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Measurement of Negative Ions Formed by Electron Impact. IV. Negative Ion Mass Spectra and Ionization Efficiency Curves of Negative Ions of *m/e* 17 and 16 from *n*-Propyl and Isopropyl Alcohols

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The negative ion mass spectra of *n*- and iso-propyl alcohols, with emphasis on their relative yields to the positive ions under 80 eV, 40 eV and 15 eV electron energies, and the ionization efficiency (IE) curves of OH^- and O^- ions to the extent of 50 eV electron energies were measured. In both cases, the electron impacts of 80 eV and 40 eV gave almost the same negative ion mass spectra, in which the relatively strong peaks of *m/e* 16 (O^-), *m/e* 17 (OH^-) and *m/e* 25 (C_2H^-) ions except for the decrement of C_2H^- ions in 40 eV for isopropyl alcohol were characteristic. For *n*-propyl alcohol, the ratio of the yield of CH_2OH^+ ions to that of O^- ions (CH_2OH^+/O^-) gave the values of 6.9×10^4 and 1.9×10^5 in 80 eV and 40 eV. For isopropyl alcohol the values of $C_2H_4OH^+/OH^-$ were 3.3×10^4 and 6.4×10^4 in 80 eV and 40 eV, respectively. The comparison of the yield of negative ion in 10 eV with that of positive ion in 15 eV gave $CH_2OH^+/O^-=2.0\times10^4$ and $C_2H_4OH^+/OH^-=2.3\times10^3$. Each appearance potential observed in IE curves is well interpreted by the following reactions. [OH^- ions], for the first process C_3H_7OH(*n*- or iso-)$+e^-\rightarrow OH^-+C_2H_4+CH_2+H$, for the second process C_3H_7OH(*n*- or iso-)$+e^-\rightarrow OH^-+CH_3+CH_2+CH_2^++e^-$ or $OH^-+C_2H_4+CH_2+H^++e^-$. [O^- ions], for the first process C_3H_7OH(*n*- or iso-)$+e^-\rightarrow O^-+C_2H_5+CH_3$, for the second process C_3H_7OH(*n*- or iso-)$+e^-\rightarrow O^-+C_2H_4+CH_3+H$ or $O^-+C_2H_3+CH_3+H_2$ and for the third process C_3H_7OH(*n*- or iso-)$+e^-\rightarrow O^-+C_3H_7$(*n*- or iso-)$+H^++e^-$ or $O^-+C_3H_5+H_2+H^++e^-$.

Recently, several studies have been reported on the measurement of negative ion mass spectra by the electron impact method.[1-6] However, they were only made for limited kinds of compounds. Furthermore, data of the ionization efficiency (IE) curves of negative ions are very limited.[7-9] On the other hand, the role of negative ions is attracting increasing attention in the field of radiation chemistry. Compounds containing oxygen atom are of particular interest. Warman *et al.*[10,11] have pointed out the occurrence of the negative ion-molecule reactions containing O^- ions.

The authors reported previously the results of measurement of negative ion mass spectra obtained from nitroalkanes in relation to electron energies,[12] and of IE curves of NO_2^-, O^-, $CH_2NO_2^-$,[12] CN^- and CNO^- [13] ions.

This work was extended to *n*- and iso-propyl alcohols. Emphasis was placed on the relative yields of negative ions to the positive ions and on the measurement of the IE curves of OH^- and O^- ions.[*1]

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[2] E. W. McDaniel, "Collision Phenomena in Ionized Gases," John Wiley & Sons Inc., New York (1964), p. 368.

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[4] R. T. Aplin, H. Budzikieweiz and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 3180 (1965).

[5] C. E. Melton and P. S. Rudolf, *J. Chem. Phys.*, **47**, 1771 (1967).

[6] D. F. Munro, J. E. Ahnell and W. S. Koski, *J. Phys. Chem.*, **72**, 2682 (1968).

[7] L. G. Christophorou, R. N. Compton, G. S. Hurst and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 536 (1966).

[8] L. G. Christophorou and R. N. Compton, *Health Physics*, **13**, 1277 (1967).

[9] T. Sugiura, T. Seguchi and K. Arakawa, This Bulletin, **40**, 2992 (1967).

[10] J. M. Warman, *Nature*, **213**, 382 (1967); *J. Phys. Chem.*, **72**, 52 (1968).

[11] S. J. Rzad and J. M. Warman, *ibid.*, **72**, 3013 (1968).

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

[13] S. Tsuda, A. Yokohata and M. Kawai, *ibid.*, **42**, 1515 (1969).

[*1] Recently, the measurement of ethyl alcohol was reported. However, no detailed discussion was made. (H. Hotta, T. Sugiura and H. Kurihara, The 11th Meeting of Radiation Chemistry, Tokyo (1968)).

Experimental

Experiments were performed on a Hitachi RMU-6D mass spectrometer equipped with the T-2M ion source having a rhenium filament. The ion detection circuit consisted of a ten stage electron multiplier and of a Faraday collector. Conditions for the experiment and the method for correction of the electron energy scale were the same as those described previously[12] except for the use of accelerating voltage of 2.4 kV and electron multiplier voltage of 1.8 kV. The compounds used were of research grade and no further purifications were made.

Results and Discussion

Negative Ion Mass Spectra. Figures 1 and 2 show the negative ion mass spectra for *n*- and iso-propyl alcohols in 80 eV, 40 eV and 10 eV electron energies, in relation to the positive ion mass spectra in 80 eV, 40 eV and 15 eV.*2

For the electron impact of 80 eV and 40 eV, the peaks of negative ions obtained commonly in both samples are as follows; m/e 12 (C^-), m/e 13 (CH^-), m/e 14 (CH_2^-), m/e 16 (O^-), m/e 17 (OH^-), m/e 24 (C_2^-), m/e 25 (C_2H^-), m/e 41 (C_2HO^-), m/e 43 ($C_2H_3O^-$), m/e 57 ($C_3H_5O^-$) and m/e 59 ($C_3H_7O^-$).

The formation of m/e 41, 43, 57 and 59 ions shows that loss of hydrogen by negative ion formation is almost entirely restricted to that of an odd number of hydrogen atoms.

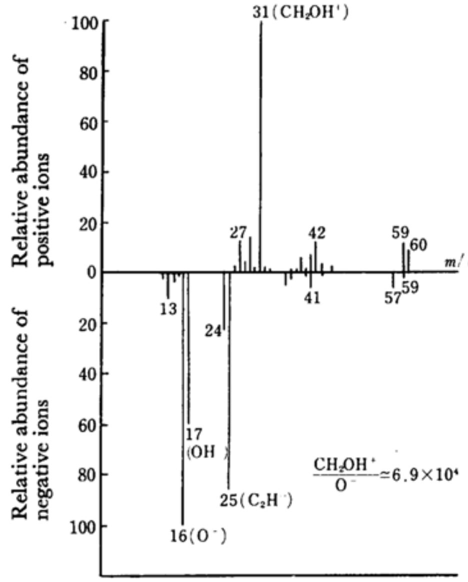

Fig. 1a.

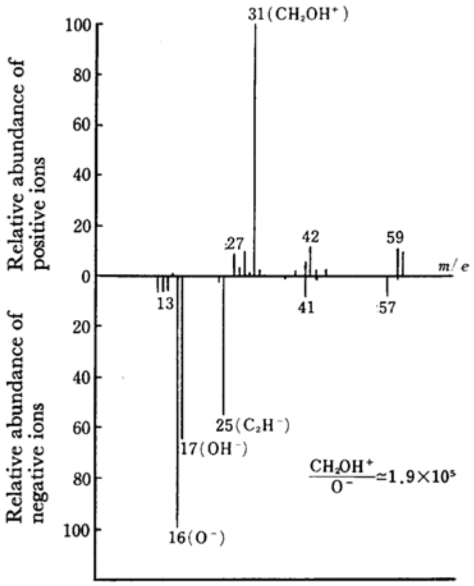

Fig. 1b.

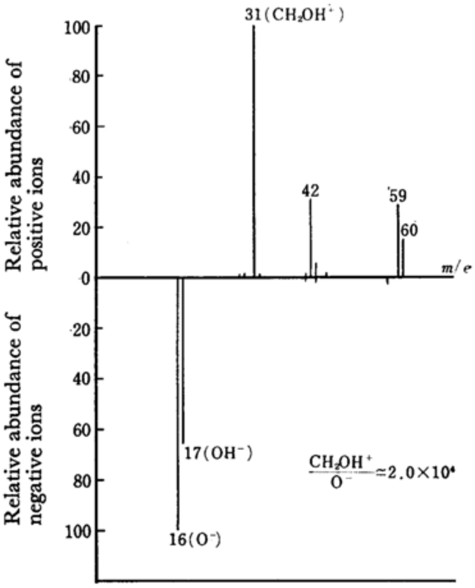

Fig. 1c.

Fig. 1. Positive and negative ion mass spectra of *n*-propyl alcohol.
(a) 80 eV
(b) 40 eV
(c) 15 eV for positive ions, 10 eV for negative ions

The most intense peaks were O^- ions for *n*-propyl alcohol and OH^- ions for isopropyl alcohol. A relatively large change in their relative yields with electron energies (80→40 eV) was found especially in C^-, C_2^- and C_3^- ions for *n*-propyl alcohol, and O^-, C_2^-, C_2H^-, C_3^- and C_2O^- ions for isopropyl alcohol. The general patterns of spectra in 80 eV

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*2 Since the positive ions obtained in 10 eV electron energies are very limited, the data for 15 eV were conveniently used for comparison with the yield of negative ions in 10 eV.

showed a relatively good consistency with those obtained by Melton[1] in 90 eV except for a smaller peak of $C_3H_7O^-$ ions for the two samples.

The comparsion of the yield of O^- ions with of CH_2OH^+ ions (the most intense peak among the positive ions) for *n*-propyl alcohol and of OH^- ions with $C_2H_4OH^+$ ions (the most intense peak among the positive ions) for isopropyl alcohol gave $CH_2OH^+/O^-=6.9\times10^4$ and $C_2H_4OH^+/OH^-=3.3\times10^4$ for 80 eV electron energies, $CH_2OH^+/O^-=1.9\times10^5$ and $C_2H_4OH^+/OH^-=6.4\times10^4$ for 40 eV electron energies respectively.

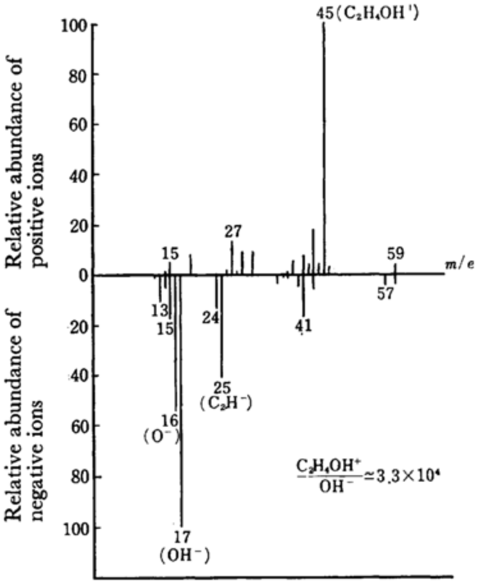

Fig. 2a.

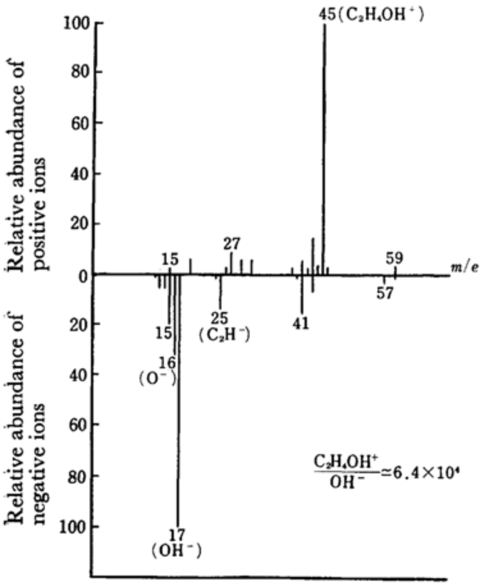

Fig. 2b.

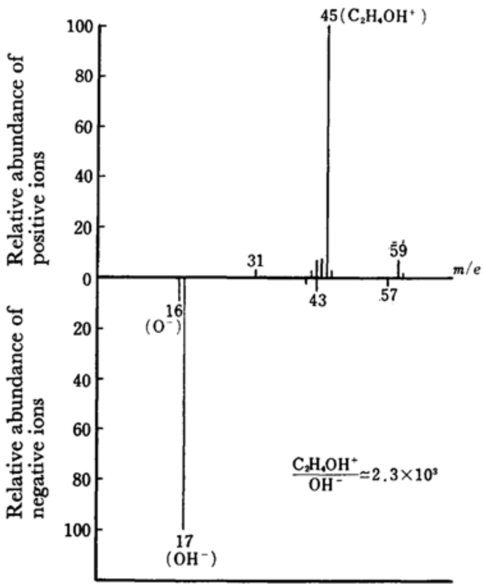

Fig. 2c.

Fig. 2. Positive and negative ion mass spectra of isopropyl alcohol.
(a) 80 eV
(b) 40 eV
(c) 15 eV for positive ions, 10 eV for negative ions

In 10 eV electron energies, O^- and OH^- ions for *n*-propyl alcohol and OH^- ions for isopropyl alcohol predominated other negative ions. When the yields of O^- and OH^- ions in 10 eV electron energies are compared with those of positive ions of the most intense peak obtained in 15 eV electron energies, $CH_2OH^+/O^-=2.0\times10^4$ for *n*-propyl alcohol and $C_2H_4OH^+/OH^-=2.3\times10^3$ for isopropyl alcohol were obtained respectively.

Since the data were taken at a pressure of $\sim10^{-6}$ mmHg, the possibility of ions induced by ion-molecule reactions would be ruled out.

The differences in negative ion mass spectra in both samples, especially of O^- and OH^- ions, will be also discussed later in relation to electron energies on the basis of measurement results of IE curves.

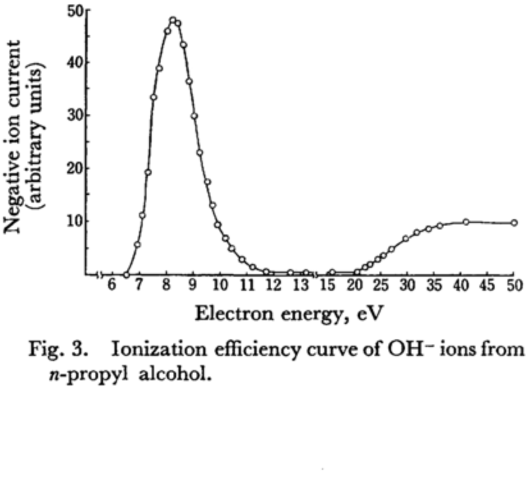

Fig. 3. Ionization efficiency curve of OH^- ions from *n*-propyl alcohol.

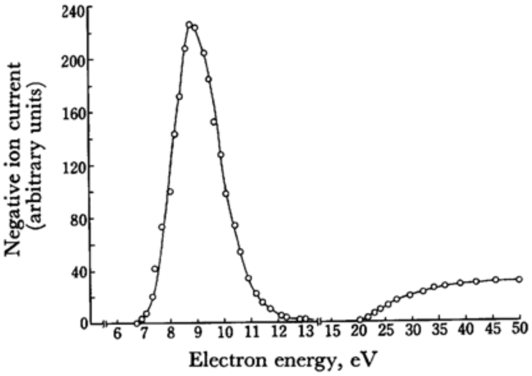

Fig. 4. Ionization efficiency curve of OH^- ions from isopropyl alcohol.

IE Curves. *OH^- Ions.* Figures 3 and 4 show the IE curves for *m/e* 17 (OH^-) ions obtained from *n*- and iso-propyl alcohols respectively. It can be understood that in both cases two processes contribute to their formation. The first process appears at ~6.5 eV for *n*-propyl alcohol and at ~6.7 eV for isopropyl alcohol. The second process appears at ~20.5 eV and ~20.1 eV. The shape of IE curves suggests clearly the dissociative electron capture for the first process and the ion pair formation for the second process.

Generally speaking, the appearance potential (AP) of reaction (1) can be experssed by Eq. (2), if the kinetic energies of fragment are ignored and the ions formed are in ground state.

$$XYZ + e^- \rightarrow X^- + Y + Z \tag{1}$$

$$AP_{calc} = \Delta H = \Delta H_f(X^-) + \Delta H_f(Y) + \Delta H_f(Z) - \Delta H_f(XYZ) \tag{2}^{*3}$$

In the case of ion pair formation ($Y \rightarrow Y^+$), the following equation holds.

$$AP_{calc} = \Delta H = \Delta H_f(X^-) + \Delta H_f(Y^+) + \Delta H_f(Z) - \Delta H_f(XYZ) \tag{3}$$

From Eqs. (2) and (3), the schemes of the most plausible reactions expected to occur at the onset values of each AP_{obs} were sought.

For the first process, the following reactions may be considered.

$$n\text{-}C_3H_7OH + e^- \rightarrow OH^- + C_3H_7 \quad (AP_{calc}=2.22\text{ eV}) \tag{4}$$

$$\rightarrow OH^- + CH_3 + C_2H_4 \quad (AP_{calc}=3.19\text{ eV}) \tag{5}$$

$$\rightarrow OH^- + C_2H_5 + CH_2 \quad (AP_{calc}=4.86\text{ eV}) \tag{6}$$

$$\rightarrow OH^- + CH_2 + H + C_2H_4 \quad (AP_{calc}=6.56\text{ eV}) \tag{7}$$

$$\rightarrow OH^- + CH_3 + 2CH_2 \quad (AP_{calc}=7.65\text{ eV}) \tag{8}$$

In the estimation of AP_{calc}, the values of ΔH_f (n-C_3H_7OH)$=-2.70$ eV, $\Delta H_f(OH^-)=-1.44$ eV,[*4] $\Delta H_f(C_3H_7)=0.96$ eV, $\Delta H_f(CH_3)=1.39$ eV, ΔH_f(C_2H_4)$=0.54$ eV, $\Delta H_f(C_2H_5)=1.10$ eV, $\Delta H_f(CH_2)=2.5$ eV and $\Delta H_f(H)=2.26$ eV were used.[14] Among reactions (4)—(8), the reaction (7) is strongly expected because the consistency of AP_{calc} with AP_{obs} (~6.5 eV) is best for reaction (7).

For the second process,[*5] the following reactions may be considered.

$$n\text{-}C_3H_7OH + e^- \rightarrow OH^- + C_3H_7^+ + e^- \quad (AP_{calc}=10.91\text{ eV}) \tag{9}$$

$$\rightarrow OH^- + CH_3^+ + C_2H_4 + e^- \quad (AP_{calc}=13.03\text{ eV}) \tag{10}$$

$$\rightarrow OH^- + C_2H_5^+ + CH_2 + e^- \quad (AP_{calc}=13.64\text{ eV}) \tag{11}$$

$$\rightarrow OH^- + C_2H_4^+ + CH_3 + e^- \quad (AP_{calc}=13.70\text{ eV}) \tag{12}$$

$$\rightarrow OH^- + CH_2^+ + C_2H_5 + e^- \quad (AP_{calc}=16.76\text{ eV}) \tag{13}$$

$$\rightarrow OH^- + CH_3^+ + 2CH_2 + e^- \quad (AP_{calc}=17.49\text{ eV}) \tag{14}$$

$$\rightarrow OH^- + CH_2^+ + CH_3 + CH_2 + e^- \quad (AP_{calc}=19.55\text{ eV}) \tag{15}$$

$$\rightarrow OH^- + H^+ + CH_2 + C_2H_4 + e^- \quad (AP_{calc}=20.16\text{ eV}) \tag{16}$$

A relatively good consistency of AP_{calc} of reaction (16) with AP_{obs} (~20.5 eV) suggests the possibility of the occurrence of reaction (16). A small allowance of the excess kinetic energies of the fragment ions, however, may also permit the possibility of reaction (15). In the present stage when their details are not well known, it is difficult to discuss this problem further.

The same reactions would also be assigned for the first and second processes in isopropyl alcohol, in which the use of ΔH_f(i-C_3H_7OH)$=-2.84$ eV is required.[*6]

O^- Ions. Figures 5 and 6 show the IE curves for *m/e* 16 (O^-) ions obtained from *n*- and iso-propyl alcohols respectively. The two samples gave similar curves except for a small peak at ~11.2 eV for *n*-propyl alcohol. If this peak is ignored, we see that the first process appears at ~6.2 eV and ~6.4 eV, the second process at the same value,

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[*3] $\Delta H_f(X)$: heat of formation of X.

[*4] To be estimated from $\Delta H_f(OH)=0.39$ eV and $EA(OH)=1.83$ eV (L. M. Branscob, *Phys. Rev.*, **148**, 11 (1966)).

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

[*5] For the value of $H_f(Y^+)$, see Ref. 14.

[*6] In some cases, rearrangement should be taken into consideration.

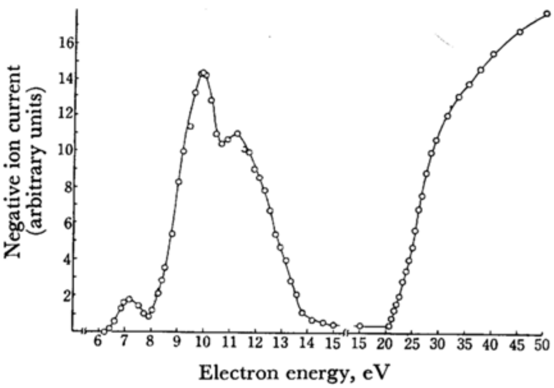

Fig. 5. Ionization efficiency curve of O⁻ ions from *n*-propyl alcohol.

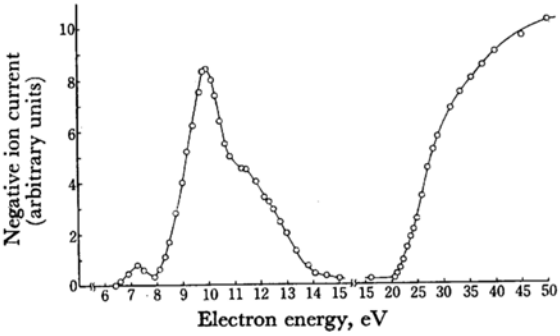

Fig. 6. Ionization efficiency curve of O⁻ ions from isopropyl alcohol.

~7.9 eV[*7] and the third process at ~20.8 eV and ~20.5 eV.

In the same manner as OH⁻ ions, the reaction schemes which correspond to each AP_{obs} value were sought by using $\Delta H_f(O^-)=1.09$ eV[*8] and the known values of ΔH_f(products).[14] For the first process, the following reactions may be considered.

$$n\text{-}C_3H_7OH + e^- \rightarrow O^- + C_3H_6 + H_2 \quad (AP_{calc}=4.00\text{ eV}) \quad (17)$$

$$\rightarrow O^- + C_2H_5 + CH_3 \quad (AP_{calc}=6.28\text{ eV}) \quad (18)$$

For the second process,

$$n\text{-}C_3H_7OH + e^- \rightarrow O^- + C_3H_7 + H \quad (AP_{calc}=7.01\text{ eV}) \quad (19)$$

$$\rightarrow O^- + C_3H_5 + H_2 + H \quad (AP_{calc}=7.35\text{ eV}) \quad (20)$$

$$\rightarrow O^- + C_2H_4 + CH_3 + H \quad (AP_{calc}=7.98\text{ eV}) \quad (21)$$

$$\rightarrow O^- + C_2H_3 + H_2 + CH_3 \quad (AP_{calc}=8.01\text{ eV}) \quad (22)$$

$$\rightarrow O^- + C_3H_6 + 2H \quad (AP_{calc}=8.52\text{ eV}) \quad (23)$$

$$\rightarrow O^- + C_3H_4 + H_2 + 2H \quad (AP_{calc}=10.23\text{ eV}) \quad (24)$$

For the third process,

$$n\text{-}C_3H_7OH + e^- \rightarrow O^- + CH_3^+ + H + C_2H_4 + e^- \quad (AP_{calc}=17.82\text{ eV}) \quad (25)$$

$$\rightarrow O^- + C_2H_4^+ + H + CH_3 + e^- \quad (AP_{calc}=18.49\text{ eV}) \quad (26)$$

$$\rightarrow O^- + H^+ + C_3H_7 + e^- \quad (AP_{calc}=20.61\text{ eV}) \quad (27)$$

$$\rightarrow O^- + H^+ + C_3H_5 + H_2 + e^- \quad (AP_{calc}=20.95\text{ eV}) \quad (28)$$

Among these reactions, the possibility of reaction (18) for the first proc[illegible] of reaction (21) or (22) for the second process and of reaction (27) or (28) for the third process can be strongly expected because their AP_{calc} values are almost consistent with each AP_{obs} value of ~6.2 eV, ~7.9 eV and ~20.8 eV respectively. For the same reason as described in the case of OH⁻ ions, however, we cannot exclude the possibility of reactions (19), (20) or (25) and (26). The same interpretation is also applied for isopropyl alcohol. Reaction (24) might correspond to the process appearing at ~11.2 eV of the third peak observed for *n*-propyl alcohol. This is, however, a tentative interpretation and still open to question.

The yield of negative ions (OH⁻, O⁻ ions) depends on the cross section of formation process of negative ions. Figures 3 and 4 show that the maximum yield of OH⁻ ions is obtained at 8.2 eV for *n*-propyl alcohol and at 8.7 eV for isopropyl alcohol and is larger in isopropyl alcohol. The cross section of reaction (7) expected to occur at 8.2 eV and 8.7 eV electron energies is larger by a factor of 5 in isopropyl alcohol. On the other hand, Figs. 5 and 6 show that the maximum yield of O⁻ ions is obtained at almost the same electron energies, ~10 eV in the range of zero to 30 eV, and their yield is larger by a factor of ~1.6 in *n*-propyl alcohol.

It should be noted that (1) O⁻ ions for *n*-propyl alcohol and OH⁻ ions for isopropyl alcohol showed always the most intense peaks irrespective of electron energies used, (2) their yields under 80 eV and

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[*7] Since the tailing due to the first process might overlap with the appearance of the second process, the exact determination of appearance potential of the second process is difficult. In this work, the minimum values in IE curves have been taken into consideration (G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959)).

[*8] $\Delta H_f(O^-)=\Delta H_f(O)-EA(O^-)=2.56-1.47=1.09$ (eV) (L. M. Baranskob, D. S. Burch, S. J. Smith and S. Geltman, *Phys. Rev.*, **111**, 504 (1958)).

40 eV electron energies were lower by a factor of 10^5—10^4 than those of positive ions, (3) even if the energy is decreased to 10 eV, their yields were still lower by a factor of 10^4—10^3 compared with those of positive ions in 15 eV, and (4) contrary to our expectation, the simple dissociative electron capture and ion pair processes such as reactions (4) and (9)*9 could not be found.

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*9 An apparatus with extremely high sensitivity seems to be required for the detection of reaction (9), $C_3H_7^+ + OH^- + e^-$. The cross section of this reaction appears to be extremely small. (S. Tsuda and W. H. Hamill, *Advan. Mass Spectry.*, **3**, 249 (1965))