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Measurement of Negative Ions Formed by Electron Impact. III. The Ionization Efficiency Curves of Negative Ions of *m/e* 26 and 42 from Nitroalkanes

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The studies of this series were extended to the negative ions of *m/e* 26 and 42 obtained from nitroalkanes; nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. For *m/e* 26 (probably, CN^-) ions, the contribution of three or two processes in the range from zero to ~20 eV of electron energy was observed for nitromethane or other samples. On the basis of ΔH_f values of the reactants and products, and of the value of EA(CN), the plausible reactions to be assigned to each process were presented. For the first process, $CH_3NO_2+e^-\rightarrow CN^-+H_2O+OH$, $RNO_2+e^-\rightarrow CN^-+R_1OH+OH$. For the second process, $CH_3NO_2+e^-\rightarrow CN^-+H_2O+O+H$, $CH_3NO_2+e^-\rightarrow CN^-+H_2+O_2+H$, $RNO_2+e^-\rightarrow CN^-+R_1+HO_2+H$, and $C_3H_7NO_2+e^-\rightarrow CN^-+C_2H_4+H_2+O+OH$ irrespective of kind of nitropropane. For the third process, $CH_3NO_2+e^-\rightarrow CN^-+3H+O_2$. For *m/e* 42 (probably, CNO^-) ions, the contribution of two processes was observed. By taking $\Delta H_f(CNO)=x$ (eV), $EA(CNO)=y$ (eV), and also combining the observed onset values with the calculated values of appearance potential of reactions to be assigned for each process — for the first process, $CH_3NO_2+e^-\rightarrow CNO^-+H_2+OH$, $RNO_2+e^-\rightarrow CNO^-+R_1OH+H$; for the second process, $CH_3NO_2+e^-\rightarrow CNO^-+HO+2H$, $CH_3NO_2+e^-\rightarrow CNO^-+H_2+O+H$, $RNO_2+e^-\rightarrow CNO^-+R_1O+2H$—a relation of $x-y\simeq 2$(eV) was derived.

Recently, several studies have been reported on the measurement of negative ion mass spectra by the electron impact method.1-4) However, they were only made for limited kinds of compounds. Furthermore, data on the ionization efficiency (*IE*) curves of negative ions are very limited.5-7) We published previously the results of measurement of *IE* curves of NO_2^-, O^- and $CH_2NO_2^-$ ions from nitroalkanes; nitromethane, nitroethane, 1-nitropropane and 2-nitropropane.8) This work has been extended to the measurements of negative ions of *m/e* 26 and 42 and affords information on *IE* curves of these negative ions for which as far as the authors know few reports have been found.

Experimental

This investigation was carried out using a Hitachi RMU-6D mass spectrometer equipped with a 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 and the correction method of electron energy scale were identical to those previously described.8)

The materials used were of research grade and no further purifications have been done.

Results and Discussion

Formation of *m/e* 26 Ions. In nitromethane, *m/e* 26 ions can be assigned to CN^-. Although the possibility of $C_2H_2^-$ ions in other samples might be considered, little formation1) of $C_2H_2^-$ ions from alcohols appears to rule out this possibility. Figure 1 shows that, except for nitromethane, two processes contribute to the formation of CN^- ions. The first process appears at a considerably lower energy than 3 eV irrespective of the compounds and the second one seems to appear at ~5.2 eV in nitroethane, ~4.4 eV in 1-nitropropane

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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.

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

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

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

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

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

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

8) S. Tsuda, A. Yokohata and M. Kawai, *ibid.*, **42**, 607, 614 (1969).

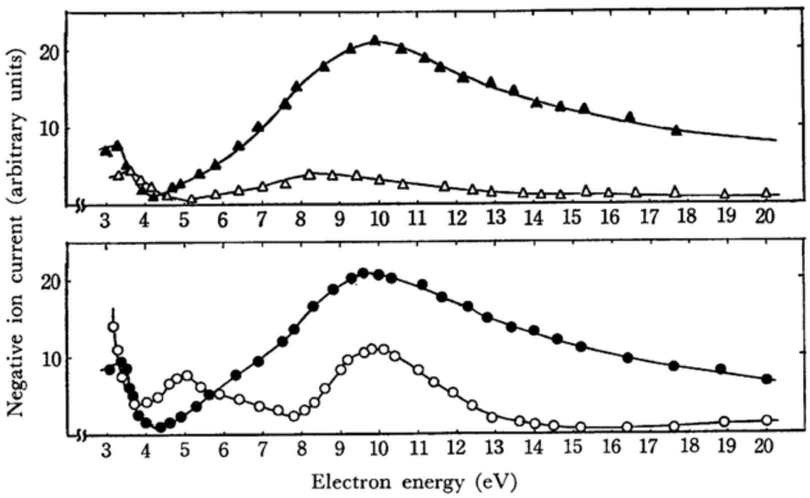

Fig. 1. Ionization efficiency curves of negative ions of *m/e* 26 from nitroalkanes.
○ CH_3NO_2 ● $1\text{-}C_3H_7NO_2$ △ $C_2H_5NO_2$ ▲ $2\text{-}C_3H_7NO_2$

and 2-nitropropane.[*1] In nitromethane three processes can be found; the second one seems to appear at ~3.7 eV and the third at ~7.8 eV.

For the first process in nitromethane, reactions (1), (2) and (3) are expected. Their appearance potentials can be estimated to be −0.85 eV, 1.47 eV and 2.12 eV, respectively,[*2] by using $\Delta H_f(CH_3NO_2) = -0.8$ eV,⁹⁾ $\Delta H_f(CN) = 3.87$ eV,¹⁰⁾ $\Delta H_f(H_2O) = -2.50$ eV, $\Delta H_f(OH) = 0.38$ eV, $\Delta H_f(HO)_2 = 0.2$ eV, $\Delta H_f(H_2) = 0.00$ eV, $\Delta H_f(H_2O_2) = -1.41$ eV, $\Delta H_f(H) = 2.26$ eV[*3] and $EA(CN) = 3.4$ eV[*4]

$$CH_3NO_2 + e^- \rightarrow CN^- + H_2O + OH \qquad (1)$$
$$(AP_{calc} = -0.85\ \text{eV})$$

$$CH_3NO_2 + e^- \rightarrow CN^- + HO_2 + H_2 \qquad (2)$$
$$(AP_{calc} = 1.47\ \text{eV})$$

$$CH_3NO_2 + e^- \rightarrow CN^- + H_2O_2 + H \qquad (3)$$
$$(AP_{calc} = 2.12\ \text{eV})$$

Among these reactions, the possibility of reaction (1) is very great, because the appearance potential of the first process has been qualitatively found to be very low. Thus, the process which appears at a considerably lower energy than 3 eV may be concluded to be due to reaction (1). A negative value of the appearance potential of this reaction means that the occurrence of this reaction is possible even with the electrons of thermal energy. The situation is quite similar to that of NO_2^- from nitromethane in which the appearance potential of dissociative electron capture shows a negative value because of $EA(NO_2) > D(CH_3\text{–}NO_2)$.

For the other samples, the occurrence of reactions (4) or (5) resulting in the formation of alcohols can be strongly expected under the analogy with reaction (1). The appearance potentials of reactions (4) and (5) can be estimated to be −0.53 eV and −0.96 eV, by using $\Delta H_f(CH_3OH) = -2.08$ eV, $\Delta H_f(C_2H_5OH) = -2.44$ eV, $\Delta H_f(C_2H_5NO_2) = -0.70$ eV and $\Delta H_f(1\text{-}C_3H_7NO_2) = -0.63$ eV.[*5]

[*1] Since the tailing due to the first process might be overlapped 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 up as the object of discussion.

[*2] These values mean the lowest value of the energy needed for the appearance of the reaction.

9) R. J. Kandel, *J. Chem. Phys.*, **23**, 84 (1955).

10) V. H. Dilbeler, R. M. Reese and J. L. Franklin, *J. Am. Chem. Soc.*, **83**, 1813 (1961).

[*3] For the values of ΔH_f, see the report of Bernecker. (R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961)).

[*4] For the electron affinity (*EA*) of CN, the values of 3.2 eV and 3.6 eV have been published. In this work, 3.4 eV (the mean value) was used. (J. T. Herron and V. H. Dibeler, *J. Am. Chem. Soc.*, **82**, 1555 (1960); E. Lederle, *Z. Physik. Chem.*, **B17**, 362 (1932).

[*5] The value of $\Delta H_f(C_2H_5NO_2)$ can be estimated in the following way.

$NH \rightarrow N + H, \qquad \Delta H = 3.61$ eV
$NO \rightarrow N + O, \qquad \Delta H = 6.52$ eV
$NO_2 \rightarrow NO + O, \qquad \Delta H = 3.16$ eV

Therefore, $\Delta H_f(NO_2) = 0.32$ eV can be obtained by using the known values of $\Delta H_f(NH)$, $\Delta H_f(H)$ and $\Delta H_f(O)$. Combining the appearance potential (10.9 eV) of the reaction ($C_2H_5NO_2 + e^- \rightarrow C_2H_5^+ + NO_2 + 2e^-$) with $\Delta H_f(NO_2) = 0.32$eV, we obtain a value of −0.70 eV for $\Delta H_f(C_2H_5NO_2)$; S. Tsuda and W. H. Hamill, *Advan. Mass Spectry.*, **3**, 249 (1965).

In the same way, $\Delta H_f(1-C_3H_7NO_2) = -0.63$ eV can be also estimated; 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 Ltd., London (1966), p. 80.

$$C_2H_5NO_2 + e^- \rightarrow CN^- + CH_3OH + OH \quad (4)$$
$$(AP_{calc} = -0.53\,\text{eV})$$
$$1\text{-}C_3H_7NO_2 + e^- \rightarrow CN^- + C_2H_5OH + OH \quad (5)$$
$$(AP_{calc} = -0.96\,\text{eV})$$

For 2-nitropropane, the same interpretation would be also applied.

For the second process of nitromethane, reactions (6) and (7) might be considered. The values of their appearance potential can be estimated to be 3.53 eV and 3.59 eV which are almost consistent with the observed onset value of 3.7 eV.

$$CH_3NO_2 + e^- \rightarrow CN^- + H_2 + O_2 + H \quad (6)$$
$$(AP_{calc} = 3.53\,\text{eV})$$
$$CH_3NO_2 + e^- \rightarrow CN^- + H_2O + O + H \quad (7)$$
$$(AP_{calc} = 3.59\,\text{eV})$$

In other words, the second process can be interpreted with other complicated electron capture processes different from reaction (1) or resulting in a further dissociation of product of reaction (1).

For the second process of nitroethane and 1-nitropropane, the possibility of reactions (8), (9) or (10) would be pointed out. Their appearance potentials give the values of 5.02 eV, and 4.56 eV or 4.59 eV which are almost consistent with the observed onset values; 5.2 eV (for nitroethane) and ~4.4 eV (for 1-nitropropane)

$$C_2H_5NO_2 + e^- \rightarrow CN^- + CH_3 + HO_2 + H \quad (8)$$
$$(AP_{calc} = 5.02\,\text{eV})$$
$$1\text{-}C_3H_7NO_2 + e^- \rightarrow CN^- + C_2H_5 + HO_2 + H \quad (9)$$
$$(AP_{calc} = 4.56\,\text{eV})$$
$$1\text{-}C_3H_7NO_2 + e^- \rightarrow CN^- + C_2H_4 + H_2 + OH + O$$
$$(AP_{calc} = 4.59\,\text{eV}) \quad (10)$$

For the third process in nitromethane, reaction (11) resulting in a further dissociation of product accompanied with the rearrangement might be assigned. This reaction gives a value of 8.05 eV for the appearance potential which is almost consistent with the observed onset value, ~7.8 eV.

$$CH_3NO_2 + e^- \rightarrow CN^- + 3H + O_2 \quad (11)$$
$$(AP_{calc} = 8.05\,\text{eV})$$

Formation of *m*/*e* 42 Ions. In nitromethane, the ions of *m*/*e* 42 can be assigned to CNO^-. In other samples, however, the possibility of $C_2H_4N^-$ ions exists. Figure 2 shows[*6] that two processes contribute to the formation of these ions. The first process appears at ~3 eV in nitromethane, nitroethane and 2-nitropropane and at ~2.6 eV[*7] in 1-nitropropane, and the second ones seem to appear at ~7.5 eV in nitromethane, ~7.2 eV in nitroethane and ~6.8 eV in 1-nitropropane and 2-nitropropane.

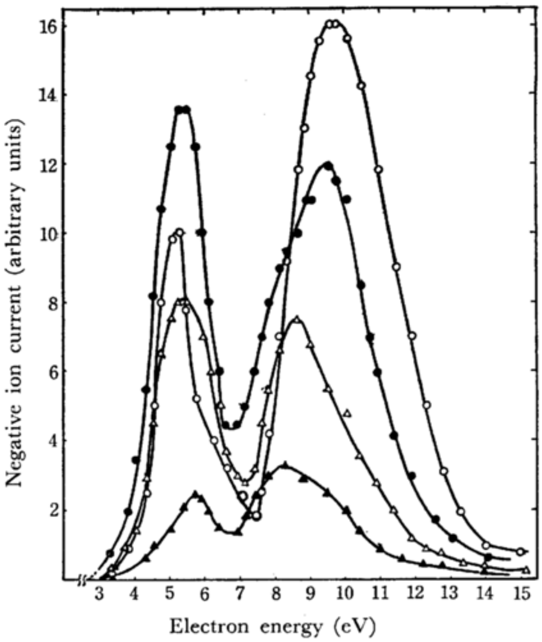

Fig. 2. Ionization efficiency curves of negative ions of *m*/*e* 42 from nitroalkanes.

○ CH_3NO_2 ● $1\text{-}C_3H_7NO_2$
△ $C_2H_5NO_2$ ▲ $2\text{-}C_3H_7NO_2$

In the case of CNO^- ions, the lack of knowledge of the values of $\Delta H_f(CNO)$ and $EA(CNO)$ makes difficult the assignment of reactions which correspond to each process. It is possible, however, to have some interesting discussions. Now, taking $\Delta H_f(CNO)=x(\text{eV})$ and $EA(CNO)=y(\text{eV})$, the appearance potentials of reactions to be expected would be estimated as follows.

For the first process;

$$CH_3NO_2 + e^- \rightarrow CNO^- + H_2O + H \quad (12)$$
$$CH_3NO_2 + e^- \rightarrow CNO^- + H_2 + OH \quad (13)$$
$$C_2H_5NO_2 + e^- \rightarrow CNO^- + CH_3OH + H \quad (14)$$
$$1\text{-}C_3H_7NO_2 + e^- \rightarrow CNO^- + C_2H_5OH + H \quad (15)$$

Then, the appearance potentials of each reaction can be estimated as follows, by using the known values of ΔH_f.

$$AP_{12} = x - y + 0.56, \quad AP_{13} = x - y + 1.18$$
$$AP_{14} = x - y + 0.88, \quad AP_{15} = x - y + 0.45$$

Combining these values with the observed onset values leads to the following results.

For nitromethane; $x-y=2.44$ or $x-y=1.82$.

For nitroethane; $x-y=2.12$, for 1-nitropropane; $x-y=2.15$.

For the second process;

[*6] In general the *IE* curve of resonance type appears to correspond to the electron capture process. If so, the possibility of ion pair formation ($R^+ + NO_2^-$) discussed in the second report[8] might be required to be replaced with another mechanism (for example, $CH_3NO_2 + e^- \rightarrow NO_2^- + CH + 2H$; $AP_{calc} = 7.9$ eV.

[*7] estimated by extrapolation.

$$CH_3NO_2 + e^- \rightarrow CNO^- + OH + 2H \quad (16)$$

$$CH_3NO_2 + e^- \rightarrow CNO^- + H_2 + O + H \quad (17)$$

$$C_2H_5NO_2 + e^- \rightarrow CNO^- + CH_3O + 2H \quad (18)$$

$$1\text{-}C_3H_7NO_2 + e^- \rightarrow CNO^- + C_2H_5O + 2H \quad (19)$$

By the same treatment, the following results can be obtained.

For nitromethane; $x-y=1.79$ or $x-y=1.88$, for nitroethane and 1-nitropropane; $x-y=2.02$, $x-y=2.02$.

If the value of 2.44 eV is excluded,*[8] a value of 1.97 ± 0.13 eV can be estimated for the mean value of $(x-y)$. Here, it should be noticed that a relatively good constancy of $(x-y)$ has been found. In other words, this suggests that the assignments above mentioned are plausible ones.

On the other hand, the appearance potential of the reactions resulting in the formation of C_2H_4N species from nitroethane (for specific example) can be approximately estimated to be 9.6 or 8.9 eV*[9] by taking $D(NO\text{-}O)=3.2$ eV, $D(N\text{-}O)=6.6$ eV, $D(H\text{-}C_2H_5)=4.2$eV, $D(O\text{-}H)=4.4$eV and $D(O\text{-}O)=5.1$ eV.*[10] Of course, this estimation is the approximate one in the meaning that there are assumed to be $D(H\text{-}C_2H_4NO_2)=D(H\text{-}C_2H_5)$, $D(C_2H_4NO\text{-}O)=D(NO\text{-}O)$ and $D(C_2H_4N\text{-}O)=D(N\text{-}O)$. Although the nitro group has a tendency to weaken the carbon-hydrogen bond,[9] its effect cannot be considered to be great. Now, combining the value of 9.6 or 8.9 eV with the observed value ($\sim$3 eV) of appearance potential, we can obtain the value of 6.6 or 5.9 eV for the electron affinity of C_2H_4N species. Judging from the values of electron affinity of various species published hitherto, however, this is too high. At any rate, few reports on the formation of $C_2H_4N^-$ ions and the lack of knowledges of $\Delta H_f(C_2H_4N)$ and $EA(C_2H_4N)$ make difficult a further discussion. Thus, in this work the possibility of $C_2H_4N^-$ ions was not taken into consideration.

In the range of electron energy higher than 16—20 eV, ion pair formations might be expected. The determination of onset values, however, was difficult because of little change of ion current in addition to the weak intensity.

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*[8] This means that reaction (12) is to be rejected.

*[9] Products to be assigned; $OH+O$ or $H+O_2$.

*[10] For each D value, see the article of Vedeneyev *et al.,* in *5.