Measurement of Negative Ions Formed by Electron Impact. VIII. Ionization Efficiency Curves of Negative Ions from Methyl and Ethyl Cyanides

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The ionization efficiency (I.E) curves of *m/e* 26(CN^-), 27(HCN^-), 38(C_2N^-) and 39($CHCN^-$) ions from methyl and ethyl cyanides, besides 40(CH_2CN^-) ions from methyl cyanide, and 50(C_3N^-) ions from ethyl cyanide were measured to the extent of about 25 eV electron energies under the pressure of $\sim10^{-6}$ mmHg by a Hitachi RMU-6D mass spectrometer. Schemes of plausible reactions expected to appear at each onset value observed in the respective IE curves were sought thermochemically by using ΔH_f values of the reactants and products. The estimation method of unknown ΔH_f values is described also. It should be noted that for CN^- ions one process (probably, $R+CN^-$) was observed in lower energies than 2 eV; C_2N^- ions are expected to be formed with excess energy; also, for CN^- and HCN^- ions rather strange phenomena of the decrement of their signal intensities with increasing electron energies were observed in the range of higher energies. Moreover, the IE curves of C_3N^- ions in the higher energy region were well interpreted in terms of the overlapping phenomena of dissociative capture process with ion pair formation process. It was found from this work that EA(HCN) $\gtrsim$1 eV, $\Delta H_f(CHCN^-)$ $\sim$3.2 eV, EA(CHCN) $\gtrsim$1.1 eV and EA(CH_2CN) $\gtrsim$1.6 eV. For the electron affinity of C_2N a value $\gtrsim$2.3 eV is tentatively introduced on the basis of EA(C_3N)=2.4 eV, EA(C_5N)=2.3 eV, and EA(CN)=3.4 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 restricted to a limited number of compounds. Data on the ionization efficiency (IE) curves of negative ions are limited[7-12] and hardly any detailed discussions are given.

The authors reported the measurement results of the IE curves of NO_2^-, O^-, $CH_2NO_2^-$, CN^-, and CNO^- ions from nitroalkanes,[13] of O^- and OH^- ions from *n*-propyl and isopropyl alcohols,[14] O^-, C_2H^-, and C_2HO^- ions from tetrahydrofuran,[15] and Cl^- ions from alkyl chlorides,[16] and discussed plausible reaction schemes expected to appear at respective onset values from a thermochemical viewpoint. The work was extended to methyl and ethyl cyanides.[17] Emphasis was placed on the measurements of the IE curves of CN^-, HCN^-, C_2N^-, and $CHCN^-$ ions from both compounds, and CH_2CN^- ions from methyl cyanide and C_3N^- ions from ethyl cyanide.

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 a Faraday collector. All measurements were made with a total emission current of 20 μA, an accelerating voltage of 3.6 kV and an electron multiplier voltage of 2.8 kV, under a pressure of $\sim10^{-6}$ mmHg in the source. The ionizing current then varied from 10.5 μA at above 10 eV to 6.4 μA at $\sim$3 eV.[16] The energy scale was calibrated in every measurement by the vanishing current method as compared with the appearance potential of *m/e* 16(O^-) ions from carbon monoxide, carbon dioxide and oxygen, as described previously.[16] The repeller voltage was adjusted to the best condition for collecting the ions. The chemicals used were of research grade.

Results and Discussion

IE curves. *CN^- Ions*: Figure 1 shows the IE curves of *m/e* 26 (CN^-) ions[18] obtained from methyl and ethyl cyanides. It can be seen that in every case at least two processes contribute to their formation. The first process appears at the energies lower than 2 eV and the second processes[19] do at $\sim$5.3 eV and

1) C. E. Melton, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press, New York, N. Y. (1963), p. 163.
2) E. W. McDaniel, "Collision Phenomena in Ionized Gases," John Wiley & Sons Inc., New York (1964), p. 368.
3) F. Fiquat-Fayard, *Actions Chim. Biol. Radiations*, **8**, 31 (1965).
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) R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967).
10) T. Sugiura, T. Seguchi, and K. Arakawa, This Bulletin, **40**, 2992 (1967).
11) W. T. Nalf and C. D. Cooper, *J. Chem. Phys.*, **49**, 2784 (1968).
12) R. N. Compton, J. A. Stockdale, and P. W. Reinhardt, *Phys. Rev.*, **180**, 111 (1969).
13) S. Tsuda, A. Yokohata, and M. Kawai, This Bulletin., **42** 614, 1515 (1969).
14) S. Tsuda, A. Yokohata, and M. Kawai, *ibid.*, **42**, 2514 (1969).
15) S. Tsuda, A. Yokohata, and M. Kawai, *ibid.*, **42**, 3115 (1969).
16) S. Tsuda, A. Yokohata, and M. Kawai, *ibid.*, **43**, 1649 (1970).

17) A report was recently made on the measurement of methyl cyanide in which the isotope effect and mechanism of formation of CH_3CN^- ions were mainly discussed. Hardly any detailed discussions were given on fragment negative ions. (T. Sugiura and K. Arakawa. The 22nd Annual Meeting of Chemical Society of Japan, Tokyo (1969)).
18) The possibility of $C_2H_2^-$ for *m/e* 26 ions can be excluded because of few signals of $C_2H_2^-$ ions from hydrocarbons.[1]
19) Since the tailing from the 1st process may overlap with the appearance of the 2nd process, it is generally difficult to determine exactly the appearance potential of the latter. In this case, however, it was not so difficult.

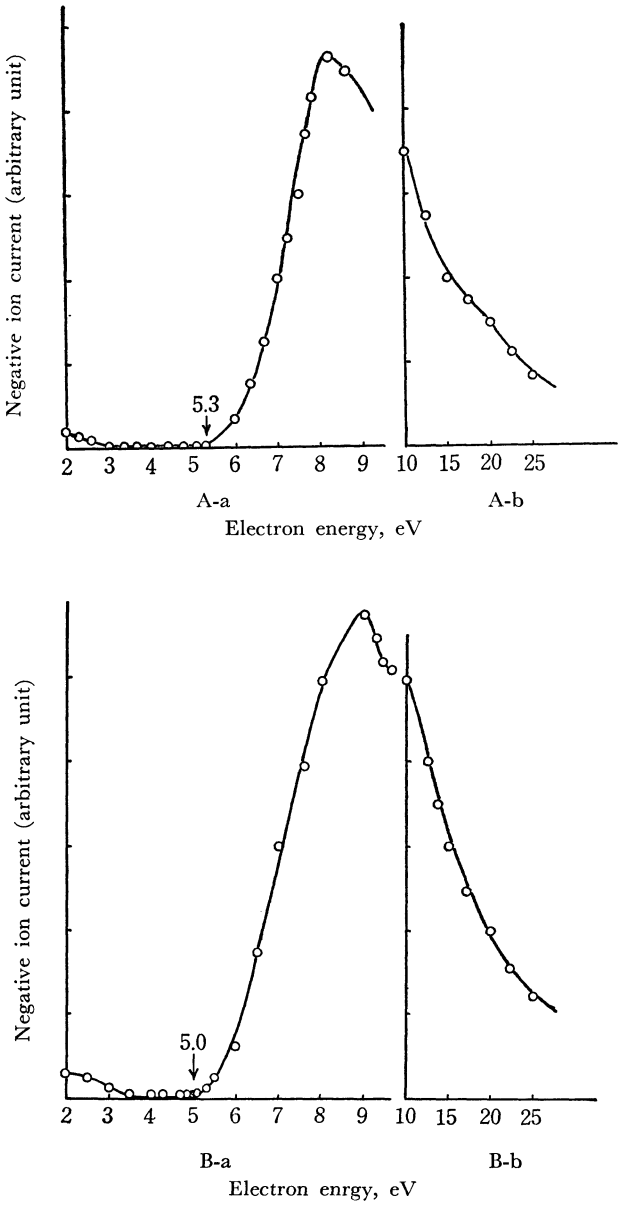

Fig. 1. Ionization efficiency curves of m/e 26(CN^-) ions from CH_3CN and C_2H_5CN.
A: CH_3CN B: C_2H_5CN

~5.0 eV, respectively, being of almost the same shape as the IE curves. They suggest dissociative electron capture processes except for the part in a higher energy region in which there is the possibility of an ion pair formation process.

The appearance potential (AP) of reaction (1) can be expressed by Eq. (2), if the kinetic energies of fragments are ignored and the ions formed are in ground state.

$$XYZ + e^- \rightarrow X^- + YZ \quad (1)$$

$$AP_{calc} = \Delta H = \Delta H_f(X^-) + \Delta H_f(YZ) - \Delta H_f(XYZ) \quad (2)^{20)}$$

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

20) $\Delta H_f(X)$: heat of formation of X.

$$AP_{calc} = \Delta H = \Delta H_f(X^-) + \Delta H_f(YZ^+) - \Delta H_f(XYZ) \quad (3)$$

The schemes of plausible reactions expected to appear at each onset value (AP_{obs}) observed in the IE curves were sought thermochemically from Eqs. (2) and (3). For the first process, the following reactions might be assigned.

$$CH_3CN + e^- \rightarrow CN^- + CH_3 \quad (AP_{calc} = 1.08\,eV) \quad (4)$$

$$C_2H_5CN + e^- \rightarrow CN^- + C_2H_5 \quad (AP_{calc} = 1.08\,eV) \quad (5)$$

In the estimation of AP_{calc}, the values of $\Delta H_f(CH_3\text{-}CN) = 0.78$ eV,[21] $\Delta H_f(C_2H_5CN) = 0.49$ eV, $\Delta H_f(CH_3) = 1.39$ eV, $\Delta H_f(C_2H_5) = 1.10$ eV and $\Delta H_f(CN^-) = 0.47$ eV[22] were used.

The correspondence of AP_{calc} values to AP_{obs} values (below 2 eV) suggests the possibility of reactions (4) and (5). However, the cross section of these reactions seems to be very small. McDowell and Warren[23] failed to detect CN^- signals in this region, but this would probably be due to the fact that their detection method was not so improved as in the present time.

For the second process, although complicated, the following reactions might be considered.

$$CH_3CN + e^- \rightarrow CN^- + CH_2 + H \quad (AP_{calc} \simeq 4.45\,eV) \quad (6)$$

$$CH_3CN + e^- \rightarrow CN^- + CH + H_2 \quad (AP_{calc} \simeq 5.85\,eV) \quad (7)$$

$$C_2H_5CN + e^- \rightarrow CN^- + C_2H_3 + H_2 \quad (AP_{calc} \simeq 2.6\,eV) \quad (8)$$

$$C_2H_5CN + e^- \rightarrow CN^- + C_2H_4 + H \quad (AP_{calc} \simeq 2.78\,eV) \quad (9)$$

$$C_2H_5CN + e^- \rightarrow CN^- + C_2H_2 + H + H_2 \quad (AP_{calc} \simeq 4.59\,eV) \quad (10)$$

Estimation of each AP_{calc} value was made by use of values of $\Delta H_f(CH_2) = 2.5$ eV, $\Delta H_f(H) = 2.26$ eV, $\Delta H_f(CH) = 6.16$ eV, $\Delta H_f(C_2H_3) = 2.83$ eV, $\Delta H_f(C_2H_4) = 0.54$ eV and $\Delta H_f(C_2H_2) = 2.35$ eV.[24] Although the consistency of AP_{calc} values with AP_{obs} values is not so good, reactions (6) and (10) would probably correspond to each onset value. In these cases, the difference of 0.8—0.4 eV between AP_{calc}

21) By combining $D(CH_3\text{-}CN) = 4.48$ eV with $\Delta H_f(CH_3) = 1.39$ eV and $\Delta H_f(CN) = 3.87$ eV, a value of 0.78 eV for $\Delta H_f(CH_3\text{-}CN)$ can be estimated. Also, by assuming $D(CH_3\text{-}CN) = D(C_2H_5\text{-}CN)$, and using $\Delta H_f(C_2H_5) = 1.10$ eV, a value of $\Delta H_f(C_2H_5CN) = 0.49$ eV is obtained. (T. L. Cottrell, "The Strengths of Chemical Bonds," London, Butterworths (1958), p. 197. R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961). C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

22) To be estimated from $EA(CN) = 3.4$ eV and $\Delta H_f(CN) = 3.87$ eV (refer to (13)). EA(CN): electron affinity of CN.

23) C. A. McDowell and J. W. Warren, *Trans. Faraday Soc.*, **48**, 1084 (1952).

24) refer to Bernecker's paper in Ref. 21. The use of another value (4.23 eV) of $\Delta H_f(CH)$, as described in Ref. 25, gives $AP_{calc} = 3.92$ eV for the occurrence of reaction (7). However, the possibility of reaction (7) accompanied with the formation of H_2 due to the rearrangement would be probably smaller than that of reaction (6).

values (4.45 eV and 4.59 eV) and AP_{obs} values (5.3 eV and ~5.0 eV) might be assessed to the excess kinetic energy of fragments. Although McDowell and Warren[23] reported the value of ~5.6 eV for the appearance of CN^- ions from methyl cyanide, it might be interpreted to correspond to the second process in this work. However, they failed to detect the CN^- signals in the range below ~5.6 eV and no discussions were made in detail for CN^- ions from methyl cyanide. If a value of ~5.6 eV corresponds to the reaction of (CH_3+ CN^-), the excess kinetic energy of fragments seems to be too high. It would be reasonable to expect the occurrence of reaction (6). It is possible at least energetically.

Reasons for the existence of a long tail extending to the range from ~10 eV to the higher energies are not well known. Even if the overlapping of ion pair formation (reaction (11) or (12)) with reactions (6) or (10) is taken into consideration, the decrement of signal intensity with an increasing electron energy is a little strange. The possibility of the ion pair formation could be excluded.

$$CH_3CN + e^- \rightarrow CN^- + CH_3^+ + e^- \quad (AP_{calc} = 10.92\ eV) \quad (11)$$

$$C_2H_5CN + e^- \rightarrow CN^- + C_2H_5^+ + e^- \quad (AP_{calc} = 9.78\ eV) \quad (12)$$

HCN^- Ions: Figure 2 shows the IE curves of *m/e* 27 ions from methyl and ethyl cyanides. The possibility of $C_2H_3^-$ ions might be excluded from the fact that there is no occurrence of $C_2H_3^-$ ions from ethyl alcohol, propyl alcohol,[1] and tetrahydrofuran.[15] The two cyanides gave curves similar to each other. We see that the first process appears at ~2 eV for methyl cyanide and below 2 eV for ethyl cyanide, and the second process at ~6.0 eV and ~5.0 eV, respectively.

The appearance potential of reactions (13) and (14) can be estimated to be AP_{calc}=3.02 eV and AP_{calc}= 1.45 eV by using $\Delta H_f(HCN)$=1.30 eV[23]

$$CH_3CN \rightarrow HCN + CH_2 \quad (AP_{calc} = \Delta H_{calc} = 3.02\ eV) \quad (13)$$

$$C_2H_5CN \rightarrow HCN + C_2H_4 \quad (AP_{calc} = \Delta H_{calc} = 1.45\ eV) \quad (14)$$

Combining of AP_{calc}=3.02 eV with AP_{obs} ≃2 eV leads to EA(HCN) ≃1 eV.[25] Then, the appearance potential of the reaction containing HCN^- ion in (14) can be estimated to be ≲0.45 eV.

For the second process, reactions (15) and (16) might be expected, where a value of ΔH(CH)=4.23 eV[26] and a value of $\Delta H_f(HCN^-)$=0.3 eV are used.

$$CH_3CN + e^- \rightarrow HCN^- + CH + H \quad (AP_{calc} \simeq 6.01\ eV) \quad (15)$$

$$C_2H_5CN + e^- \rightarrow HCN^- + C_2H_3 + H \quad (AP_{calc} \simeq 4.90\ eV) \quad (16)$$

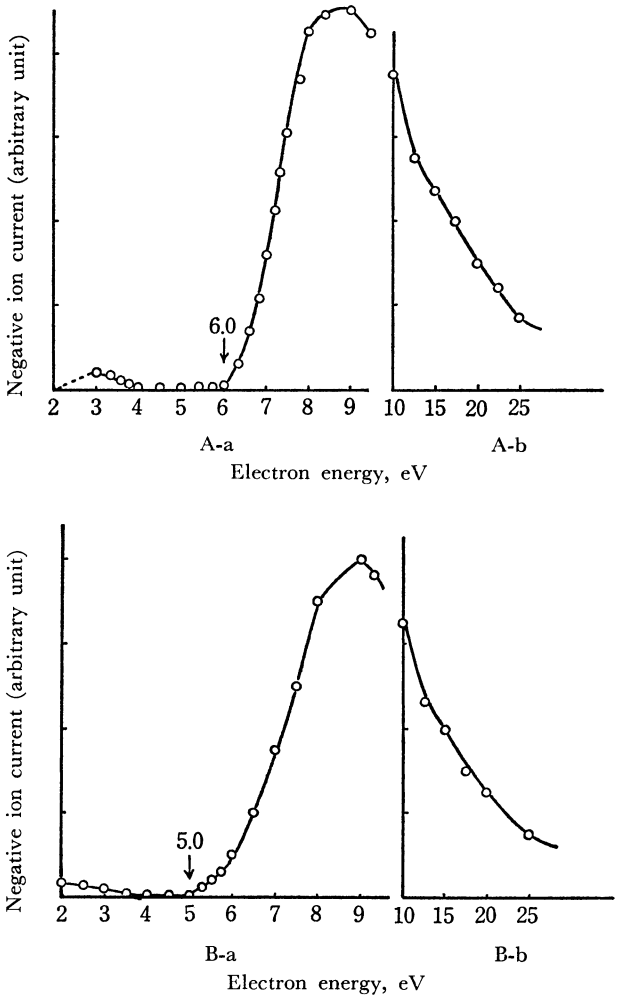

Fig. 2. Ionization efficiency curves of *m/e* 27(HCN^-) ions from CH_3CN and C_2H_5CN.
A: CH_3CN B: C_2H_5CN

The AP_{calc} values are in good agreement with the AP_{obs} values (~6.0 eV and ~5.0 eV).

Let us discuss the possibility of $C_2H_3^-$ ions. On the basis of $\Delta H_f(N)$=4.9 eV,[27] the AP_{calc} value of reaction (17) can be estimated as follows.

$$CH_3CN \rightarrow C_2H_3 + N \quad (AP_{calc} = \Delta H_{calc} = 6.95\ eV) \quad (17)$$

Thus, if an electron affinity of C_2H_3 is assumed to be ~0.95 eV, the value of AP_{obs} ≃6.0 eV can be reasonably interpreted. If so, AP_{calc} of reaction (18) is given as ~5.2 eV which is almost consistent with AP_{obs} ≃5.0 eV.

$$C_2H_5CN + e^- \rightarrow C_2H_3^- + H_2 + CN \quad (AP_{calc} \simeq 5.2\ eV) \quad (18)$$

However, no formation of $C_2H_3^-$ ions from ethyl alcohol, propyl alcohol, and tetrahydrofuran would exclude the possibility of this ion. Moreover, the difficulty of interpretation of the first process by $C_2H_3^-$ ions affords additional evidence for their exclusion.

C_2N^- Ions: Figure 3 shows that we have

25) Since the ions might be formed with an excess kinetic energy, this shows the lowest value.

26) To be estimated from D(CH–H)=3.99 eV, ΔH_f(H)=2.26 eV and $\Delta H_f(CH_2)$=2.5 eV (refer to Cottrell's article Ref. 21, p. 174).

27) V. I. Vedeneyev, L. V. Gurvich, V. N. Kandrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Bulter Tranner Ltd., London (1966), p. 118.

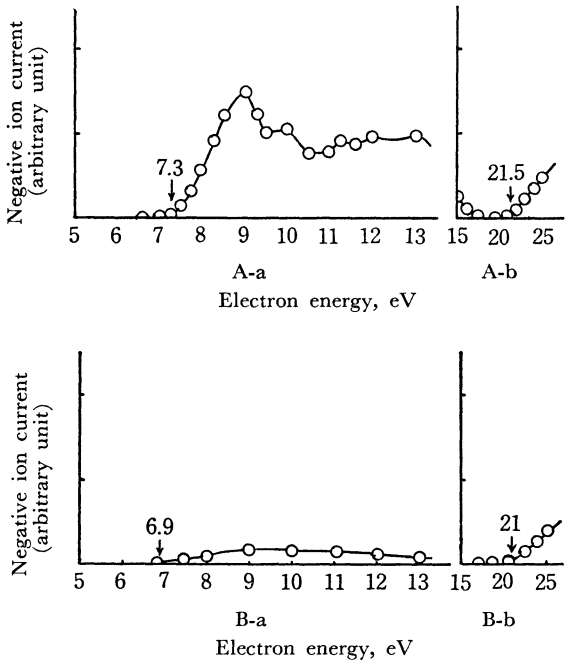

Fig. 3. Ionization efficiency curves of m/e 38(C_2N^-) ions from CH_3CN and C_2H_5CN.
A: CH_3CN B: C_2H_5CN

$AP_{obs} \simeq 7.3$ eV for the first process and $AP_{obs} \simeq 21.5$ eV for the second process in methyl cyanide, and $AP_{obs} \simeq 6.9$ eV and $AP_{obs} \simeq 21$ eV for the respective processes in ethyl cyanide. The IE curves from methyl cyanide show a relatively complicated shape for the first process, and a simple shape for that in ethyl cyanide. For the first process, we have

$$CH_3CN + e^- \rightarrow C_2N^- + H_2 + H \quad (AP_{calc} \leq 4.48\ eV) \quad (19)$$

$$CH_3CN + e^- \rightarrow C_2N^- + 3H \quad (AP_{calc} \leq 9.00\ eV) \quad (20)$$

$$C_2H_5CN + e^- \rightarrow C_2N^- + CH_3 + H_2 \quad (AP_{calc} \leq 3.90\ eV) \quad (21)$$

$$C_2H_5CN + e^- \rightarrow C_2N^- + CH_4 + H \quad (AP_{calc} \leq 3.99\ eV) \quad (22)$$

$$C_2H_5CN + e^- \rightarrow C_2N^- + CH_2 + H_2 + H \quad (AP_{calc} \leq 7.25\ eV) \quad (23)$$

$$C_2H_5CN + e^- \rightarrow C_2N^- + CH_3 + 2H \quad (AP_{calc} \leq 8.42\ eV) \quad (24)$$

In the estimation of AP_{calc}, a value of $\Delta H_f(C_2N^-) \leq 3$ eV was used which can be computed from $\Delta H_f(C_2N) = 5.3$ eV[28] and $EA(C_2N) \geq 2.3$ eV assumed tentatively. Evidently, we have no value of $EA(C_2N)$ while $EA(C_3N)$ and $EA(C_5N)$ are known to be 2.4 eV and 2.3 eV,[28] being $EA(CN) = 3.4$ eV. Here, a value of ≥ 2.3 eV was assigned tentatively for $EA(C_2N)$.

If reaction (19) is assumed to correspond to the first process, the difference (≥ 2.8 eV) between AP_{obs} ($\simeq 7.3$ eV) and AP_{calc} ≤ 4.48 eV might be ascribed to the excess kinetic energy of fragments. In the same way, the assignment of reaction (21) or (22) for the first process in ethyl cyanide may give a value $\gtrsim 3$ eV as the excess kinetic energy of fragments. In the present stage, however, this is still open to question.

For the second process, we have

$$CH_3CN + e^- \rightarrow C_2N^- + H^+ + H_2 + e^- \quad (AP_{calc} \leq 18.08\ eV) \quad (25)$$

$$C_2H_5CN + e^- \rightarrow C_2N^- + CH_3^+ + H_2 + e^- \quad (AP_{calc} \leq 13.70\ eV) \quad (26)$$

$$C_2H_5CN + e^- \rightarrow C_2N^- + H^+ + CH_4 + e^- \quad (AP_{calc} \leq 17.59\ eV) \quad (27)$$

The assignment of reactions (25) and (27) seems also to require a kinetic energy $\gtrsim 3.5$ eV for the fragments.

CHCN⁻ Ions: The IE curves (Fig. 4) show that three processes in methyl cyanide and two processes in ethyl cyanide contribute to the formation of m/e 39 ($CHCN^-$) ions, where in the former the first process appears at $\sim$2.3 eV, the second process at $\sim$7.0 eV and the third process at $\sim$20 eV; in the latter the respective processes appear at $\sim$6.5 eV and $\sim$16.5 eV.

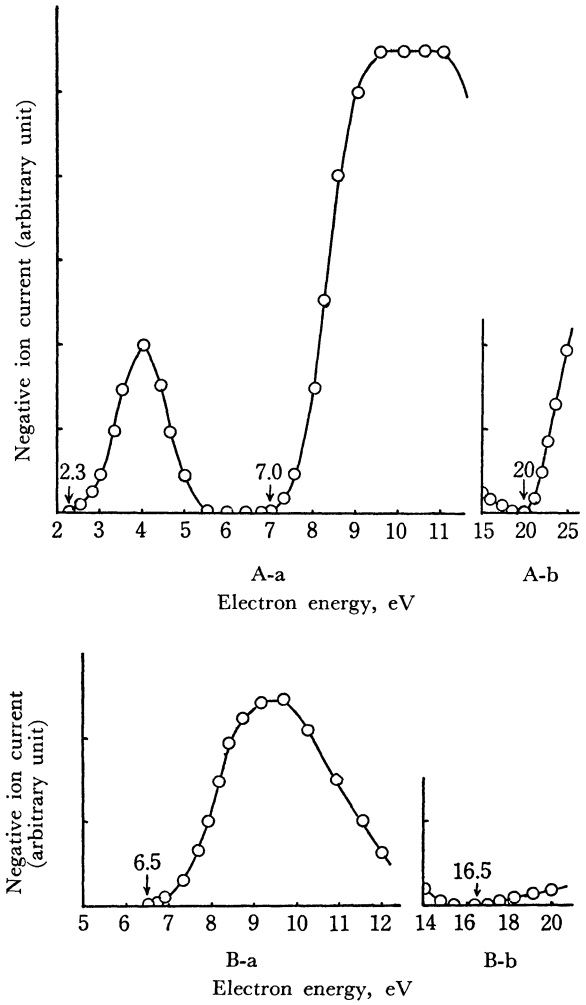

Fig. 4. Ionization efficiency curves of m/e 39 ($CHCN^-$) ions from CH_3CN and C_2H_5CN.
A: CH_3CN B: C_2H_5CN

28) V. H. Dibeler, R. M. Reese, and J. L. Franklin, *J. Amer. Chem. Soc.*, **83**, 1813 (1961).

Since the ΔH_f(CHCN) and EA(CHCN) values are not known, it is impossible to estimate AP_{calc} values of the reactions assigned for each process. By setting $\Delta H_f(CHCN^-) = \Delta H_f(CHCN) - EA(CHCN) = X$ (eV), let us estimate the AP_{calc} values of the reactions to be assigned for each onset value in the IE curves.

For the first process in methyl cyanide,

$$CH_3CN + e^- \rightarrow CHCN^- + H_2$$
$$(AP_{calc} = X - 0.78 \text{ (eV)}) \quad (28)$$

For the second process in methyl cyanide and the first process in ethyl cyanide,

$$CH_3CN + e^- \rightarrow CHCN^- + 2H$$
$$(AP_{calc} = X + 3.74 \text{ (eV)}) \quad (29)$$
$$C_2H_5CN + e^- \rightarrow CHCN^- + CH_3 + H$$
$$(AP_{calc} = X + 3.16 \text{ (eV)}) \quad (30)$$

Combining these values with AP_{obs} values (2.3 eV, 7.0 eV, and 6.5 eV) we obtain the results 3.08 eV, 3.26 eV, and 3.34 eV for X; $\bar{X}$=3.23 eV. Then the AP_{calc} values of reactions expected for the last process can be estimated as follows.

For the third process in methyl cyanide and the second process in ethyl cyanide.

$$CH_3CN + e^- \rightarrow CHCN^- + H^+ + e^-$$
$$(AP_{calc} = 20.56 \text{ eV}) \quad (31)$$
$$C_2H_5CN + e^- \rightarrow CHCN^- + CH_3^+ + H + e^-$$
$$(AP_{calc} = 16.23 \text{ eV}) \quad (32)$$

The consistency of the AP_{calc} values with the AP_{obs} values ($\sim$20 eV and $\sim$16.5 eV) is relatively good. In other words, the assignment of each reaction and a value of $\Delta H_f(CHCN^-) \simeq 3.2$ eV might be reasonable.

Next, let us estimate a value of ΔH_f(CHCN). The appearance potential of reaction (33) gives the value of $\Delta H_f(CHCN^+) \simeq 15.9$ eV.[29] An estimation of ΔH_f(CHCN) is needed for the value of IP(CHCN)[30] but it is not known.

$$CH_3CN \rightarrow CHCN^+ + H_2 + e^- \quad (AP = 15.1 \text{ eV}) \quad (33)$$

According to Mulliken's assignment, the values of $IP(C_2H_6)$ (=11.65 eV[31]) and the onset ($\sim$11.7 eV)[32] in the IE curves of $C_2H_5OH^+$ ions from ethyl alcohol are considered to correspond to the removal of an electron from the C–C orbital. On the other hand, the removal of an electron from the C–H π orbital requires a value of about 13 eV.[33] Thus, let us assign tentatively IP(CHCN)$\simeq$11.7 eV, the energy required for the removal of an electron from the C–C orbital. We can then get a value of 4.2 eV for ΔH_f(CHCN). If so, a value of $\Delta H_f(CH_2CN) = 1.96$ eV[34] would lead to D(H–CHCN)$\simeq$4.5 eV. Judging from the usual C–H bond energy, this value seems to be reasonable.

Thus, EA(CHCN) could be estimated by combining the values of ΔH_f(CHCN) and $\Delta H_f(CHCN^-)$. Since the fragment ions may be formed with an excess kinetic energy, the following procedure is preferable. Let us assume EA(CHCN)=Y (eV) and excess kinetic energy=Z (eV). Then, the AP_{calc} of reaction (34) is estimated as follows.

$$CH_3CN + e^- \rightarrow CHCN^- + H_2$$
$$(AP_{calc} = 3.4 - Y + Z) \quad (34)$$

By combining this value with $AP_{obs} \simeq 2.3$ eV, we can get a value of EA(CHCN)$\gtrsim$1.1 eV.

CH_2CN^- Ions: The IE curves (Fig. 5) represent the typical dissociative electron capture process. We have $AP_{obs} \simeq 1.8$ eV.

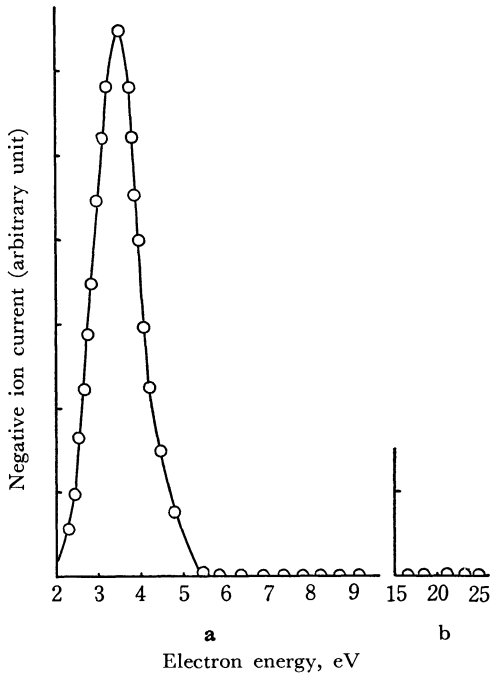

Fig. 5. Ionization efficiency curves of *m/e* 40 $(CH_2CN)^-$ ion from CH_3CN.

The appearance potential of reaction (35)[34] has been reported to be 3.44 eV which gives a value of $\Delta H_f(CH_2CN) = 1.96$ eV.

$$CH_3CN \rightarrow CH_2CN + H$$
$$(AP_{calc} = \Delta H_{calc} = 3.44 \text{ eV}) \quad (35)$$

The value EA(CH_2CN)$\geq$1.64 eV is obtained by combining AP_{calc} (=3.44 eV) with AP_{obs} (1.8 eV).

For the ion pair formation the following reaction is expected.

$$CH_3CN + e^- \rightarrow CH_2CN^- + H^+ + e^-$$
$$(AP_{calc} = 15.4 \text{ eV}) \quad (36)$$

However, few signals in the range of energies from $\sim$5.4 eV to 25 eV appear to exclude the possibility of ion pair formation.

C_3N^- Ions: Figure 6 shows that the first process appears at $\sim$9.4 eV and the second process at $\sim$13.9 eV, although their cross sections are small.

On the basis of $\Delta H_f(C_3N) = 131$ kcal/mol[28] and EA(C_3N)=55 kcal/mol,[28] the AP_{calc} values of reac-

29) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic press, New York, N. Y. (1957), p. 274.
30) IP(X): ionization potential of X.
31) R. S. Mulliken, *J. Chem. Phys.*, **3**, 519 (1935).
32) S. Tsuda and W. H. Hamill, *Advan. Mass Spectry.*, **3**, 249 (1965).
33) C. A. McDowell and B. C. Cox, *J. Chem. Phys.*, **22**, 946 (1954).
34) R. F. Pottie and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 4737 (1961).

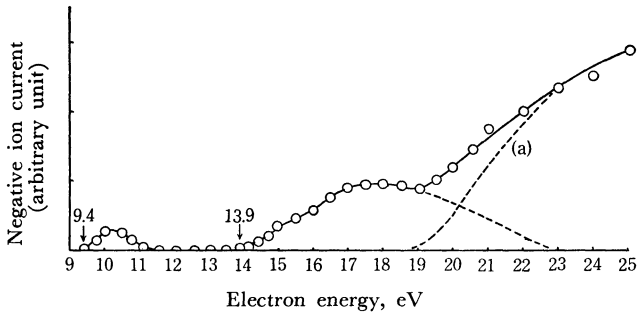

Fig. 6. Ionization efficiency curves of m/e 50(C_3N^-) ions from C_2H_5CN.

tions (37), (38), (39), and (40) can be estimated as follows:

$$C_2H_5CN + e^- \rightarrow C_3N^- + 2H_2 + H \quad (AP_{calc} = 5.09\,eV) \quad (37)$$

$$C_2H_5CN + e^- \rightarrow C_3N^- + H_2 + 3H \quad (AP_{calc} = 9.59\,eV) \quad (38)$$

$$C_2H_5CN + e^- \rightarrow C_3N^- + 5H \quad (AP_{calc} = 14.09\,eV) \quad (39)$$

$$C_2H_5CN + e^- \rightarrow C_3N^- + 2H_2 + H^+ + e^- \quad (AP_{calc} = 18.69\,eV) \quad (40)$$

Relatively good consistencies of AP_{calc} values (9.59 and 14.09 eV) with AP_{obs} values ($\sim$9.4 and $\sim$13.9 eV) suggest the possibility of reactions (38) and (39). Reaction (37) could be excluded.

The shape of the IE curve in the energy region higher than $\sim$18.7 eV can be well interpreted in terms of the overlapping due to the ion pair formation (reaction (40)) appearing at 18.69 eV. The IE curves expected from the ion pair formation process are expressed by a dotted curve, (a) in Fig. 6, which is consistent with the usual picture presumed for the ion pair formation.