High-kinetic Energy Fragment Ions from Organic Compounds under Electron Impact. IV. Methanol

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It has long been known[1,2] that fragment ions formed from polyatomic molecules under electron impact often have excess kinetic energy,* and studies of KE fragment ions from hydrocarbons have been reported.[1-7] Hustrulid et al.[1] suggested that these ions with a high kinetic energy result from the dissociation of doubly-charged ions formed by electron impact. Mohler et al.[3] computed the repulsive energies of ions fromed from various compounds on this assumption.

In the present ariticle, some findings on the KE fragment ions from methanol will be reported, and a mechanism of the production of the KE ions will be suggested according to the proposal made by Hustrulid and Mohler.

Measurement

Methanol was a special-grade reagent obtained from the Nippon Rikagaku Shiyaku Co. and was purified by distillation. It was found to be mass-spectroscopically pure. The procedure for the measurement of KE ions has previously been reported.[6]

The results of measurement are given in Table I. Column two gives the kinetic energy, E, of the KE ions CH_2^+, CH_3^+ and OH^+, while columns three and four give the intensity of the KE ion, I_k, and that of TE ion, I_t, respectively in arbitrary units. The last column gives the lowest electron energy, A, at which the KE ions could be detected. In each instance, the given result is the mean value of four measurements. The reproducibility of E values was ± 0.2 eV. The + mark in the I_k column indicates the presence of a weak peak.

Table I. Ions of high kinetic energy in the mass spectrum of methanol

m/e	E, eV.	I_k	I_t	A, eV.
14		+		
15	2.7	0.7	74.3	37
17	1.9	1.3	2.0	36

E, kinetic energy
I_k, intensity of the high kinetic-energy peak,
I_t, intensity of the thermal energy peak,
A, minimum electron energy at which the kinetic-energy peak was observed.
+ indicates the presence of a weak peak.

Discussion

KE peaks appear at m/e 14, 15 and 17, which indicate CH_2^+, CH_3^+ and OH^+ ions respectively. The kinetic energy of the CH_2^+ ion could not be measured, as its intensity was too small. CH_3^+ and OH^+ KE ions may be produced individually or simultaneously from methanol by one or more of the following reactions:

$$CH_3OH \rightarrow CH_3OH^+ \rightarrow \begin{cases} CH_3^+ + OH & 19.2 \quad (1) \\ CH_3^+ + O + H & 23.6 \quad (2) \\ OH^+ + CH_3 & 21.0 \quad (3) \\ OH^+ + CH_2 + H & 24.5 \quad (4) \\ OH^+ + CH + 2H & 28.8 \quad (5) \\ OH^+ + C + 3H & 31.2 \quad (6) \end{cases}$$

$$CH_3OH \rightarrow CH_3OH^{2+} \rightarrow CH_3^+ + OH^+ \qquad 31.5 \quad (7)$$

The figures after each formula indicate the energy of formation in eV. computed from the measured kinetic energy in Table I and from other appropriate data,[8] assuming the conservation of the momentum of fragments.

Since the intensities of KE ions were rather weak over a fairly wide range of electron energies, the precise values of the appearance potentials could not be estimated. A comparison of the tangent of the ionization efficiency curves of the ions with that of neon indicates that the appearance potentials of the KE ions are somewhat lower than the minimum electron energy given in Table I. Hence, in the following discussions, we will confine our

1) A. Hustrulid, P. Kusch and J. T. Tate, *Phys. Rev.*, **54**, 1037 (1938).
2) J. A. Hipple, R. E. Fox and E. U. Condon, ibid., **69**, 347 (1946).
* For convenience, ions with excess kinetic energies will hereafter be described as KE ions, and ions with thermal energies corresponding to the temperature of the ion-source, as TE ions. The peak height of the KE and TE ions will be indicated by I_k and I_t respectively.
3) F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Chem. Phys.*, **22**, 394 (1954).
4) H. E. Stanton, *J. Chem. Phys.*, **30**, 1116 (1959).
5) T. Tsuchiya, *J. Chem. Phys.*, **36**, 568 (1962).
6) T. Tsuchiya, This Bulletin, **35**, 1221 (1962).
7) T. Tsuchiya, ibid., **36**, 1290 (1963).
8) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York (1957); M. B. Wallenstein, Thesis, Univ. of Utah (1951).

investigation to these reactions that require energies larger than about 30 eV. Thus, reactions 1—4 were discarded, assuming the produced fragments are not in excited states.

The peak height of the OH^+ KE ion is larger than that of the CH_3^+ KE ion, as may be seen from Table I. As both ions are focused at about the same ion acceleration voltage, their "sensitivities" are considered to be approximately equal.[9] Under the present experimental conditions, the number of ions produced in the ion source is considered to be proportional to the area of the recorded ion peak rather than to the height of the peak, and it is expected that the higher the initial kinetic energy of the ions, the larger the recorded ion peak width.[10] Even taking such circumstances and the amount of kinetic energies of the OH^+ ion and the CH_3^+ ion in Table I into consideration, the number of CH_3^+ ions of high energy is considered to be smaller than that of the OH^+ ion. Since, by reaction 7, CH_3^+ and OH^+ are expected to be produced in the same amount, reactions 5 and 6, which should produce the OH^+ KE ion only, must be considered. In the investigation described above, the possibility of a simultaneous production of CH_2^+ and OH^+ KE ions was disregarded, as the intensity of CH_2^+ was very small.

The CH_3^+ KE ion is expected to be produced only by reaction 7, which involves the disruption of a doubly-charged ion proposed by Hustrulid[1] and Mohler[3]. On this base, the two ions produced simultaneously are expected to have the same momentum. From the measured kinetic energies given Table I, the momenta of CH_3^+ and OH^+ are computed to be proportional to 9.2 and 8.0 respectively. Even taking into account the experimental errors, these two values are not expected to coincide with each other. The discrepancy may be explained as follows. Hitherto we have assumed that the two fragments produced in reaction 7 have only translational energies. However, the circumstances are quite different if we suppose that the OH^+ KE ion can carry away energy in some other form, such as rotational energy, because of the particular molecular structure of the mother substance.

Lyman,[11] in a study of the band spectrum of the hydroxyl radical produced by a discharge through water vapor, pointed out that a part of the OH radical exhibits "abnormal rotation." Many authors have studied the abnormal rotation of the hydroxyl radical,[12-15] and similar phenomena have been reported in a study of water vapor bombarded by electrons.[14,15] This phenomenon has been explained as follows. A water molecule has the equilibrium form of an isosceles triangle at the ground state, two hydrogen atoms bonding with an oxygen atom at about 105°. When a water molecule is excited to an unstable excited state by vacuum discharge or electron bombardment, however, one of the two hydrogen atoms will fly off in a direction normal to the line joining the initial position and the oxygen atom, leaving the other to rotate about the oxygen atom. The amount of the abnormal rotational energy is reported to be about 0.4 eV.[14] in this event. A similar abnormal rotation of OH is also observed in the case of ethanol.[13]

More recently Chupka,[16] in a study of appearance potentials, has pointed out that appreciable excess rotational energy may be present where the dissociation into fragments with excess kinetic energy occurs in a direction not along the line connecting the centers of the mass of the two fragments.

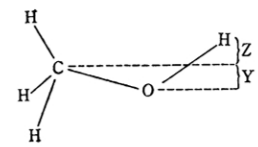

Fig. 1. Molecular structure of methanol.

C-H	1.096±0.010 Å
C-O	1.427±0.007 Å
O-H	0.956±0.015 Å
y	0.083±0.005 Å
z	0.802 Å
∠HCH	109.03±0.75°
∠COH	108.9±2°

P. Venkateswarlu and W. Gordy, *J. Chem. Phys.*, **23**, 1200 (1955).

The molecular structure of methanol is shown in Fig. 1,[17] the C–O–H angle is about 108°. If it is assumed that, according to the mechanism proposed by Hustrulid and Mohler, at first two electrons are removed from the methanol molecule, leaving a positive charge on the CH_3 and OH groups, and that then the doubly-charged molecular ion dissociates into CH_3^+ and OH^+ KE ions by means of the Coulomb repulsion, a part of the Coulomb

9) C. Berry, *Phys. Rev.*, **78**, 597 (1950).
10) C. A. McDowell and J. W. Warren, *Discussions Faraday Soc.*, **10**, 53 (1951).
11) T. Lyman, *Phys. Rev.*, **53**, 379 (1938).
12) R. J. Dwyer and O. Oldenberg, *J. Chem. Phys.*, **12**, 35 (1944).
13) K. Niira, *Busseironkenkyu*, **11**, 1 (1948) (in Japanese).
14) K. Niira, *J. Phys. Soc. Japan*, **4**, 230 (1949).
15) C. Hayakawa, *Proc. Phys. Math. Soc. Japan*, **26**, 78 (1944).
16) W. A. Chupka, *J. Chem. Phys.*, **30**, 191 (1959).
17) J. D. Swalen, ibid., **23**, 1739 (1955); P. Venkateswarlu and W. Gordy, ibid., **23** 1200 (1955).

energy may be considered to be transferred to the rotational energy of the fragment ions. Because of the structure of the parent ion, OH^+ rather than CH_3^+ is expected to obtain rotational energy in the main. If OH^+ is assumed to carry away energy by rotational motion, we may judiciously elucidate the phenomenon that the momenta of the two fragment ions in reaction 7 differ greatly, the OH^+ ion having the smaller momentum.

The difference between the sum of the measured kinetic energies of the two fragments and the total energy computed from the kinetic energy of the CH_3^+ ion is 0.5 eV. If it is assumed that the CH_3^+ ion has only a translational energy, and that vibrational motion of OH^+ is only slightly excited, a value of 0.5 eV. may be assigned to the rotational energy of the OH^+ ion. This value is considered to be compatible in order of magnitude with the value reported for the abnormal rotational energy of the OH molecule from water,[14] taking the accuracy of the present experiment into account. According to Mohler et al., the distance between two charges in the present case is estimated to 2.8 Å. However, since nothing is known about the actual distance between the charges in CH_3OH^{2+}, the postulate given above cannot be corroborated from this point of view, although the assumed distance would not be unacceptable. If the CH_3^+ ion has additional excitation energy, a smaller distance may be assumed.[3]

Summary

Fragment ions with high kinetic energies have been produced from methanol by electron impact, as in the cases of many hydrocarbons. Assuming that a fragment has a rotational energy of the order of 0.5 eV. most of the high-energy ions from methanol can be ascribed to a doubly-charged molecule ion that dissociates into two singly-charged fragments.

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