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Measurement of Negative Ions Formed by Electron Impact. V. Negative Ion Mass Spectra and Ionization Efficiency Curves of Negative Ions of *m/e* 16, 25 and 41 from Tetrahydrofuran

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The negative ion mass spectra of tetrahydrofuran, with an emphasis on their relative abundances to the positive ions under 80 eV and 40 eV electron energies, and the ionization efficiency (IE) curves of *m/e* 16(O^-), *m/e* 25(C_2H^-) and *m/e* 41(C_2HO^-) ions to the extent of 40 eV electron energies were measured. The electron impacts of 80 eV and 40 eV gave almost the same distribution of *m/e* for negative ion mass spectra. The relatively strong peaks were observed at *m/e* 24(C_2^-) ions for 80 eV and *m/e* 14(CH_2^-) ions for 40 eV, besides the commonly strong peaks of *m/e* 25(C_2H^-), *m/e* 16(O^-) and *m/e* 41(C_2HO^-) ions. The comparison of the yield of C_2H^- ions with that of $C_3H_6^+$ gave the values 9.4×10^3 and 2.7×10^4 for $C_3H_6^+/C_2H^-$ at 80 eV and 40 eV electron energies, respectively. The reaction schemes expected to occur at each onset observed in the IE curves were also discussed. It is of interest to note that C_2H^- ions are not obtained in the range of low energy of electrons, but become observable at $\sim$23.5 eV.

Recently, several studies have been reported on the measurement of negative ion mass spectra by the electron impact method.[1-6] However, they were made for a limited number of compounds, and data for the ionization efficiency curves of negative ions are very limited.[7-9] The role of negative ions is attracting increasing attention in the field of radiation chemistry. Compounds containing oxygen atom are of special interest. Warman,[10] Rzad[11] and Henz[12] have pointed out the occurrence of the negative ion-molecule reactions containing O^- ions.

This work was extended to tetrahydrofuran (C_4H_8O). Recently, the importance[13] of negative ions was suggested on the radiolysis of tetrahydrofuran-nitrous oxide system, but we haven't any informations about negative ions from tetrahydrofuran. In this paper negative ion mass spectra from tetrahydrofuran, with emphasis on their relative abundances to the positive ions, and the ionization efficiency (IE) curves of *m/e* 16 (O^-), *m/e* 25 (C_2H^-) and *m/e* 41 (C_2HO^-) ions are reported. There seem to be few papers so far on this subject.

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1) C. E. Melton, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press, New York, N. Y. (1963), p. 163.

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Experimentals

Experiments were performed on a Hitachi RMU-6D mass spectrometer equipped with T-2M ion source having a rhenium filament. The ion detection circuit consisted of a ten stage electron multiplier and of a Faraday collector. The experimental condition was as follows: total emission=20 μA, accelerating voltage =3.6 kV and electron multiplier voltage=2.5 kV. The correction method of electron energy scale was the same as that used previously.[14] The sample was of reagent grade.

Results and Discussion

Negative Ion Mass Spectra. Table 1 shows the relative abundances of negative ions at 80 eV and 40 eV electron energies. The electron impacts of 80 eV and 40 eV gave almost the same distribution of *m/e* for negative ion mass spectra. The spectra obtained are shown as follows; *m/e* 12 (C^-), *m/e* 13 (CH^-), *m/e* 14 (CH_2^-), *m/e* 15 (CH_3^-), *m/e* 16 (O^-), *m/e* 17 (OH^-), *m/e* 24 (C_2^-), *m/e* 25 (C_2H^-), *m/e* 26 ($C_2H_2^-$), *m/e* 29 ($C_2H_5^-$), *m/e* 36 (C_3^-), *m/e* 37 (C_3H^-), *m/e* 38 ($C_3H_2^-$), *m/e* 40 (C_2O^-),[*1] *m/e* 41 (C_2HO^-),[*1] *m/e* 42 ($C_2H_2O^-$) and *m/e* 43 ($C_2H_3O^-$), in which parent ion ($C_4H_8O^-$) was not detected. Since their data were taken at a pressure of 10^{-6} mmHg in the source, the possibility of ions induced by ion-molecule reactions would be ruled out.

TABLE 1. RELATIVE ABUNDANCES OF NEGATIVE IONS (NORMALIZED TO $[C_2H^-]=100$)

m/e	Probable negative ion	Relative abundances	
		80 eV	40 eV
12	C	3.0	1.0
13	CH	14.8	15.0
14	CH_2	10.9	28.3
15	CH_3	trace	—
16	O	55.5	63.4
17	OH	4.2	12.7
24	C_2	29.9	8.4
25	C_2H	100.0	100.0
26	C_2H_2	2.4	4.3
29	C_2H_5	0.7	2.3
36	C_3	8.8	3.3
37	C_3H	4.5	3.3
38	C_3H_2	1.9	8.3
40	C_2O	6.6	14.0
41	C_2HO	27.7	86.7
42	C_2H_2O	trace	2.3
43	C_2H_3O	5.39	21.7

The relatively strong peaks were observed at *m/e* 24 (C_2^-) ions for 80 eV and *m/e* 14 (CH_2^-) ions for 40 eV, besides the commonly strong peaks of *m/e* 25 (C_2H^-), *m/e* 16 (O^-) and *m/e* 41 (C_2HO^-) ions.

The reason for the absence of fragment ions such as $x=4$ at CH_x^-, $x=3$, 4 and 6 at $C_2H_x^-$, $x=3$—8 at $C_3H_x^-$, $y=4$ at C_y^-, $z=1$, 3 and 4 at C_zO^-, $u=1$—4 at CH_uO^-, $u=4$ at $C_2H_uO^-$, $u=1$—6 at $C_3H_uO^-$, and $u=1$—8 at $C_4H_uO^-$ is not well known. As described by MacNeil and Thynne,[15] however, they may be explained from the size, symmetry and bonding of the molecule, or the electron affinity of each radical. Ferguson *et al.*[16] reported the geometrical considerations for

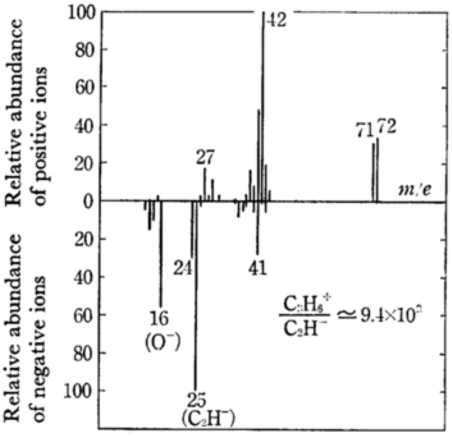

Fig. 1a

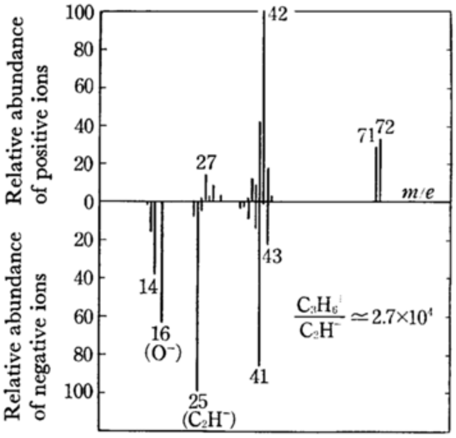

Fig. 1b

Fig. 1. Positive and negative ion mass spectra of tetrahydrofuran (source pressure; $\sim 10^{-6}$ mmHg).
a 80 eV b 40 eV

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[14] S. Tsuda, A. Yokohata and M. Kawai, This Bulletin, **42**, 614 (1969).

[*1] Since no formation of $C_3H_4^-$ (*m/e* 40) and $C_3H_5^-$ (*m/e* 41) ions from butane,[1] nitropropane[14] and propylalcohol[1,20] was observed, these ions might be ruled out.

[15] K. A. G. MacNeil and J. C. J. Thynne, *Trans, Faraday Soc.*, **64**, 2112 (1968).

[16] E. E. Ferguson, F. C. Fehsenfeld and A. L. Schmeltekopf, *J. Chem. Phys.*, **47**, 3085 (1967).

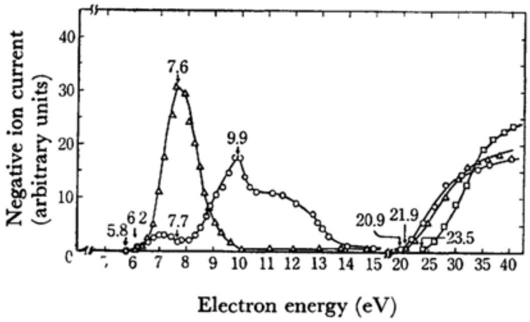

Fig. 2. Ionization efficiency curves of negative ions of m/e 16, 25 and 41 obtained from tetrahydrofuran.
○ m/e 16 (O^-) □ m/e 25 (C_2H^-)
△ m/e 41 (C_2HO^-)

negative ion processes but their discussions are only made for a few simple molecules.

The most intense peak was observed at C_2H^- ions. The situation is quite similar to acetylene, ethane, *n*-butane and *n*-butyl alcohol.1) This finding seems to show that C_2H^- ion is relatively stable and its electron affinity is relatively high.

A relatively large change in their relative abundances with electron energies (80→40 eV) was found at C^-, CH_2^-, OH^-, C_2^-, $C_2H_5^-$, C_3^-, $C_3H_2^-$, C_2HO^- and $C_2H_3O^-$ ions. This would be interpreted by electron energy dependency of cross section of the reaction (ion pair formation) which governs the formation of each ion.

Figure 1 shows the negative ions mass spectra at 80 eV and 40 eV electron energies, in relation to the positive ion mass spectra.

The comparison of the yield of C_2H^- ions with that of $C_3H_6^+$ ions (the most intense peak among the positive ions) gave $C_3H_6^+/C_2H^- \simeq 9.4\times 10^3$ and 2.7×10^4 at 80 eV and 40 eV electron energies, respectively.

IE Curves. Figure 2 shows the IE curves of O^-, C_2H^- and C_2HO^- ions to the extent of 40 eV.

O^- Ions. It can be understood that three processes contribute to their formation. The first process appears at ~5.8 eV, the second process at ~7.7 eV[*2] and the third process at ~20.9 eV. The shape of IE curves suggests the dissociative capture process and ion pair formation.

The onset of ~5.8 eV would be interpreted with reaction (1), because it gives a reasonable value of ~3.64 eV17) for D(RC–O),[*3] by combining 5.8 eV with EA(O)=1.47 eV.18)

$$C_4H_8O + e^- \rightarrow C_4H_8 + O^- \qquad (1)$$

Then, $\Delta H_f(C_4H_8O) = -2.2$ eV19) and $\Delta H_f(O^-) = 1.09$ eV20) result in $\Delta H_f(C_4H_8) \simeq 2.51$ eV.[*4]

For the second and third processes, the following reactions may be assigned.

$$C_4H_8O + e^- \rightarrow C_4H_8{}^* + O^- \qquad (2)$$

$$C_4H_8O + e^- \rightarrow C_4H_7 + H + O^- \qquad (3)$$

$$C_4H_8O + e^- \rightarrow C_4H_7^+ + H + O^- + e^- \qquad (4)$$

However, the appearance potential (~5.8 eV) of reaction (1) and C–H bond energy (4.3 eV15)) would give a value of ~10.1 eV for the appearance of reaction (3) which is inconsistent with ~7.7 eV. Thus, reaction (3) is excluded. Although speculative because of unknown value of C_4H_8,* reaction (2) appears to fit the second process.

On the other hand, the formation of reaction (4) requires a higher energy than reaction (3)—energy to be required for at least ionizing C_4H_7. The appearance potential of ~20.9 eV gives $IP(C_4H_7) \approx 10.8$ eV, which seems a little too large to be accepted.21) However, a small allowance of the kinetic energy of fragment ions at AP≈20.9 eV acts for $IP(C_4H_7)$ toward its decrement. Hence, the assignment of reaction (4) for the third process would be reasonable.

C_2H^- Ions. It is characteristic that C_2H^- ions are not obtained in the range of low energy and become observable at electron energy of ~23.5 eV. Probably, ion pair formation would responsible for this onset value.

C_2HO^- Ions. These ions show the typical dissociative electron capture process in the range of electron energies from ~6.2 to ~10 eV. Appearance potential of ~21.9 eV seems to correspond to ion pair formation.

For each onset value of these ions the reactions (5), (6) and (7) may be expected.[*5] However, their exact determination is difficult, because of difficulty of the assignment of ΔH_f values which is due to the unknown structure of negative ions and radicals produced.

For C_2H^- ions;

$$C_4H_8O + e^- \rightarrow C_2H^- + C_2H_4O^+ + H_2 + H + e^- \qquad (5)$$

[*2] Since the tailing due to the 1st process might be overlapped with the appearance of the 2nd process, the exact determination of appearance potential of the 2nd process is difficult. In this work, the minimum values in the IE curves have been discussed as by Schulz (G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959)).

17) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London (1958), p. 275.

[*3] Tetrahydrofuran contains two C–O bonds. D(RC–O) means the average value of C–O bond energy.

18) B. Edlen, *J. Chem. Phys.*, **33**, 98 (1960).

19) R. C. Cass, S. E. Fletcher, C. T. Moltimer, H. D. Springall and C. T. White, *J. Chem. Soc.*, **1958**, 1406.

20) S. Tsuda, A. Yokohata and M. Kawai, to be published.

[*4] The structure of C_4H_8 shown in reaction (1) is not well known. It is probably in the form of tetramethylene.

21) R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

[*5] There are other possibilities too.

For C_2HO^- ions;

$$C_4H_8O + e^- \rightarrow C_2HO^- + C_2H_5 + H_2 \quad (6)$$

$$\rightarrow C_2HO^- + C_2H_4^+ + H + H_2 + e^- \quad (7)$$

It should be emphasized that the main negative ionic species to be considered on the radiolysis of tetrahydrofuran are not parent ions but *m/e* 25 (C_2H^-), *m/e* 41 (C_2HO^-) and *m/e* 16 (O^-) ions.

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