BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 614—618 (1969)

Measurement of Negative Ions Formed by Electron Impact. II. The Ionization Efficiency Curves of Negative Nitro, Oxygen Atom and Nitromethylene Ions from Nitroalkanes

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(Received June 17, 1968)

The ionization efficiency (IE) curves of NO_2^-, O^- and $CH_2NO_2^-$ ions from nitroalkanes (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) have been measured with a Hitachi RMU-6D mass spectrometer. Based on each authorized value of IP(CH_3, C_2H_5, C_3H_7, O and H), D(C–NO_2, C–H, C–C, NO–O and N–O), EA(NO_2 and O) and the excitation energy of CH_3, the respective onsets observed for the electron energies above $\sim$3 eV on the IE curves were suggested to be interpreted as appearance potentials of the following reactions. For NO_2^- ions, $RNO_2+e\rightarrow R^*+NO_2^-$, $RNO_2+e\rightarrow R^++NO_2^-+e$; for O^- ions, $RNO_2+e\rightarrow RNO+O^-$, $RNO_2+e\rightarrow RN+O+O^-$, $RNO_2+e\rightarrow RN^++O+O^-+e$; for $CH_2NO_2^-$ ions, $CH_3NO_2+e\rightarrow H^+\ \ CH_2NO_2^-+e$, $RNO_2+e\rightarrow H+R_1+CH_2NO_2^-$. On the other hand, the strong peak of NO_2^- ions due to the dissociative electron capture process ($RNO_2+e\rightarrow R+NO_2^-$) was observed at the lower electoron energy. Furthermore, a value of EA(CH_2NO_2) was presented to be $\sim$0.5 eV.

Recently, several studies have been reported on the measurement of negative ion mass spectra by the electron impact method.1-5) However, they have only been made for the limited kinds of compounds. Furthermore, the data of the ionization efficiency (IE) curves of negative ions are very limited. On the other hand, the role of negative ions is attracting increasing attention in the field of radiation chemistry.6) Especially, the compounds containing nitrogen and oxygen atoms are of

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1) C. E. Melton in "Mass Spectrometry of Organic Ions," ed. by F. W. Mclafferty, Academic Press, Inc., 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. Budzikiewez 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) T. Sugiura, T. Seguchi and K. Arakawa, This Bulletin, **40**, 2992 (1967).

interest.

The present work provides information on the IE curves of negative nitro, oxygen atom and nitromethylene ions (NO_2^-, O^- and $CH_2NO_2^-$) from nitroalkanes for which, as far as the authors know, few reports have been published.

Experimental

The investigation was carried out using a Hitachi RMU-6D mass spectrometer equipped with a T-2M ion source having a straight line rhenium filament. The ion detection circuit consisted of an electron multiplier and of a Faraday collector.

All experiments were made with an ionizing current of 80 μA down to the electron energy of $\sim$3 eV, though it decreased considerably in intensity at lower energies. The accerelating voltage used was always 1.8 kV and the electron multiplier was operated at 1.4 kV. The energy scale was corrected by using the values (9.4 eV and 20.9 eV) of appearance potential of O^- ions from carbon monoxide[7] and those (4.4 eV and 17.3 eV) of O^- ions from oxygen.[8] The reliability of this work, however, is restricted to electron energies above $\sim$3 eV, because of instrumental difficulties.

The research grade nitroalkanes (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) were used without further purification. Measurements for each of the compounds were made at a pressure of about 1×10^{-6} mmHg in the source and a pressure of about 2×10^{-7} mmHg in the analyzer tube.

Results and Discussion

Formation of NO_2^- Ion. Figures 1A-a, 1B-a, 1C-a and 1D-a show respectively the IE curves of NO_2^- ions produced from nitromethane, nitroethane, 1-nitropropane and 2-nitropropane. Figures 1A-b, 1B-b, 1C-b and 1D-b show the same curves, respectively, in the range of electron energy from 3 eV to 15 eV on an expanded scale.

Through all the samples, three resonance peaks were commonly found. In addition, for nitromethane a small peak at 12 eV was found. The first resonance peak lies at a considerably lower electron energy, the second at 4.6 eV for nitromethane, 5.4 eV for nitroethane, 5.5 eV for 1-nitropropane and 5.5 eV for 2-nitropropane, and the last at 8.5 eV, 9.7 eV, 9.8 eV and 9.9 eV, respectively.

These facts show clearly that three processes contribute to the formation of NO_2^- ions. The first process can be easily understood as the dissociative electron capture. Because $D<EA$ (D:

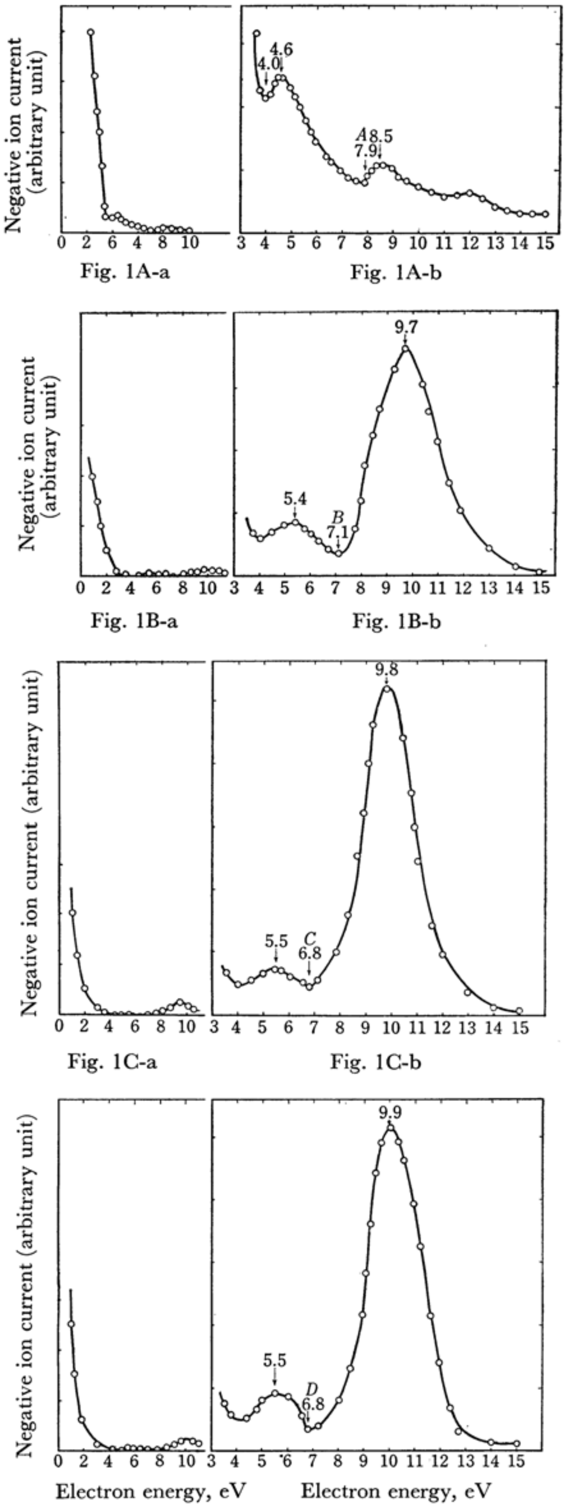

Fig. 1A-a Fig. 1A-b

Fig. 1B-a Fig. 1B-b

Fig. 1C-a Fig. 1C-b

Fig. 1D-a Fig. 1D-b

Fig. 1. Ionization efficiency curves of NO_2^- from nitroalkanes.

A	CH_3NO_2	B	$C_2H_5NO_2$
C	1-$C_3H_7NO_2$	D	2-$C_3H_7NO_2$

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6) R. B. Cundall, A. W. Locke and G. C. Street, *Nature*, **210**, 1354 (1966).

7) M. A. Fineman and A. w. Petrocelli, *J. Chem. Phys.*, **36**, 25 (1962).

8) D. c. Frost and C. A. McDowell, *J. Am. Chem. Soc.*, **80**, 6183 (1958).

dissociation energy of C–N bond, *EA*: electron affinity of NO_2), the dissociative electron capture is energetically possible even with thermal electrons. The appearance potential of NO_2^- ions due to this process can be expected to be below zero, *e. g.*, for nitromethane, -1.4—-1.6 eV.*1

The second process which can be expected to appear at 4.0 eV is not well known. Following Schulz's interpretation made for the formation of H^- ions from hydrogen,[9] however, it seems to correspond to the process of $R^*+NO_2^-$ (R^*: excited state of radical). If a value of 4.0 eV in nitromethane is taken as the value of appearance potential of $CH_3^*+NO_2^-$, the excitation energy of methyl radical can be estimated to be 5.4—5.6 eV. The agreement with the value (5.7 eV) reported by Herzberg *et al.*[10] is relatively good. Of course, this interpretation is a tentative one which demonstrates the need for further work.*2

The third process seems to correspond to that of an ion pair formation $[R^++NO_2^-]$. Each value marked by B, C and D in Fig. 1 coincides well with the corresponding value[11] obtained by one of the authors except for nitromethane. Thus, the third process can be concluded as the ion pair formation. For nitromethane an ion pair seems to appear at ~7.9 eV (the value marked by A in Fig. 1) which is not inconsistent with the value (8.2 eV) estimated by taking $D(C\text{–}NO_2)=2.3$ eV, $IP(CH_3)=9.8$ eV and $EA(NO_2)=3.9$ eV. A small change in negative ion current around 8 eV, however, suggests that the cross section for ion pair formation is very small compared with that of other nitroalkanes.

The present work confirms also that the IE curve for 2-nitropropane is the same as that for 1-nitropropane. It is of interest that the peak due to the ion pair formation process has been found in ~8.5 eV for nitromethane and ~9.8 eV for other three compounds irrespective of the change of alkyl group. These results indicate that the cross section for ion pair formation $[R^++NO_2^-]$ varies strongly with the electron energy and has a maximum value around 8.5 eV or 9.8 eV.

The relative intensity of NO_2^- ions produced from each compound is shown in Table 1. The peak height of the third process in nitromethane was almost the same as that of negative oxygen atom ions (O^-)*3 produced from carbon monoxide under the same experimental condition. Therefore, the cross section for negative nitro ion formation due to the first process should be very large.

TABLE 1. RELATIVE INTENSITY OF NO_2^- IONS PRODUCED FROM NITROALKANES

Process / Compound	Relative intensity of peak by each process*		
	1st process	2nd rpocess	3rd process
CH_3NO_2	(> 240)	~ 3	~ 3.5
$C_2H_5NO_2$	(> 130)	1	~ 6
1-$C_3H_7NO_2$	(> 150)	~ 1	~ 8
2-$C_3H_7NO_2$	(> 200)	~ 1.5	~ 8.5

* Normalized to the peak of 2 nd process in IE curve of NO_2^- from $C_2H_5NO_2$ (yield=1).

Formation of O^- Ion. Figures 2A, 2B, 2C and 2D show respectively the IE curves of O^- ions from nitromethane, nitroethane, 1-nitropropane and 2-nitropropane. Although the negative ions of *m/e* 16 may be assigned to the species (*e. g.* NH_2^-) other than O^- ion, their possibility might be ruled out in the range of low electron energy because the complicated rearrangement is necessary for its formation.

All of the results show the possibility of three processes. The first process appears at ~3.1 eV and peaks at ~ 6.6 eV irrespective of the compounds. Thus, this process seems to be the dissociative electron capture for which the reaction (1) or (2) can be expected.

$$RNO_2 + e \longrightarrow RNO + O^- \qquad (1)$$

$$\longrightarrow RN + O + O^- \qquad (2)$$

However, the reaction (2) would require much higher energy than ~3.1 eV, because the values of D(RNO–O) and D(RN–O) are expected to be higher than D(NO–O) and D(N–O)[12] respectively, as pointed out by Kandel.[13] At this stage we would prefer the reaction (1), although this problem is not fully resolved.

The second process seems to appear at ~8.3 eV for nitromethane, at ~8.6 eV for other three compounds and peaks at 9.5 eV and ~10.1 eV respectively. Possibly, this corresponds to the reaction (2). Then, the values of $D(CH_3NO_2\rightarrow CH_3N+O+O)$ and $D(RNO_2\rightarrow RN+O+O)$ are estimated to be ~9.8 eV and ~10.1 eV respectively.

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*1 $D(CH_3\text{–}NO_2) \simeq 2.5$—$2.3$ eV (R. I. Reed, "Ion Production by Electron Impact," Academic Press, London (1962), p. 35). $EA(NO_2)\simeq 3.9$ eV (See Ref. 11).

9) G. J. Schulz, *Phys. Rev.*, **113**, 816 (1959).

10) G. Herzberg and J. Shovsmith, *Can. J. Phys.*, **34**, 523 (1956).

*2 Although a series of optical absorption bands for nitrite ions (NO_2^-) from 330 mμ to 390 mμ has been measured by Pringsheim, this does not fit the value of 5.4≃5.6 eV; P. Pringsheim, *J. Chem. Phys.*, **23**, 369 (1955).

11) S. Tsuda and W. H. Hamill, *Advan. Mass. Spectry.*, **3**, 249 (1965).

*3 Cross section: 1.6×10^{-19} cm^2 (G. J. Schulz, *Phys. Rev.*, **128**, 178 (1962)).

12) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Bulter Tanner Ltd., London (1966), p. 29: D(NO–O)≃3.2 eV, D(N–O)≃6.6 eV.

13) R. J. Kandell, *J. Chem. Phys.*, **23**, 84 (1955).

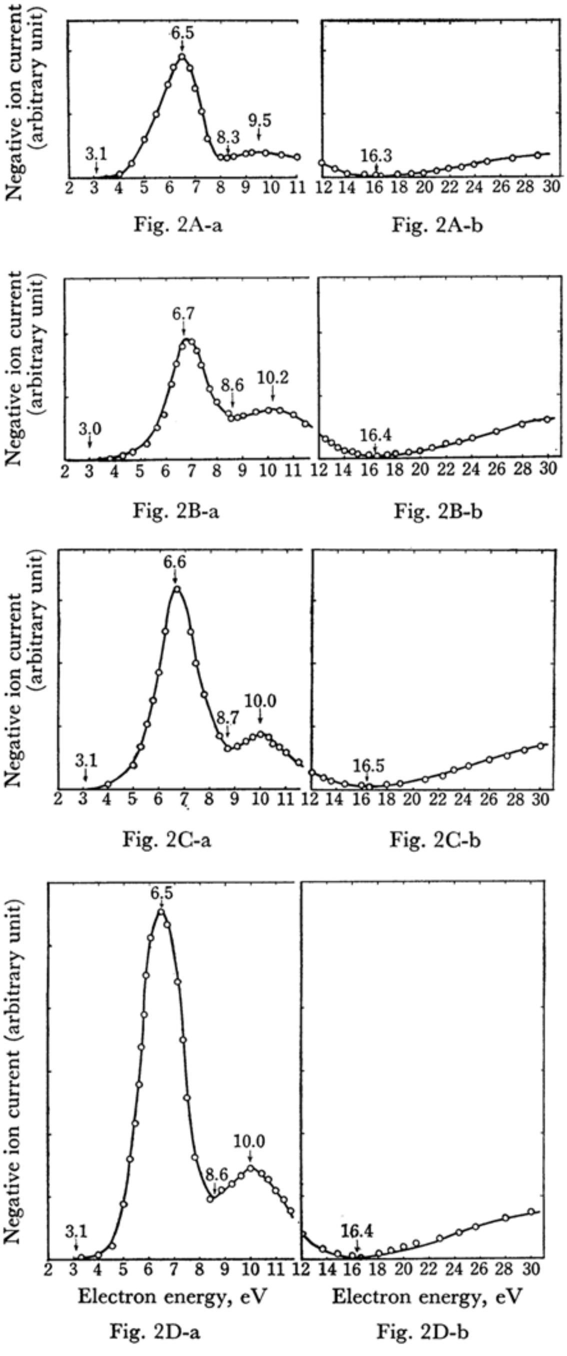

Fig. 2A-a Fig. 2A-b

Fig. 2B-a Fig. 2B-b

Fig. 2C-a Fig. 2C-b

Fig. 2D-a Fig. 2D-b

Fig. 2. Ionization efficiency curves of O^- from nitroalkanes.

A CH_3NO_2 B $C_2H_5NO_2$
C $1\text{-}C_3H_7NO_2$ D $2\text{-}C_3H_7NO_2$

The third process appears to ~16.4 eV irrespective of the compounds. The following ion pair formation might be considered.

$$RNO_2 + e \longrightarrow RN^+ + O + O^- + e \qquad (3)$$

For nitromethane the appearnace potential of the reaction (3) can be estimated to be ~16 eV, taking $\Delta H_f(CH_3N^+) \simeq 11.4$ eV,[14] $\Delta H_f(CH_3NO_2) \simeq -0.8$ eV,[13] $\Delta H_f(O) \simeq 2.6$ eV[15] and $EA(O) = 1.45$ eV.[16] It agrees approximately with 16.3 eV observed for nitromethane.

TABLE 2. RELATIVE INTENSITY OF O^- IONS PRODUCED FROM NITROALKANES

Process / Compound	Relative intensity of peak due to each process*	
	1st process	2nd process
CH_3NO_2	~ 3.2	~ 0.8
$C_2H_5NO_2$	~ 3	~ 1.3
$1\text{-}C_3H_7NO_2$	~ 5	~ 1.5
$2\text{-}C_3H_7NO_2$	~ 8.5	~ 2.5

* Normalized to the peak of 2nd process in IE curve of NO_2^- from $C_2H_5NO_2$ (yield=1).

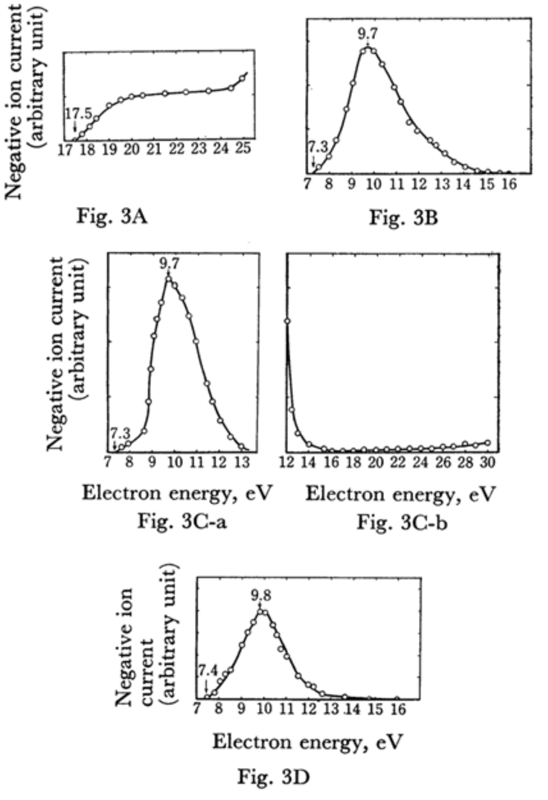

Fig. 3A Fig. 3B

Fig. 3C-a Fig. 3C-b

Fig. 3D

Fig. 3. Ionization efficiency curves of $CH_2NO_2^-$.

A CH_3NO_2 B $C_2H_5NO_2$
C $1\text{-}C_3H_7NO_2$ D $2\text{-}C_3H_7NO_2$

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[14] F. H. Field and J. J. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York (1957), p. 274.

[15] R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

[16] D. C. Frost and C. A. McDowell, *J. Am. Chem. Soc.*, **80**, 6183 (1958).

Table 2 shows the relative intensity of the peaks of O^- ions produced from each compound.

Formation of $CH_2NO_2^-$ (*m/e* 60) Ion. Figures 3(A), 3(B), 3(C) and 3 (D) show respectively the IE curves of $CH_2NO_2^-$ ions*[4] from nitromethane, nitroethane, 1-nitropropane and 2-nitropropane. All of the results except for nitromethane showed a broad resonance peak in the range of electron energy from 7.3 eV to ~16 eV. The peaks were respectively at 9.7 eV for nitroethane, at 9.7 eV for 1-nitropropane, and at 9.8 eV for 2-nitropropane.

A relatively high value of appearance potential (~7.3 eV) rules out the possibility of the dissociative electron capture process; $R+CH_2NO_2^-$ (R: radical).

In the discussion on IE curves of NO_2^- ions, the authors pointed out the possibility of ion pair formation in the range of electron energy from 6.8 eV to 15 eV. If the process of ion pair formation corresponds also to a value of ~7.3 eV, the electron affinity of CH_2NO_2 radical can be estimated to be 4.5 eV from the reaction (4) by using the values of $D(C_2H_5\text{–}CH_3)=3.5$ eV[12] and $IP(C_2H_5)=$ 8.3 eV[17]

$$1\text{-}C_3H_7NO_2 + e \longrightarrow C_2H_5^+ + CH_2NO_2^- + e \quad (4)$$

On the other hand, the reaction (5)[17] gives the value of 6.1 eV.

$$C_2H_5NO_2 + e \longrightarrow CH_3^+ + CH_2NO_2^- + e \quad (5)$$

In addition to their high values, their inconsistency rules out the possibility of the ion pair formation. Then, the possibility of reaction (6) or (7) is expected.*[5]

$$RNO_2 + e \longrightarrow H + R_1 + CH_2NO_2^- \quad (6)$$

$$RNO_2 + e \longrightarrow CH_3 + CH_2 + CH_2NO_2^- \quad (7)$$

However, the same value*[6] of onset suggests the possibility of the reaction (6).

For 1-nitropropane in which the formation of $CH_2NO_2^-$ ions was successively observed for the electron energies higher than ~17 eV, the onset of ion pair formation might be expected in this range. Because of a very slow slope of IE curve (Fig. 3 C-b), however, it was very difficult to determine the value of onset.

On the other hand, a high onset value (17.5 eV) in nitromethane suggests strongly the possibility of the following ion pair formation.

$$CH_3NO_2 + e \longrightarrow H^+ + CH_2NO_2^- + e \quad (8)$$

Then, the electron affinity of CH_2NO_2 radical can be estimated to be 0.5 eV, by using $D(C\text{–}H)=4.4$ eV and $IP(H)=13.6$ eV. This value is also consistent with the value (0.6 eV) estimated from reaction (6), by taking $D(C\text{–}H)=4.4$ eV, $D(C\text{–}C)=$ 3.5 eV. However, because of a very small yield of $CH_2NO_2^-$ ion the reliability of this value is not so high.

TABLE 3. RELATIVE INTENSITY OF THE PEAKS OF $CH_2NO_2^-$ IONS

Compound	Relative intensity*
$C_2H_5NO_2$	~0.05
$1\text{-}C_3H_7NO_2$	~5
$2\text{-}C_3H_7NO_2$	~0.12

* Normalized to the peak of 2nd process in IE curve of NO_2^- from $C_2H_5NO_2$ (yield=1).

Table 3 shows the relative intensity of the peaks of $CH_2NO_2^-$ ion from each compound.*[7] It should be emphasized that the intensity of $CH_2NO_2^-$ from 1-nitropropane is much stronger (about 100—40 times) than that from nitroethane and 2-nitropropane. This might be useful for the identification of 1-nitropropane.

The authors are indebted to Professor William H. Hamill, Radiation Laboratory, University of Notre Dame, Indiana, U. S. A. for helpful suggestions and discussions.

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*[4] The possibility of $C_2H_4O_2$ ion may be ruled out, because (1) in spite of the complicated rearrangement required for the formation of $C_2H_4O_2^-$ from $1\text{-}C_3H_7NO_2$, a relatively large peak of *m/e* 60 ion was found, and (2) the appearance potential observed cannot be explained with the formation of this ion.

17) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 3464 (1964).

*[5] The $CH_2NO_2^-$ ion from 2-nitropropane is considered to be the rearrangement ion.

*[6] The appearance potential of the reaction (6) is shown as follows.

$$AP=D(C\text{–}H)+D(C\text{–}C)-EA(CH_2NO_2)$$

where the excess kinetic energy of fragment ions is ignored.

*[7] The relative intensity of $CH_2NO_2^-$ ion from CH_3NO_2 was very samll (~0.02) in the range of electron energy from 20 eV to 23 eV.