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Measurement of Negative Ions Formed by Electron Impact. VII. Negative Ion Mass Spectra from Alkyl Cyanides

Satoru TSUDA, Akira YOKOHATA and Toshikatsu UMABA

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

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The negative ion mass spectra from alkyl (methyl, ethyl, *n*- and *iso*-propyl) cyanides with electron energies of 80 eV, 40 eV and 9.5 eV were measured by a Hitachi RMU-6D mass spectrometer with emphasis on the relative abundance of negative ions to positive ions with electron energies of 80 eV, 40 eV and 15 eV. In every sample, the electron impacts with 80 eV and 40 eV gave almost the same distribution of *m/e* for negative ion mass spectra. Then, the peak of *m/e* 26(CN^-) ions was the most intense and also the relatively strong peak of 25(C_2H^-) ions was found through all samples. On the other hand, the formations of 38(C_2N^-), 39($CHCN^-$) and 41(CH_3CN^-) ions from methyl cyanide, of 50(C_3N^-) ions from ethyl cyanide, *n*- and *iso*-propyl cyanides, of 40(CH_2CN^-) ion from *n*-propyl cyanide were characteristic of each sample. The ratio of the yield of negative ions to positive ions was respectively of the order of $\sim 10^4$ for CH_3CN^+/CN^- (CH_3CN), $C_2H_4^+/CN^-$ (C_2H_5CN), $C_3H_5^+/CN^-$ (*n*-C_3H_7CN) and $C_3H_6^+/CN^-$ (*iso*-C_3H_7CN) at 80 eV and 40 eV electron energies. At 9.5 eV, *m/e* 26 (CN^-) ions predominated over other negative ions for all the samples and a much larger peak of 40 (CH_2CN^-) ions in *n*-C_3H_7CN than in *iso*-C_3H_7CN was also observed. Then, we got the values of 19~65 for CH_3CN^+/CN^-, $C_2H_4^+/CN^-$, $C_3H_5^+/CN^-$ and $C_3H_6^+/CN^-$ (15 eV for positive ions). This work also gave linear relationship of the yield of each negative ion to the pressure in the range used for an usual chemical analysis.

Collisions of electrons of low velocity with molecules may produce charged fragments of the molecules. The data on the minimum electron energy necessary to produce these fragments, their identification, and the processes involved may permit one to determine the electron affinity of fragments and the heat of dissociation of the molecule. The relative abundance of ion products and the probability of a process as a function of the electron energy are also of interest.

If the kinetic energy of the electron in a gaseous medium is below the ionization potential of the molecules, the electron would lose energy to electronic excitation as long as its kinetic energy is above the first excitation potential of the medium. When the electron energy is below the first excitation potential, moderation occurs through elastic and inelastic collisions leading to vibrational and rotational excitation of the molecules. A subexcitation electron may lose energy also through various types of electron attachment processes and the excitation of compound negative ion states. Compound negative ion states can decay purely elastically, give vibrationally excited molecules, or lead to dissociative attachment.[1-6]

Especially, of interest and practical importance are the processes which result in the formation of negative ions. As described frequently,[7] they are classified into the following types: a) resonance capture, b) dissociative resonance capture and c) ion pair formation. Under the normal operating conditions (80—40 eV) of a mass spectrometer, all processes may occur. As they are pressure dependent, the relative ion intensities in negative ion mass spectra would change with the sample pressure. In the formation of $CH_2NO_2^-$ ions from *n*- and *iso*-nitropropanes,[8] the authors reported the linear relationship of their yield to the pressure in the region used for an usual analysis, and also their yield is ~100 times greater in *n*-nitropropane than in isonitropropnane. This shows clearly the usefulness of the measurement of

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1) G. J. Schulz and R. E. Fox, *Phys. Rev.*, **106**, 1179 (1957).

2) G. J. Schulz, *Phys. Rev. Lett.*, **10**, 104 (1963).

3) C. R. Bowman and W. D. Miller, *J. Chem. Phys.*, **42**, 681 (1965).

4) H. G. M. Heideman, C. E. Kuyatt and G. E. Chamberlain, *J. Chem. Phys.*, **44**, 440 (1966).

5) M. G. Menedez and H. K. Holt, *ibid.*, **45**, 2743 (1966).

6) R. N. Compton, L. G. Christophorou and R. H. Huebner, *Phys. Lett.*, **23**, 656 (1966).

7) C. E. Melton in "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press Inc., New York, N. Y. (1963), Chapter 4.

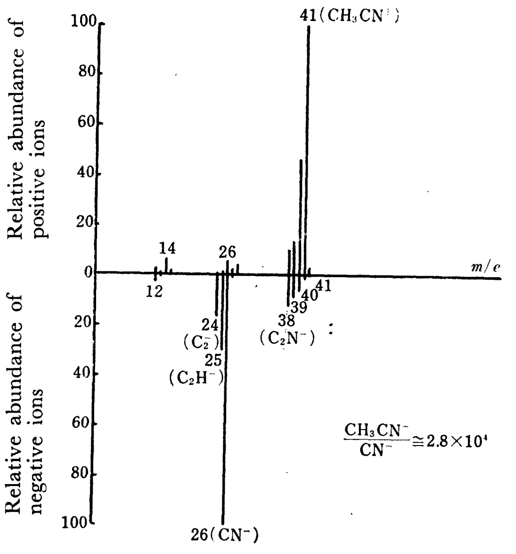
8) S. Tsuda, A. Yokohata and M. Kawai, This Bulletin, **42**, 607 (1969).

negative ions for chemical analysis. Also, the formation of molecular anions by resonance capture would permit the determination of the molecular weight, and in some cases might be useful for structural and stereochemical problems.[9]

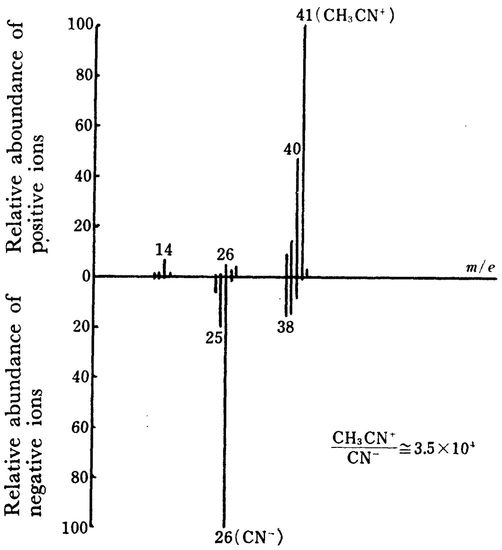
Unfortunately, however, a very little has been published on negative ion mass spectrometry. There also appear to be discrepancies in the published experimental results which calls for further work. For the purpose of gathering the data of negative ions and establishing their pattern in comparison with positive ions under various electron energies, this series of studies[10] has been begun. This work is an extension to alkyl cyanides, with emphasis on a comparative study of negative and positive ions.

Experimental

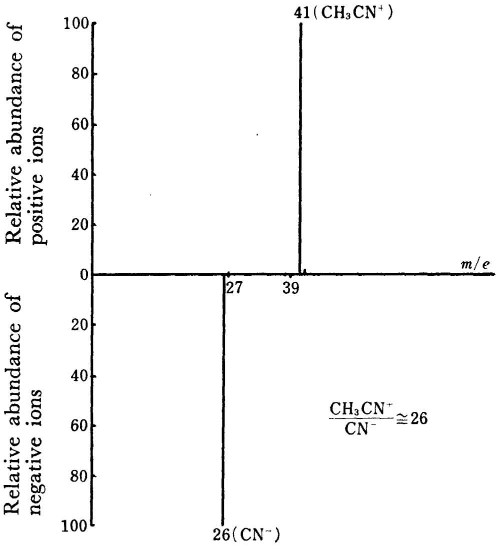
Experiments were performed on a Hitachi RMU-6D mass spectrometer equipped with the T-2M ion source having a rhenium filament. The ion detection circuit consisted of a ten stage electron multiplier having Ag–Mg dynode and of a Faraday collector. All the spectra were measured with a total emission current of 20 μA, an accelerating voltage of 3.6 kV and an electron multiplier voltage of 2.5 kV, under the electron energies of 80 eV, 40 eV, 9.5 eV (80 eV, 40 eV and 15 eV for positive ions) and a pressure of $\sim 10^{-6}$ mmHg in the source. An ionizing current showed a constant value of 10.5 μA down to $\sim$10 eV. The energy scale was calibrated in every measurement by the vanishing current method as compared to the ionization potential of argon or the appearance potential of m/e 16(O^-) ions from carbon monoxide, carbon dioxide and oxygen as described previously.[10] The repeller voltage was adjusted respectively to the best condition to collect the ions in positive and negative ion measurements. All chemicals were of research grade.



1a



1b



1c

Fig. 1. Positive and negative ion mass spectra of CH_3CN.
a 80 eV, b 40 eV, c 15 eV for positive ions, 9.5 eV for negative ions

Results and Discussion

Negative Ion Mass Spectra. *Methyl Cyanide.* In 80 eV electron impact experiments (Fig. 1a), the foregoing spectra were observed where they are shown in decreasing order of yield; m/e 26

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9) R. T. Aplin, H. Budzikiewiez and C. Djerassi, *J. Amer. Chem. Soc.*, **87**, 3180 (1965).

10) S. Tsuda, A. Yokohata and M. Kawai, This Bulletin, **42**, 614, 1515, 2514 (1969).

(CN^-), 25 (C_2H^-), 24 (C_2^-), 38 (C_2N^-), 39 ($CHCN^-$), 40 (CH_2CN^-), 12 (C^-), 27 (HCN^-), 13 (CH^-), 41 (CH_3CN^-) and 14 (CH_2^-). The comparison of the yield of CN^- ion with that of CH_3CN^+ (*m/e* 41, the most intense peak among the positive ions) gave a value of $\sim 2.8\times 10^4$ for CH_3CN^+/CN^-.

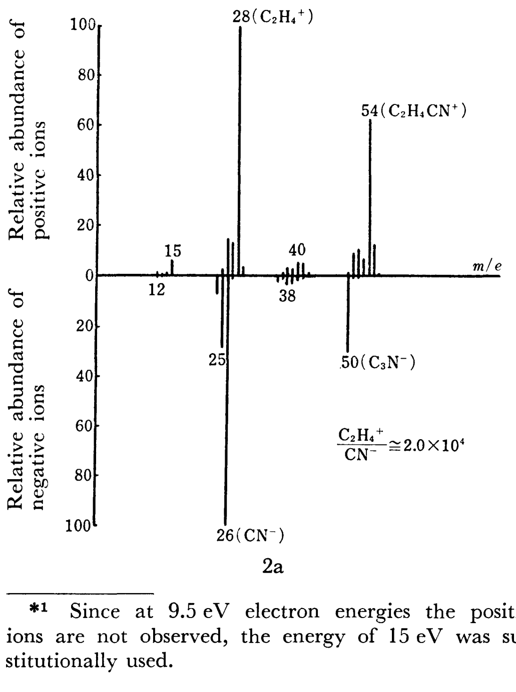
For 40 eV electron energies (Fig. 1b) the pattern of the negative ions was almost the same as that for 80 eV except for a small change in the relative abundance of C_2H^-, C_2^- and $CHCN^-$ ions, and the ratio of CH_3CN^+ to CN^- was $\sim 3.5\times 10^4$.

For 9.5 eV electron energies (Fig. 1c) CN^- ions predominated over other negative ions. A value of ~ 26 for CH_3CN^+/CN^- was obtained where 15 eV electron energies are used for positive ions.[*1]. Table 1 shows the yield of minor negative ions for 80 eV, 40 eV and 9.5 eV.

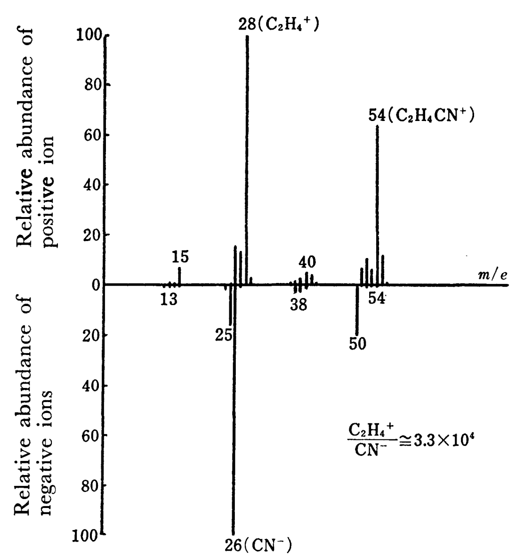
TABLE 1. MINOR NEGATIVE IONS FROM CH_3CN

m/e	Relative intensities at electron energies of		
	80 eV	40 eV	9.5 eV
12	2.56	1.07	
13	1.24	1.34	
14	0.17	0.40	0.05
15		trace	0.09
27	1.47	1.89	1.31
38	12.00	15.80	0.24
39	8.66	15.00	1.03
40	6.18	8.67	0.23
41	0.83	1.08	

Normalized to CN^- (yield=100)



2a



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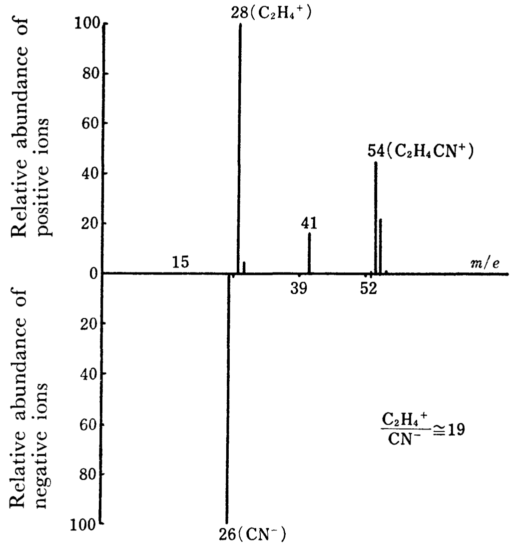

2c

Fig. 2. Positive and negative ion mass spectra of C_2H_5CN.
a 80 eV, b 40 eV, c 15 eV for positive ions, 9.5 eV for negative ions

Then, the formation of parent negative ion, CH_3CN^- at 80 eV and 40 eV was observed while at 9.5 eV it was not. It is noticed[11] that the appearance potential, AP_{obs} value of CH_3CN^- ions from methyl cyanide is ~ 23 eV and the effect of an additive xenon suggests the possibility of the occurrence of the reaction; $Xe^*+CH_3CN\rightarrow Xe^+ + CH_3CN^-$. Also, the formation of C_2H^- and C_2^-

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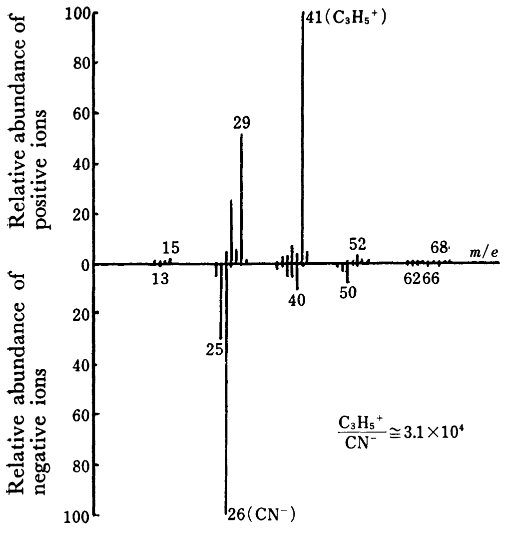
[*1] Since at 9.5 eV electron energies the positive ions are not observed, the energy of 15 eV was substitutionally used.

11) T. Sugiura and T. Arakawa, presented at the annual meeting of 22nd Chemical Society of Japan, Tokyo (1969).

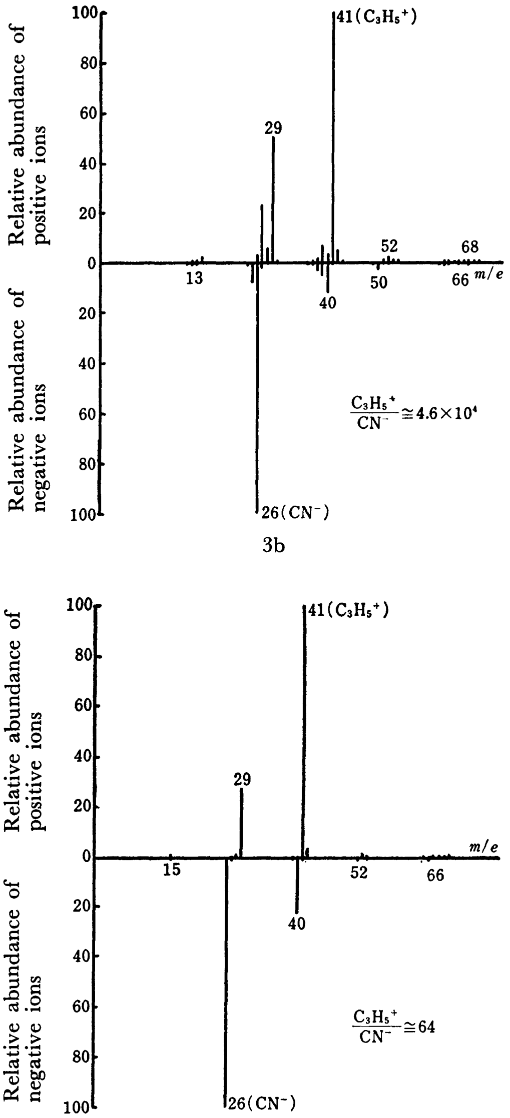
ions from the compounds containing two carbon atoms besides hydrogen atoms may be regarded to be a general phenomenon as found in ethane,[7] nitroethane[10] and ethyl chloride.[12] Furthermore, in the case of compounds containing cyano group, CN^- and C_2N^- ions should be added to them. These are qualitatively understood on the basis of EA(C_2)$\simeq$3.1 eV[13] and EA (CN)$\simeq$ 3.4 eV[8] while a value of $\gtrsim$2.3 eV is expected for EA (C_2N).[14] The data on EA (HCN), EA (CHCN) and EA (CH_2CN) will be reported in the next paper.

Ethyl Cyanide. The 80 eV electron impact gave the following spectra (Fig. 2a), being shown in the decreasing order of yield: *m/e* 26 (CN^-), 50 (C_3N^-), 25 (C_2H^-), 24 (C_2^-), 38 (C_2N^-), 39 ($CHCN^-$), 36 (C_3^-), 40 (CH_2CN^-), 51 (HC_3N^-), 27 (HCN^-), 12 (C^-), 13 (CH^-), 52 ($H_2C_3N^-$), 37 (C_3H^-), 14 (CH_2^-), 53 ($H_3C_3N^-$) and 54 ($H_4C_3N^-$). The comparison with $C_2H_4^+$ ions (*m/e* 28, the most intense peak among the positive ions) gave a value of $\sim 2.0\times10^4$ for $C_2H_4^+/CN^-$.

For 40 eV electron energies (Fig. 2b), almost the same pattern as 80 eV was observed except for a relatively small change in the yield of C_2H^-, C_2^-, and C_3N^- ions, and a value of $C_2H_4^+/CN^-$ was estimated to be $\sim 3.3\times10^4$.



3a



3b

3c

Fig. 3. Positive and negative ion mass spectra of n-C_3H_7CN.
a 80 eV, b 40 eV, c 15 eV for positive ions, 9.5 eV for negative ions

For 9.5 eV electron energies (Fig. 2c), CN^- ions predominated over other negative ions, where a value of $C_2H_4^+/CN^-\simeq 19$ was found. Table 2 shows the yield of minor negative ions for 80 eV, 40 eV and 9.5 eV.

It is of interest to note that a relatively strong peak of C_3N^- ions was observed. This can be understood on the basis of a relatively high value (55 kcal/mol) of EA(C_3N) obtained by Dibeler *et al.*[14] in a mass spectrometric study of cyanogen and cyanoacetylenes, in which the measurement of appearance potentials of positive ions was made mainly. On the other hand, C_2N^- ions decrease in a considerable amount when compared with those in methyl cyanide. Another difference

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12) S. Tsuda, A. Yokohata and M. Kawai, This Bulletin, to be published.

13) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold Ltd., London (1966), p. 192. EA: electron affinity.

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

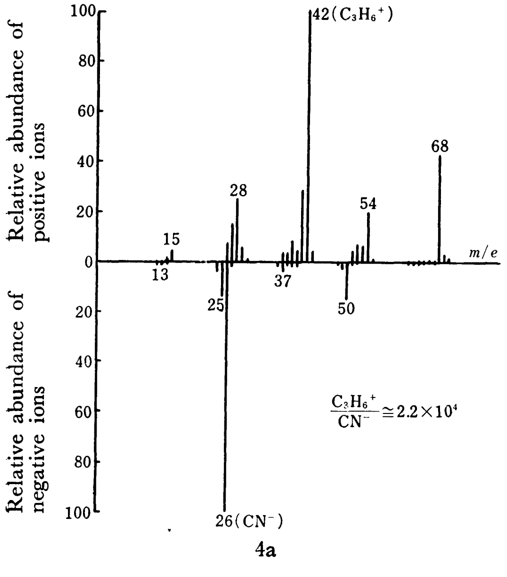
TABLE 2. MINOR NEGATIVE IONS FROM C_2H_5CN

m/e	Relative intensities at electron energies of		
	80 eV	40 eV	9.5 eV
12	1.23	0.51	
13	0.92	0.64	trace
14	0.25	0.59	0.01
15		0.22	0.02
24	7.07	2.21	
25	30.70	16.10	0.04
27	1.25	1.40	1.37
36	2.07	0.11	
37	0.37	0.24	
38	3.64	3.49	0.04
39	2.65	2.76	0.30
40	1.88	1.66	0.13
50	30.80	20.20	0.02
51	1.30	0.93	trace
52	0.57	0.97	1.23
53	trace		0.12
54	trace	0.19	0.04

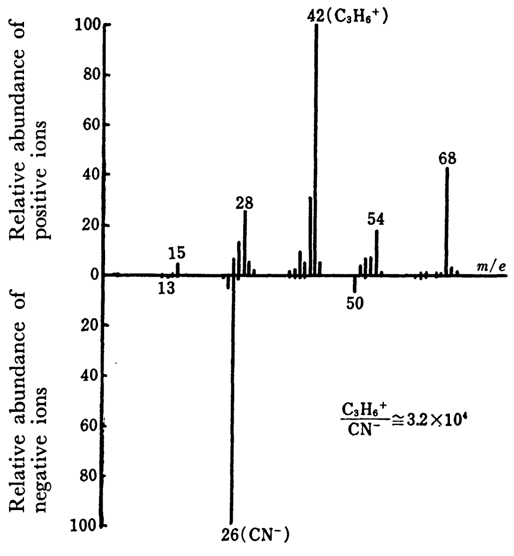
Normalized to CN^- (yield=100)

from methyl cyanide is that there is no formation of parent negative ion, $C_2H_5CN^-$, which was not observed throughout the whole range of electron energies used.

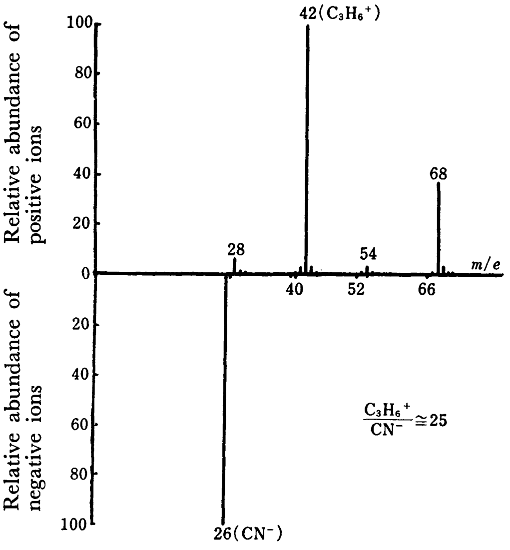
n- and iso-Propyl Cyanides. For the impacts of 80 eV and 40 eV electron energies (Figs. 3a, 4a and 3b, 4b), the two samples gave almost the same negative ions; *m/e* 26 (CN^-), 25 (C_2H^-), 50 (C_3N^-), 24 (C_2^-), 39 ($CHCN^-$), 38 (C_2N^-), 49 (C_4H^-), 36 (C_3^-), 27 (CHN^-), 48 (C_4^-), 37 (C_3H^-), 13 (CH^-), 62 (C_4N^-), 63 (C_4HN^-), 12 (C^-), 64 ($C_3H_2CN^-$), 66 ($C_3H_4CN^-$), 52 ($C_2H_2CN^-$), 51 (C_2HCN^-), 14 (CH_2^-), 41 (CH_3CN^-), 68 (C_3H_6-CN^-), and 65 ($C_3H_3CN^-$), except for a relatively large peak of 40 (CH_2CN^-) ion in *n*-C_3H_7CN. The parent ion, *m/e* 69 ($C_3H_7CN^-$) was not observed for both compounds.



4a



4b



4c

Fig. 4. Positive and negative ion mass spectra of *iso*-C_3H_7CN.
a 80 eV, b 40 eV, c 15 eV for positive ions, 9.5 eV for negative ions

It is of great interest to note that a relatively strong peak of *m/e* 25 (C_2H^-) ion has been observed among the negative ions arising from the propyl group. This is consistent with the situation in propyl alcohol[7] and nitropropane.[8] Also, *m/e* 50 (C_3N^-) ion was observed to be comparatively strong as in the case of C_2H_5CN.

Especially, we should like to emphasize here that a relatively strong peak of *m/e* 40 (CH_2CN^-) was found only in *n*-C_3H_7CN, the situation being very similar to that[8] of *m/e* 60 ($CH_3NO_2^-$) obtained from nitropropanes. The comparison of the yield of CN^- ion with that of $C_3H_5^+$ and $C_3H_6^+$ ions (*m/e* 41 and 42, the most intense peaks among the positive ions from *n*- and *iso*-propyl cyanides) gave the following values for $C_3H_5^+/CN^-$ and $C_3H_6^+/CN^-$; $\sim 3.1\times 10^4$ and $\sim 2.2\times 10^4$ at 80 eV respectively, $\sim 4.6\times 10^4$ and $\sim 3.2\times 10^4$ at 40 eV, respectively.

At 9.5 eV, *m/e* 26 (CN^-) ions predominated over other negative ions (Fig. 3c and Fig. 4c). Moreover, a relatively large yield of *m/e* 40 (CH_2CN^-) from *n*-C_3H_7CN is very characteristic, while in *iso*-C_3H_7CN it is found only as a relatively small peak. This finding would be useful for one of the identification methods of *n*-C_3H_7CN. The reason for a small cross section of CH_2CN^- ion formation from *iso*-C_3H_7CN would probably be that it is the rearrangement ion. The ratio of the yield of $C_3H_5^+$ and $C_3H_6^+$ to CN^- gave values of $\sim$64 and $\sim$25, respectively. Tables 3 and 4 show the yields of minor negative ions from *n*- and *iso*-propyl cyanides in relation to the electron energy.

Table 3. Minor negative ions from *n*-C_3H_7CN

m/e	Relative intensities at electron energies of		
	80 eV	40 eV	9.5 eV
12	0.82	0.48	
13	1.33	0.97	trace
14	0.40	0.40	trace
15			0.11
24	5.83	1.33	
25	30.28	8.19	0.07
27	1.58	1.72	1.56
36	2.49	0.37	
37	1.38	0.53	
38	5.12	3.48	0.04
39	5.30	5.28	0.33
40	11.00	12.00	23.00
41	0.38	0.39	0.76
48	1.53		
49	3.37	0.26	
50	7.97	2.91	0.04
51	0.47	0.21	
52	0.48	0.62	0.69
53			0.05
62	1.17	0.40	
63	1.10	0.66	
64	0.66	0.62	0.02
65	0.04	0.06	
66	0.52	0.75	1.34
67		trace	0.15
68	0.28	0.61	0.08

Normalized to CN^- (yield=100)

Table 4. Minor negative ions from *iso*-C_3H_7CN

m/c	Relative intensities at electron energies of		
	80 eV	40 eV	9.5 eV
12	0.65	0.44	
13	1.04	0.91	
14	0.41	0.57	0.04
15	0.10	0.20	0.10
24	4.01	1.08	
25	13.99	5.61	0.03
27	1.53	1.18	1.34
36	1.53	0.40	
37	2.46	0.50	
38	1.20	1.50	
39	1.62	1.48	0.17
40	1.17	1.14	0.28
41	trace	trace	trace
42			trace
48	1.06	trace	
49	2.12	0.05	
50	15.22	6.15	trace
51	0.61	0.28	
52	0.36	0.93	0.69
53			0.1
54			0.12
62	0.64	0.28	
63	0.49	0.26	
64	0.29	0.42	
66	trace	0.11	0.36
67			0.03
68			0.02

Normalized to CN^- (yield=100)

Effect of Pressure. Figure 5 shows the relation between the yields of *m/e* 26 (CN^-), 38 (C_2N^-), 39 ($CHCN^-$), 40 (CH_2CN^-) and 50 (C_3N^-) ions and the pressure for each sample (5a for *m/e* 26 ion, 5b for *m/e* 38 ion, 5c for *m/e* 39 ion, 5d for *m/e* 40 ion and 5e for *m/e* 50 ion) under the electron energy of 80 eV. All the results show good linearities against the pressure under given experimental conditions. Also, this linear relationship was independent of the electron energy as shown in Fig. 6, where the *m/e* 26 (CN^-) ion from CH_3CN is shown as an example. A similar linear relationship had been reported for the *m/e* 1 (H^-) ion produced from hydrogen[15] under the electron energies of 6.8 eV, 10.0 eV and 14.2 eV in the range of pressure from 1×10^{-4} mmHg to 4×10^{-4} mmHg, for the *m/e* 39 (CH_3CC^-) ion[16] from methylacetylene in the range of pressure up to about 5×10^{-5} mmHg and for *m/e* 46 (NO_2^-), 16 (O^-), 26 (CN^-) and 42 (CNO^-) ions[8] from nitroalkanes in the range of pressure used for usual analysis. Of course,

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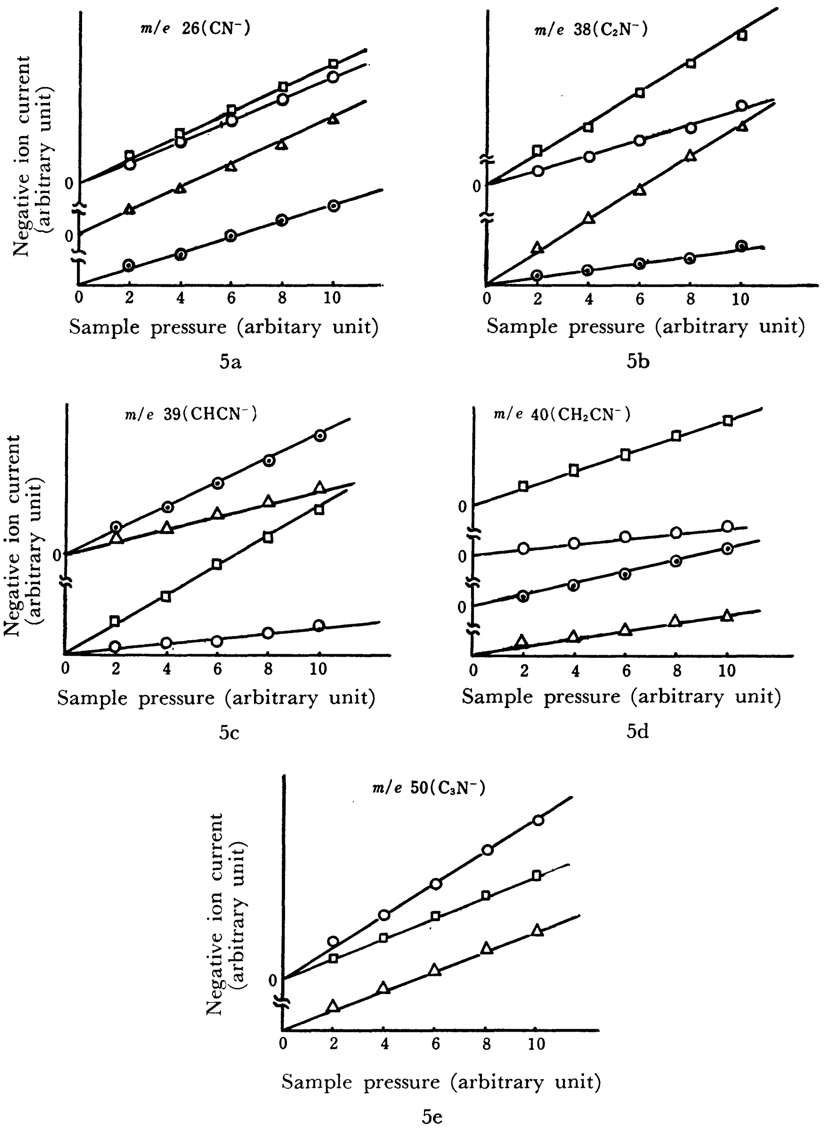
[15] G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959).

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



5a

5b

5c

5d

5e

Fig. 5. Plot of negative ion current against pressure (electron energy; 80 eV).
○ iso-C_3H_7CN, □ n-C_3H_7CN, △ C_2H_5CN, ⊙ CH_3CN

the pressure dependency may become complicated at higher pressures because of the occurrence of ion-molecule reactions. In the present work, however, such a study was not made because of instrumental difficulty.

The Formation of Negative Ions. As mentioned above, the yield of negative ions is dependent on electron energies and cross sections of formation processes which are very different from those of positive ions, especially in their behaviors in the low energy region. Here, we should like to add a few words on the formation of parent negative ions and the excitation of negative ions.

It is generally accepted that a parent negative ion is formed by the capture of a free electron by a molecule, with the vibrational excitation of the molecular ion and its subsequent stabilization in a collision with another molecule ($e^- + AB \rightarrow [AB^-]^*$; $[AB^-]^* + X \rightarrow [AB^-] + X +$ kinetic energy.[17] However, we should not overlook that electron attachment may be significantly impeded when the formation of a stable negative ion requires a substantial deformation from the neutral geometry. For example, although N_2O containing 16 valence electrons is linear in the ground electronic state,[18] a compound with 17 electrons is bent in the ground

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

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

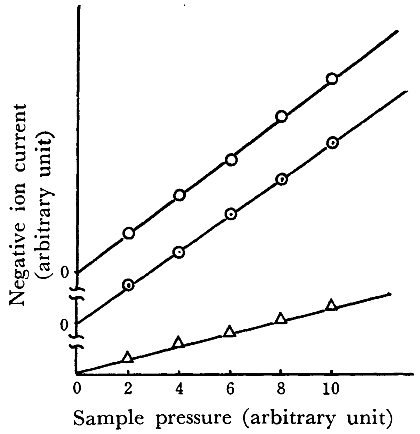

Fig. 6. Plot of negative ion (CN^-) current against pressure in CH_3CN.
△ 9.5 eV, ⊙ 40 eV, ○ 80 eV

state, *e.g.*, NO_2 with $\alpha = 134.1°$. The energy necessary to bend N_2O from 180° to 134° can be estimated to be about 1 eV, using a harmonic bending force constant. On the other hand, the appearance potential of the reaction; $e^- + N_2O \rightarrow O^- + N_2$, is said to be $\sim$0.21 eV on the basis of $D(N_2\text{-}O) = 1.677$ eV and $EA(O) = 1.465$ eV. Thus, energetic electrons do not attach to N_2O but rather cause dissociative attachment. The failure to form N_2O^- by a simple transfer of an electron*2 could be understood on this basis. Very recently, Chantry[19] showed that the prominent peak of O^- ion via dissociative attachment in N_2O occurs at or very close to zero (0—0.05 eV) in the high temperature (1050°K). This leads us to conclude that the cross section increases very rapidly with increasing vibrational excitation of the initial molecule. It seems to be a feature of many dissociative attachment processes.

MacNeil *et al.*[20] also report that production of negative ions is clearly influenced by the size, symmetry and bonding of the molecule being bombarded with electrons; in general, large, symmetrical molecules containing multiple linkages tend to undergo less fragmentation and consequently to form larger negative ions, sometimes including the molecular ion.

Next, let us discuss on the excitation of the negative ion. It is known that it is unlikely that negative ions with stable discrete excited states exist with appreciable binding energy. For example, in the case of CN^- ions it seems reasonable to assume that the electron attaching to the CN radical will go into the $(x\sigma)$ orbital*3 of N_2^+ or CO^+ ions which is isoelectronic with the CN radical.[21] Then, it leads to a molecule which is isoelectronic with the N_2 and CO molecules. Examination of the energy level diagrams of these molecules shows that the first excited singlet levels are between 8 and 9 eV above the ground state. Thus, it would seem improbable that it could be produced in a low-lying electronically excited state. Of course, the production in the vibrational excited state would be possible.

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*2 The possibility of formation of N_2O^- via ion-molecule reactions in N_2O cannot be excluded. (P. J. Chantry, *J. Chem. Phys.*, **51**, 3380 (1969)).

19) P. J. Chantry, *J. Chem. Phys.*, **51**, 3369 (1969).

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

*3 The electron configuration is shown to be $kk(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^1$.

21) J. D. Craggs, C. A. McDowell and J. W. Warren *Trans. Faraday Soc.*, **48**, 1093 (1952).