Measurement of Negative Ions Formed by Electron Impact. IX. Negative Ion Mass Spectra and Ionization Efficiency Curves of Negative Ions of *m/e* 25, 26, 27, 38, 39, 40 and 50 from Acrylonitrile

Satoru TSUDA, Akira YOKOHATA, and Toshikatsu UMABA

Department of Chemistry, Faculty of Engineering, University of Hiroshima, Senda-machi, Hiroshima 730

(Received November 4, 1972)

Negative ion mass spectra of acrylonitrile were measured for the electron energies of 80, 40 and 9.5 eV. Emphasis was laid on the abundance of the negative ions relative to the positive ions measured for the energies of 80, 40 and 15 eV, respectively. The ionization efficiency (IE) curves were also determined up to 25 eV for the ions of *m/e* 25(C_2H^-), 26(CN^-), 27(HCN^-), 38(C_2N^-), 39($CHCN^-$), 40(CH_2CN^-) and 50(C_3N^-). The electron impact of 80 eV and 40 eV gave almost the same distribution of *m/e* for negative ion mass spectra. Besides the most intense peak of CN^- ions, relatively strong peaks of C_3N^-, C_2H^-, C_2^- and C_2N^- ions were observed. In 9.5 eV, CN^- ions predominated over other ions. Yields of the ions showed a good linearity against the pressure in the range used for usual chemical analysis, irrespective of electron energy. Comparison of the yield of CN^- ions with that of $C_2H_3CN^+$ gave the values 1.2×10^4 and 1.9×10^4 for $C_2H_3CN^+/CN^-$ at 80 eV and 40 eV, respectively, and 47.6 at 9.5 eV (15 eV for the positive ions). The plausible reaction schemes expected to occur at each onset observed in the IE curves were also sought thermochemically by using ΔH_f values of the reactant and products. A value $\gtrsim 2$ eV was obtained for the electron affinity of C_2H.

Studies have been reported on the measurement of negative ion mass spectra by the electron impact method.[1–5] However, they were restricted to a limited number of compounds. Data of ionization efficiency (IE) curves of negative ions are also very limited.[6–10]

IE curves were given for NO_2^-, O^-, $CH_2NO_2^-$, CN^- and CNO^- ions from nitroalkanes,[11] O^- and OH^- ions from *n*-propyl and isopropyl alcohols,[12] O^-, C_2H^- and C_2HO^- ions from tetrahydrofuran,[13] Cl^- ions from alkyl chlorides,[13] CN^-, HCN^-, C_2N^- and $CHCN^-$ ions from methyl and ethyl cyanides.[15] Investigation was extended to acrylonitrile. In this paper we report on negative ion mass spectra for 80eV, 40eV and 9.5 eV, with emphasis on relative abundances to the positive ions for 80 eV, 40 eV and 15 eV, and the IE curves of *m/e* 25(C_2H^-), 26(CN^-), 27(HCN^-), 38(C_2N^-), 39 ($CHCN^-$), 40(CH_2CN^-) and 50(C_3N^-) ions.[16]

Experimental

Experiments were performed on a Hitachi RMU-6D mass spectrometer equipped with a T-2M ion source having a rhenium filament. The ion detector consisted of a ten-stage electron multiplier and a Faraday collector. Experimental conditions: total emission current=20 μA, ion accelerating voltage=3.6 kV, electron multiplier voltage=2.8 kV, sourve pressure $\simeq 10^{-6}$ mmHg. The ionizing current varied from 10.5 μA above 10 eV to 6.4 μA at ~3 eV.[14] The energy scale was calibrated in every measurement by the vanishing current method in comparison with the ionization potential of argon (for positive ions) and the appearance potential of *m/e* 16(O^-) from carbon monoxide, carbon dioxide and oxygen (for negative ions).[11,14] The repeller voltage was adjusted to the best condition to collect positive and negative ions. The sample used was of reagent grade.

Results and Discussion

Negative Ion Mass Spectra. The relative abundances of negative ions for 80 eV, 40 eV and 9.5 eV electron energies are shown in Table 1. Since the data were taken at a pressure of $\sim10^{-6}$ mmHg in the source, the possibility of ions being induced by ion-molecule reactions may be ruled out. The electron impact of 80 eV and 40 eV gave almost the same distribution of *m/e* for negative ion mass spectra.

The spectra obtained are as follows.

m/e 12(C^-), *m/e* 13(CH^-), *m/e* 14(CH_2^-), *m/e* 24(C_2^-), *m/e* 25(C_2H^-), *m/e* 26(CN^-), *m/e* 27(HCN^-), *m/e* 36(C_3^-), *m/e* 37(C_3H^-), *m/e* 38(C_2N^-), *m/e* 39($CHCN^-$), *m/e* 40(CH_2CN^-), *m/e* 50(C_3N^-), *m/e* 51(HC_3N^-), *m/e* 52($H_2C_3N^-$)

The parent ion (*m/e* 53, $H_3C_3N^-$) was not detected.

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 on 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. Amer. Chem. Soc.*, **87**, 3180 (1965).

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

6) L. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Rienhardt, *J. Chem. Phys.*, **45**, 536 (1966).

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

8) R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967).

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

10) R. N. Compton, J. A. Stockdale, and P. W. Reinhardt, *Phys. Rev.*, **180**, 111 (1969).

11) S. Tsuda, A. Yokohata, and M. Kawai, This Bulletin, **42**, 614, 1515 (1969).

12) S. Tsuda, A. Yokohata, and M. Kawai, *ibid.*, **42**, 2514 (1969).

13) S. Tsuda, A. Yokohata, and M. Kawai, *ibid.*, **42**, 3115 (1969).

14) S. Tsuda, A. Yokohata, and M. Kawai, *ibid.*, **43**, 1649 (1970).

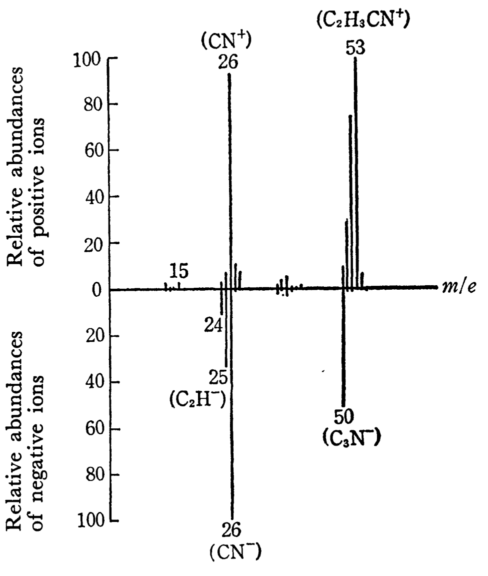
15) S. Tsuda, A. Yokohata, and T. Umaba, *ibid.*, **44**, 1486 (1971).

16) Recently, the measurement of IE curves of a few ion species was reported. However, no discussion is given on the plausible reaction schemes expected to appear at each onset value (T. Sugiura, Discussion Meeting of the Research Reactor Institute of Kyoto University, January 14, (1968)).

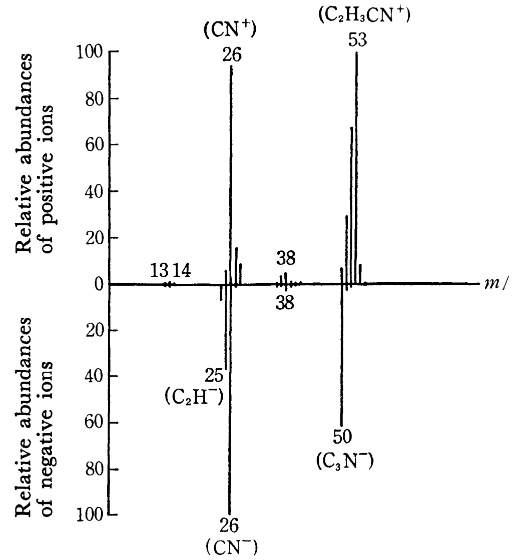
TABLE 1. RELATIVE ABUNDANCES OF NEGATIVE IONS (NORMALIZED TO $[CN^-]=100$)

m/e	Probable negative ion	Relative abundances		
		80 eV	40 eV	9.5 eV
12	C	1.46	0.76	
13	CH	0.39	0.85	0.07
14	CH_2	0.06	0.05	0.04
24	C_2	11.20	7.26	0.10
25	C_2H	34.20	36.80	0.91
26	CN	100.00	100.00	100.00
27	HCN	1.47	1.26	1.32
36	C_3	2.39	1.76	
37	C_3H	0.58	0.78	
38	C_2N	2.90	3.55	0.46
39	CHCN	0.89	0.81	2.31
40	CH_2CN	0.04	0.04	0.26
50	C_3N	50.80	61.70	4.45
51	C_2HCN	1.86	2.88	0.78
52	C_2H_2CN	0.47	0.76	0.02

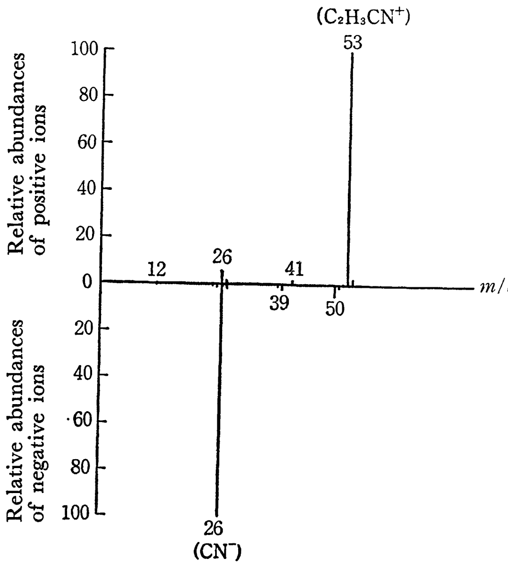
Relatively strong peaks were observed at *m/e* 50(C_3N^-), *m/e* 25(C_2H^-) and *m/e* 24(C_2^-) ions for 80 eV and 40 eV, besides the most intense peak at *m/e* 26(CN^-). The situation is quite similar to that for ethyl cyanide. This shows that C_3N^-, C_2H^- and C_2^- ions are stable, while electron affinities of C_3N and C_2 between them are known to be $EA(C_3N)=2.4$ eV[17] and $EA(C_2)=3.1$ eV.[18] However, the values of $EA(C_2H)$ and $EA(C_2N)$ are not known. The change of relative abundances with electron energies (80→40 eV) was relatively great for C^-, CH^-, C_2^-, C_3^-, C_3HN^- and $C_3H_2N^-$ ions.



(a)



(b)



(c)

Fig. 1. Positive and negative ion mass spectra of acrylonitrile (Pressure in the source, $\sim 10^{-6}$ mmHg).
(a): 80 eV, $C_2H_3CN^+/CN^- \simeq 1.2\times10^4$
(b): 40 eV, $C_2H_3CN^+/CN^- \simeq 1.9\times10^4$
(c): 15 eV for positive ions, 9.5 eV for negative ions, $C_2H_3CN^+/CN^- \simeq 47.6$

In 9.5 eV electron energy, *m/e* 26(CN^-) ions predominated over other negative ions. Since the dissociative electron capture process governs the reaction in a lower energy region, the yield should depend on the cross section of each process. The IE curves of CN^-, C_3N^-, C_2H^-, C_2N^-, HCN^-, $CHCN^-$ and CH_2CN^- ions are given.

Figure 1 shows the negative ion mass spectra for 80 eV, 40 eV and 9.5 eV electron energies in relation to the positive ion mass spectra at 80 eV, 40 eV and 15 eV.[19] Comparison of the yield of CN^- ions with

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

18) C. 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. 194.

19) Since the formation of positive fragment ions cannot be expected from the impact of 9.5 eV electrons, the data for 15 eV electrons were used for comparison for the sake of convenience.

that of $C_2H_3CN^+$ ions (the most intense peak among the positive ions) gave $C_2H_3CN^+/CN^- \simeq 1.2\times10^4$ and 1.9×10^4 at 80 eV and 40 eV electron energies, respectively. The ratio of the yield of CN^- ions at 9.5 eV to that of $C_2H_3CN^+$ ions at 15 eV gave the value $C_2H_3CN^+/CN^- \simeq 47.6$.

Effect of Pressure. Figure 2 shows the plot of the yield of *m/e* 26(CN^-), 50(C_3N^-), 38(C_2N^-) and 39($CHCN^-$) ions against pressure, where the electron energy used was 80 eV. All the results showed a good linearity, which are consistent with the findings for *m/e* 1(H^-) ion from hydrogen,[20] *m/e* 39(CH_3CC^-) ion from methylacetylene,[21] *m/e* 46(NO_2^-), 16(O^-), 26(CN^-) and 42(CNO^-) ions from nitroalkanes,[11] *m/e* 26(CN^-), 27(HCN^-), 38(C_2N^-), 39($CHCN^-$) and 40(CH_2CN^-) ions from methyl- and ethylcyanides.[22] The linear correlations against pressure were independent of electron energy. The pressure dependency may become complicated at higher pressures because of the occurrence of ion-molecule reactions.

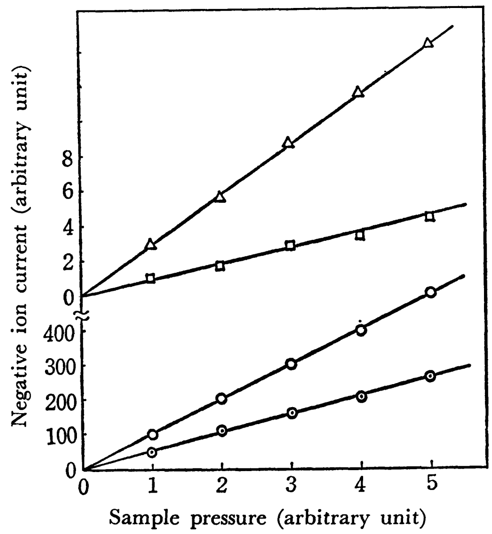


Fig. 2. Plot of negative ion current against pressure. (electron energy, 80 eV)
○ CN^- ⊙ C_3N^- △ C_2N^- □ $CHCN^-$

IE Curves; CN^- ions. Figure 3(a) shows the IE curve of *m/e* 26(CN^-) ions. At least three processes appear to take place. The first process appears at lower energies than 2 eV, the second process at ~3.0 eV[23] and the third process at ~5.8 eV. The shape of the IE curve suggests a dissociative electron capture process except for the part in a higher energy region.

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

20) G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959).
21) T. Sugiura, T. Seguchi, and K. Arakawa, This Bulletin, **40**, 2992 (1967).
22) S. Tsuda, A. Yokohata, and T. Umaba, *ibid.*, **43**, 3383 (1970).
23) Exact determination of appearance potential of the 2nd and 3rd processes is difficult, since the tailing due to the 1st and 2nd processes and their appearance might overlap. In this work, the minimum values in the IE curves have been discussed as by Schulz (G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959)).

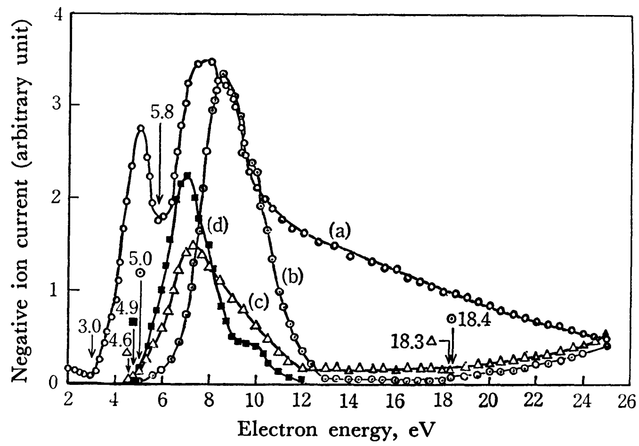


Fig. 3. Ionization efficiency curves of *m/e* 26(CN^-), *m/e* 25(C_2H^-) and *m/e* 38(C_2N^-) ions.
○ CN^- ⊙ C_3N^- △ C_2H^- ■ C_2N^-

$$XYZ + e^- \longrightarrow X^- + YZ \qquad (1)$$

$$AP_{calcd} = \Delta H = \Delta H_f(X^-) + \Delta H_f(YZ) - \Delta H_f(XYZ) \qquad (2)^{24)}$$

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

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

From Eqs. (2) and (3), schemes of the reactions expected to occur at each onset value (AP_{obsd}) were sought thermochemically.

For the first process, we have

$$C_2H_3CN + e^- \longrightarrow CN^- + C_2H_3 (AP_{calcd} = 1.3 \text{ eV}) \qquad (4)$$

In the estimation of AP_{calcd}, the values of $\Delta H_f(C_2H_3CN) = 2$ eV,[25] and $\Delta H_f(CN^-) = 0.47$ eV and $\Delta H_f(C_2H_3) = 2.83$ eV[26] were used. The first process appearing at <2 eV would probably correspond to reaction (4). Combining $\Delta H_f(C_2H_3CN) = 2$ eV with $\Delta H_f(CH_2) = 2.5$ eV[26] and $\Delta H_f(CHCN) = 4.2$ eV,[15] we obtain $D(CH_2{=}CHCN) = 4.7$ eV. This is reasonable as compared with $D(CH_2{=}CH_2) = 5.2$ eV.[18] The CN radical is expected to weaken the C=C bond. A previous value $\Delta H_f(CHCN) = 4.2$ eV[15] might also be mentioned.

For the second process, we have

$$C_2H_3CN + e^- \longrightarrow CN^- + C_2H_2 + H \quad (AP_{calcd} = 3.08 \text{ eV}) \qquad (5)$$

$$\longrightarrow CN^- + C_2H + H_2 \quad (AP_{calcd} = 3.47 \text{ eV}) \qquad (6)$$

Estimation of each AP_{calcd} value was made with the use[26] of $\Delta H_f(C_2H_2) = 2.35$ eV, $\Delta H_f(H) = 2.26$ eV and $\Delta H_f(C_2H) = 5.0$ eV. A good consistency of $AP_{calcd} = 3.08$ eV with $AP_{obsd} \simeq 3.0$ eV suggests the possibility of the occurrence of reaction (5) rather than (6).

For the third process, we have

24) ΔH (X): heat of formation of X.
25) From $\Delta H_f(C_3H_3N^+) = 12.8$ eV and $IP(C_2H_3CN) = 10.75$ eV, $\Delta H_f(C_2H_3CN) \simeq 2$ eV can be estimated (J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952)).
26) R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

$$C_2H_3CN + e^- \longrightarrow CN^- + CH_2 + CH \quad (AP_{calcd} = 7.13\ \mathrm{eV})^{27)} \quad (7)$$

$$\longrightarrow CN^- + C_2H + 2H \quad (AP_{calcd} = 7.99\ \mathrm{eV}) \quad (8)$$

$$\longrightarrow CN^- + C_2 + H + H_2 \quad (AP_{calcd} = 9.25\ \mathrm{eV})^{28)} \quad (9)$$

However, each AP_{calcd} value does not fit $AP_{obsd} \simeq 5.8$ eV. Reaction (10) might be possible. The value of C_2H_2* can be estimated to be ~2.7 eV.

$$C_2H_3CN + e^- \longrightarrow CN^- + C_2H_2^* + H \quad (10)$$

C_3N^- Ions. Figure 3(b) shows the IE curve of *m/e* 50(C_3N^-) ions with relatively strong peaks. Its shape suggests a dissociative electron capture process and an ion pair formation process. The former appears at ~5 eV and the latter at ~18.4 eV.

On the basis[17] of $\Delta H_f(C_3N)=131$ kcal/mol and $EA(C_3N)=55$ kcal/mol,[29] AP_{calcd} values of reactions (11) and (12) can be estimated as follows.

$$C_2H_3CN + e^- \longrightarrow C_3N^- + H_2 + H \quad (AP_{calcd} = 3.57\ \mathrm{eV}) \quad (11)$$

$$\longrightarrow C_3N^- + H_2 + H^+ \quad (AP_{calcd} = 17.16\ \mathrm{eV}) \quad (12)$$

The difference between AP_{obsd} and AP_{calcd}, ~1.43 eV or ~1.23 eV would be ascribed to an excess energy of C_3N^- ion.

C_2H^- Ions. Figure 3(c) shows the *IE* curve of *m/e* 25(C_2H^-) ions, where the first process appears at ~4.6 eV and the second process at ~18.3 eV. The values of $\Delta H_f(C_2H) \simeq 5$ eV, $\Delta H_f(HCN)=1.3$ eV and $\Delta H_f(CN)=3.87$ eV result in $AP_{calcd}=6.56$ eV for reaction (13) and $AP_{calcd}=6.87$ eV for reaction (14).

$$C_2H_3CN \longrightarrow C_2H+H+HCN \quad (AP_{calcd}=6.56\ \mathrm{eV}) \quad (13)$$

$$\longrightarrow C_2H+H_2+CN \quad (AP_{calcd}=6.87\ \mathrm{eV}) \quad (14)$$

If an electron affinity of C_2H is assumed to be 1.96 eV, we have the following schemes.

$$C_2H_3CN + e^- \longrightarrow C_2H^- + H + HCN \quad (AP_{calcd} = 4.6\ \mathrm{eV}) \quad (15)$$

$$\longrightarrow C_2H^- + H_2 + CN \quad (AP_{calcd} = 4.91\ \mathrm{eV}) \quad (16)$$

$$\longrightarrow C_2H^- + H^+ + HCN + e^- \quad (AP_{calcd} = 18.19\ \mathrm{eV})^{30)} \quad (17)$$

$$\longrightarrow C_2H^- + H + HCN^+ + e^- \quad (AP_{calcd} = 18.46\ \mathrm{eV})^{31)} \quad (18)$$

$$\longrightarrow C_2H^- + H_2 + CN^+ + e^- \quad (AP_{calcd} = 20.04\ \mathrm{eV})^{32)} \quad (19)$$

If we assume $EA(C_2H)=2.27$ eV we get the following results.

$$C_2H_3CN + e^- \longrightarrow C_2H^- + H + HCN \quad (AP_{calcd} = 4.29\ \mathrm{eV}) \quad (20)$$

$$\longrightarrow C_2H^- + H_2 + CN \quad (AP_{calcd} = 4.6\ \mathrm{eV}) \quad (21)$$

$$\longrightarrow C_2H^- + H^+ + HCN + e^- \quad (AP_{calcd} = 17.88\ \mathrm{eV}) \quad (22)$$

$$\longrightarrow C_2H^- + H + HCN^+ + e^- \quad (AP_{calcd} = 18.15\ \mathrm{eV}) \quad (23)$$

$$\longrightarrow C_2H^- + H_2 + CN^+ + e^- \quad (AP_{calcd} = 19.73\ \mathrm{eV}) \quad (24)$$

Reaction (19) or (24) might be excluded. This suggests the possibility of reaction (15) rather than reaction (16). Introduction of $EA(C_2H)=1.96$ eV appears to make the assignment of reactions (15) and (17) or (18) possible. To assume $EA(C_2H)=2.27$ eV requires 0.31 eV and 0.42 eV or 0.15 eV for an excess energy of C_2H^- ion under the assignment of reactions (20) and (22) or (23). Although the possibility of excess energy of the fragment makes the situation complicated, it should be noted that the value of the electron affinity of C_2H is relatively large and the value of $EA(C_2H) \gtrsim 2$ eV is reasonable.

C_2N^- Ions. As shown in Fig. 3(d), the shape of the IE curve is a little complicated in the range 9—11 eV. We got $AP_{obsd} \simeq 4.9$ eV. The values of $\Delta H_f(C_2N)=5.3$ eV and $\Delta H_f(CH_3)=1.39$ eV give a value of 4.69 eV for AP_{calcd} of reaction (25), $AP_{calcd}=8.06$ eV also for reaction (26).

$$C_2H_3CN \longrightarrow C_2N + CH_3 \quad (AP_{calcd} = 4.69\ \mathrm{eV}) \quad (25)$$

$$\longrightarrow C_2N + CH_2 + H \quad (AP_{calcd}=8.06\ \mathrm{eV}) \quad (26)$$

Combining AP_{calcd} (=8.06 eV) with AP_{obsd} ($\simeq$4.9 eV), we have $EA(C_2N) \simeq 3.16$ eV. Judging from $EA(CN)=3.4$ eV, $EA(C_3N)=2.4$ eV and $EA(C_5N)=2.3$ eV, the value of $EA(C_2N) \simeq 3.16$ eV is reasonable, in other words, the following reaction would be assigned.

$$C_2H_3CN + e^- \longrightarrow C_2N^- + CH_2 + H \quad (27)$$

The following ion-pair process was difficult to detect.

$$C_2H_3CN + e^- \longrightarrow C_2N^- + H^+ + CH_2 + e^- \quad (AP_{calcd} \simeq 18.5\ \mathrm{eV}) \quad (28)$$

HCN^-. Three processes were observed (Fig. 4(a)). The values of AP_{obsd} were $\ll 2$ eV, 3.0 eV and 5.6 eV. Although the possibility of $C_2H_3^-$ ions for *m/e* 27 ions might be considered, combining of AP_{calcd} (=4.7 eV) of reaction (29) with AP_{obsd} lower than 2 eV leads to $EA(C_2H_3)$ larger than 2.7 eV. This seems to be too large to be acceptable. Thus, it can be excluded:

$$C_2H_3CN \longrightarrow C_2H_3 + CN \quad (AP_{calcd}=4.7\ \mathrm{eV}) \quad (29)$$

Using $EA(HCN) \gtrsim 1$ eV[15] and $(C_2H_2)^*=2.7$ eV (introduced temporarily) the following reactions might be assigned.

$$C_2H_3CN + e^- \longrightarrow HCN^- + C_2H_2 \quad (AP_{calcd} \lesssim 0.65\ \mathrm{eV}) \quad (30)$$

$$\longrightarrow HCN^- + C_2H_2^* \quad (AP_{calcd} \lesssim 3.35\ \mathrm{eV}) \quad (31)$$

27) $\Delta H_f(CH)=6.16$ eV (refer to 26).
28) $\Delta H_f(C_2)=8.52$ eV (refer to 18).
29) EA(X) : electron affinity of X.
30) $IP(H)=13.59$ eV (refer to 26). IP(X): ionization potential of X.
31) $IP(HCN)=13.86$ eV (refer to 18).
32) $IP(CN)=15.13$ eV (refer to 18).

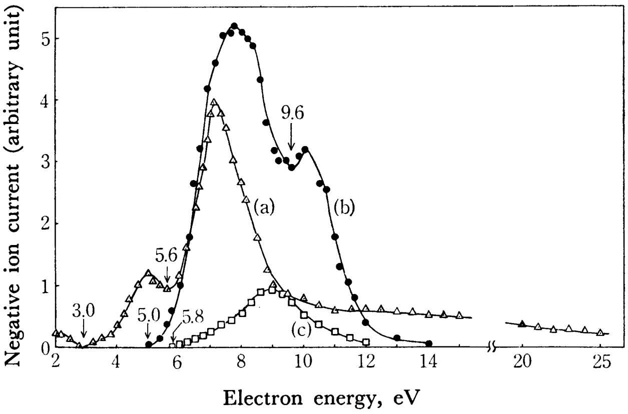


Fig. 4. Ionization efficiency curves of *m/e* 27(HCN^-), *m/e* 39($CHCN^-$) and *m/e* 40(CH_2CN^-) ions.
△ HCN^- ● $CHCN^-$ □ CH_2CN^-

$$\longrightarrow HCN^- + C_2H + H \quad (AP_{calcd} \lesssim 5.56\ eV) \quad (32)$$

$CHCN^-$ Ions. Figure 4(b) shows AP_{obsd}=5.0 eV and 9.6 eV. By using ΔH_f(CHCN)=4.2 eV[15] we have

$$C_2H_3CN \longrightarrow CHCN + CH_2 \quad (AP_{calcd} = 4.7\ eV) \quad (33)$$

Moreover, EA(CHCN)$\gtrsim$1.1 eV[15] leads to the following result.

$$C_2H_3CN + e^- \longrightarrow CHCN^- + CH_2 \quad (AP_{calcd} \lesssim 3.6\ eV) \quad (34)$$

Thus, combining of AP_{calcd} with AP_{obsd} (=5.0 eV) requires a value of $\gtrsim$1.4 eV as an excess energy of the fragment.

Next, let us consider the possibility of $C_3H_3^-$ ions.

$$C_2H_3CN \longrightarrow C_3H_3 + N \quad (AP_{calcd} = 5.9\ eV)^{33)} \quad (35)$$

Introduction of $EA(C_3H_3)$=0.9 eV appears to make possible the interpretation of AP_{obsd}=5 eV. Since no $C_3H_3^-$ ion from hydrocarbons has been obtained, they may be excluded.

For AP_{obsd}=9.6 eV, the following reaction would be assigned.

$$C_2H_3CN + e^- \longrightarrow CHCN^- + CH + H \quad (AP_{calcd} \lesssim 9.52\ eV) \quad (36)$$

CH_2CN^- Ions. These ions show only one process having the appearance potential at ~5.8 eV (Fig. 4(c)). $\Delta H_f(CH_2CN)$=1.96 eV,[15] $EA(CH_2CN)\gtrsim$ 1.64 eV[15] and ΔH_f(CH)=6.16 eV give a value of $\lesssim$4.48 eV for AP_{calcd} of the following reaction.

$$C_2H_3CN + e^- \longrightarrow CH_2CN^- + CH \quad (AP_{calcd} \lesssim 4.48\ eV) \quad (37)$$

The reaction might also be accompanied with an excess energy of fragments; $\gtrsim$1.32 eV.

33) $\Delta H_f(C_3H_3)$=3.0 eV (refer to 26). ΔH_f(N)=4.9 eV (refer to 18).