berry, *Phys. Rev.*, **78**, 597 (1950).

[7] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1951).

[8] T. M. Sugden, A. D. Walsh and W. C. Price, *Nature*, **148**, 373 (1941).

[9] R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

[10] T. Kambara, *J. Phys. Soc. Japan*, **5**, 31 (1950).

[11] T. Kambara, ibid., **5**, 36 (1950).

[12] T. Kambara, ibid., **5**, 84 (1950).

[13] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

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

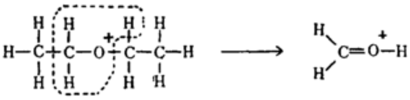
[15] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca (1939).

[16] Y. U. Syrkin and M. E. Dyatkina, "Structure of Molecules and Chemical Bond", Interscience Publishers, Inc., New York (1950).

M/e=31 $(CH_3-O-H)^+$, AP 12.3_5 eV.

The structure of this ion may be thought to be either CH_3O^+ or CH_2OH^+. Though this ion is the most abundant among those produced by 75 eV. electron impact, it can not be produced through a simple process, as the rupture of only one bond in the cases of M/e =59 and 45. Thus, in this dissociation process, rearrangement of atoms in the molecule is necessary.

The following dissociation process is energetically reasonable.



That is, it is thought that with the ionization of the oxygen atom, the rupture of bonds and the formation of O–H bond take place simultaneously. Assuming the bond energy additivity, the energy necessary for this process will be calculated as follow:

ionization of oxygen atom	9.55 eV.
rupture of C–C bond	3.6 eV.
rupture of C–O bond	3.26 eV.
rupture of C–H bond[17]	2.9 eV.
formation of O–H bond	−4.8 eV.
formation of $\rangle C=O^+-$ structure	−2.35 eV.

The sum of these energies is 12.16 eV. in total and agrees well with the appearance potential obtained.

On the contrary, if this ion is assumed to have the structure of CH_3O^+, the energy necessary for the reaction becomes more than 16 eV. Therefore the structure of M/e =31 ion is concluded to be $H_2C=O^+-H$.

M/e=29 $C_2H_5^+$ or CHO^+, AP 14.0 eV.

If the M/e=29 ion is $C_2H_5^+$, Eq. 2 leads

$$A(C_2H_5^+)=I(C_2H_5)+D(C_2H_5-OC_2H_5)$$

Then $I(C_2H_5)=14.0-3.26=10.74$ eV.

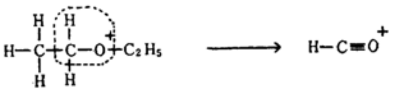
The ionization potential of C_2H_5 radical can be estimated from various data. For example, Bleakney gave a rather high value of 9.8 eV. from the decomposition of ethyl alcohol, and the mean value of the data given from various ionized decompositions of organic compounds is 8.75 eV.[5] Moreover, the energy for direct ionization of C_2H_5 radical has the rather low value of 8.60 eV.[18] Therefore, this ion should not be $C_2H_5^+$ ion, but CHO^+.

If it is assumed that radicals of H, CH_3 and C_2H_5 are produced in the course of the formation of CHO^+, the heat of reaction can be calculated from the thermochemical data as follows.

$$\begin{aligned} A(CHO^+) &= \Delta H_f(CH_3)+\Delta H_f(C_2H_5) \\ &\quad +\Delta H_f(H)+\Delta H_f(CHO^+) \\ &\quad -\Delta H_f(C_2H_5OC_2H_5)=14.3\text{ eV.} \end{aligned}$$

The calculated value agrees well with the experimental result.

From the standpoint of bond energy additivity, and the assumed reaction of



as in the case of M/e=31 ion, the energy necessary for the reaction will be calculated as follows.

ionization of the molecule	9.55 eV.
rupture of C–C bond	3.6 eV.
rupture of C–O bond	3.26 eV.
rupture of C–H bond	2.9 eV.
$H-C-O^+- \rightarrow H-C\equiv O^+$	−2.35×2 eV.

The sum of these energies is 14.6 eV. The difference between this value and the measured appearance potential is somewhat great, but this is unavoidable under such a loose assumption and rough calculation.

The total bond energy of O^+ ion in the case of CHO^+ is also calculated as in the case of M/e=59 ion. That is to say, provided that the energy of the C–O bond 3.26 eV. is conserved in one of the triple bond of CHO^+ ion, the total energy of O^+ is calculated as

$$3.26+2.35\times2=7.96\text{ eV.}=182\text{ kcal./mol.}$$

This value is rather small compared with that of M/e=59 ion.

The reason why the stabilization is smaller in this case than in the case of M/e=59 ion is thought to be due to the existence of fewer resonance structures.

Summary

A mass spectrometric study on ionization and dissociation of diethyl ether has been carried out.

The M/e=31 ion is the most abundant among the ions produced by 75 eV. electron impact and the M/e=29, 59, 45 and 74 ions are abundant in this order next to M/e=31 ion.

The appearance potential measurement of these ions leads to the following conclusion. The ions are formed by the removal of one of the lone pair electrons of the oxygen atom in the molecule.

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[17] C. E. Cumming and M. E. Bleakney, *Phys. Rev.*, 58 787 (1940).

[18] J. A. Hipple and D. P. Stevenson, ibid., 63, 121 (1943).

By considering the trivalent structure of O^{+} and by applying the bond energy additivity, which is adequate for hydrocarbons, to such an ionized dissociation process the producing processes of such ions can be satisfactorily revealed.

The stabilization energy for the formation of $\rangle C=O^{+}-$ structure is obtained as 54 kcal./mol. by such a calculation.

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