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Measurement of Negative Ions Formed by Electron Impact. I. Negative Ion Mass Spectra of Nitroalkanes

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The negative ion mass spectra of nitroalkanes (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) have been mesaured with a mass spectrometer under electron energies of 80 eV, 40 eV, 9.5 eV and 4.5 eV in the range of pressure used for usual analysis. The spectral intensities of negative ions were compared with those of positive ions. In 80 or 40 eV electron impact experiments, *m/e* 16 (O^-), 46 (NO_2^-), 26 (probably, CN^-) and 42 (probably, CNO^- or $C_2H_4N^-$) ions were commonly found. Their yields showed good linearity against pressure under the present experimental conditions. The peaks of *m/e* 61 (parent ion; $CH_3NO_2^-$) in nitromethane, of *m/e* 25 (C_2H^-) in nitroethane, 1-nitropropane and 2-nitropropane, and a relatively strong peak of *m/e* 60 ($CH_2NO_2^-$) in 1-nitropropane were characteristic. For lower electron energies, the strong dependency of the yield of negative ions on the electron energy was confirmed. The yield of negative ions as compared with positive ions for 80 eV and 40 eV of electron energy was lower by a factor of $\sim 10^4$. On the other hand, the comparison of the yield of positive ions for 15 eV electrons with that of negative ions for 9.5 eV electrons gave the value of ~ 0.2. In addition, of the role these negative ions in radiolysis has been briefly discussed.

In the last few years studies involving positive ion mass spectra have been carried out with a great variety of organic compounds. However, only a few papers have been published with respect to negative ion mass spectrometry. Also, discrepancies are seen between the published experimental results, which demonstrate the need for further work. In general, the mechanisms for formation of negative ions by electron impact can be classified into the following processes:[1] (a) The radiative capture of a free electron by a neutral atom ($e + A \rightarrow A^- + h\nu$). (b) Capture of a free electron by an atom with a third body taking up the excess energy ($e + A + B \rightarrow A^- + B +$ kinetic energy). (c) Capture of a free electron by a molecule, with the vibrational excitation of the molecular ion and its subsequent stabilization by a collision with another molecule ($e + XY \rightarrow (XY)^{-*}$; $(XY)^{-*} + A \rightarrow XY^- + A +$ kinetic energy). (d) Dissociative attachment: capture of a free electron by a mol-

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

ecule, the excess energy going into dissociation of the molecule ($e + XY \rightarrow (XY)^{-*} \rightarrow X + Y^-$). (e) Ion-pair production: noncapture dissociation of a molecule into positive and negative ions ($e + XY \rightarrow e + X^+ + Y^-$). (f) Transfer of one or more electrons to a neutral structure or a positive ion in a collision with another particle ($A + B \rightarrow A^- + B^+$; or $C^+ + D \rightarrow C^- + D^{2+}$).

Under ordinary laboratory conditions, and excluding charge-changing collisions, processes (b), (c) and (d) would be the most probable. For electron with energies in excess of about 7—20 eV, (e) will also become important.

As these processes are pressure dependent in different ways,[2] the relative intensities of negative ion mass spectra can be expected to change with sample pressure. A further complication is the low yield of negative ions as compared with positive ions in the range of 50 eV to 70 eV of electron energy. However, the recent developements of detection method and apparatus have overcome considerably these difficulties.

Moruzzi *et al.*[3] have surveyed the negative-ion species produced in oxygen and some gases containing oxygen for various pressures and E/P conditions[*1] using an rf mass spectrometer coupled to an electron drift tube operating at pressures up to 5 mmHg. Compton *et al.*[4] have studied the non-dissociative electron capture in complex molecules and negative-ion lifetimes with a modified Bendix mass spectrometer. Melton *et al.*[5] have published the results of measurement for individual and total cross sections for the production of positive ions, negative ions and free radicals by using the modified dual electron beam method. Also, Christophorou and Compton[6] have reviewed the electron swarm and electron beam techniques under the subject of interaction of low energy electrons with polyatomic molecules.

On the other hand, the role of negative ions has recently drawn increasing attention in the field of radiation chemistry. Cundall *et al.*[7] have pointed out the importance of negative ions in the radiolysis of nitroalkanes. Warman[8] has elucidated the occurrence of the ion-molecule reactions of negative oxygen atom ions with the additives such as carbon dioxide and acetone in the radiolysis of alkane-nitrous oxide systems.

Also, in the silent discharge reactions in the gas phase with which a part of our recent works are concerned, the role of negative ions has been suggested to be important.[9]

At the present stage when the negative ion mass spectra were only measured for limited compounds, further work on negative ions is strongly required. The present work deals with the negative ion mass spectra of nitroalkanes,[*2] especially in relation to the electron energy effect.

Experimental

This investigation was carried out using a standard Hitachi RMU-6D mass spectrometer equipped with a T-2M ion source having a straight line rhenium filament. The ion detection circuit consisted of a ten stage electron multiplier having Ag-Mg dynode and a Faraday collector. All the spectra were measured with an ionizing current of 80 μA and a constant accelerating voltage of 1.8 kV, under the ionizing energies of 80 eV, 40 eV, 9.5 eV and 4.5 eV.

The electron energy was calibrated by the vanishing current method as compared to the ionization potential of argon[10] or the appearance potential[11] of m/e 16 (O^-) from carbon monoxide.

The polarity of the collector ion lens was reversed for negative ion measurement. The electron multiplier was always operated at 1.4 kV.

The research grade nitroalkanes (nitromethane, nitroethane, 1-nitropropane and 2-nitropropane) were used without further purification. Data for each of the compounds were taken at a pressure of $\sim 10^{-6}$ mmHg in the source.

Results and Discussion

Nitromethane. In 80 eV electron impact experiments, negative ions of m/e 16 (O^-), 46 (NO_2^-), 26 (CN^-) and 42 (CNO^-) have mainly been observed (Fig. 1a). The result was consistent with that of Aplin *et al.*,[12] except that the relative intensity of m/e 16 (O^-) ion to m/e 26 (CN^-) ion was reversed.

It is probable that differences in the source

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[2] C. E. Melton in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, Inc., New York, N. Y. (1963), p. 163.

[3] J. L. Moruzzi and A. V. Phelps, *J. Chem. Phys.*, **45**, 4617 (1966).

[*1] E: electric field strength. P: pressure.

[4] R. N. Compton, L. G. Christophorou, G. S. Hurst and P. W. Reinhardt, *J. Chem. Phys.*, **45**, 4634 (1966).

[5] C. E. Melton and P. S. Rudolf, *ibid.*, **47**, 1771 (1967).

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

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

[8] J. M. Warman, *ibid.*, **213**, 382 (1967).

[9] A. Yokohata and S. Tsuda, Presented at the 10th Conference on Radiation Chemistry, Hiroshima, October, 1967.

[*2] Negative ion mass spectra have not yet been measured, except nitromethane which is measured only at an electron energy of 70 eV. (See Ref. 12)

[10] K. Watanabe, T. Nakayama and J. Mottl, *J. Quant, Spectrosc. Radiat. Transfer.*, **2**, 369 (1962).

[11] M. A. Fineman and W. Petrocelli, *J. Chem. Phys.*, **36**, 25 (1962).

[12] R. T. Aplin, H. Budzikiewiez and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 3180 (1965).

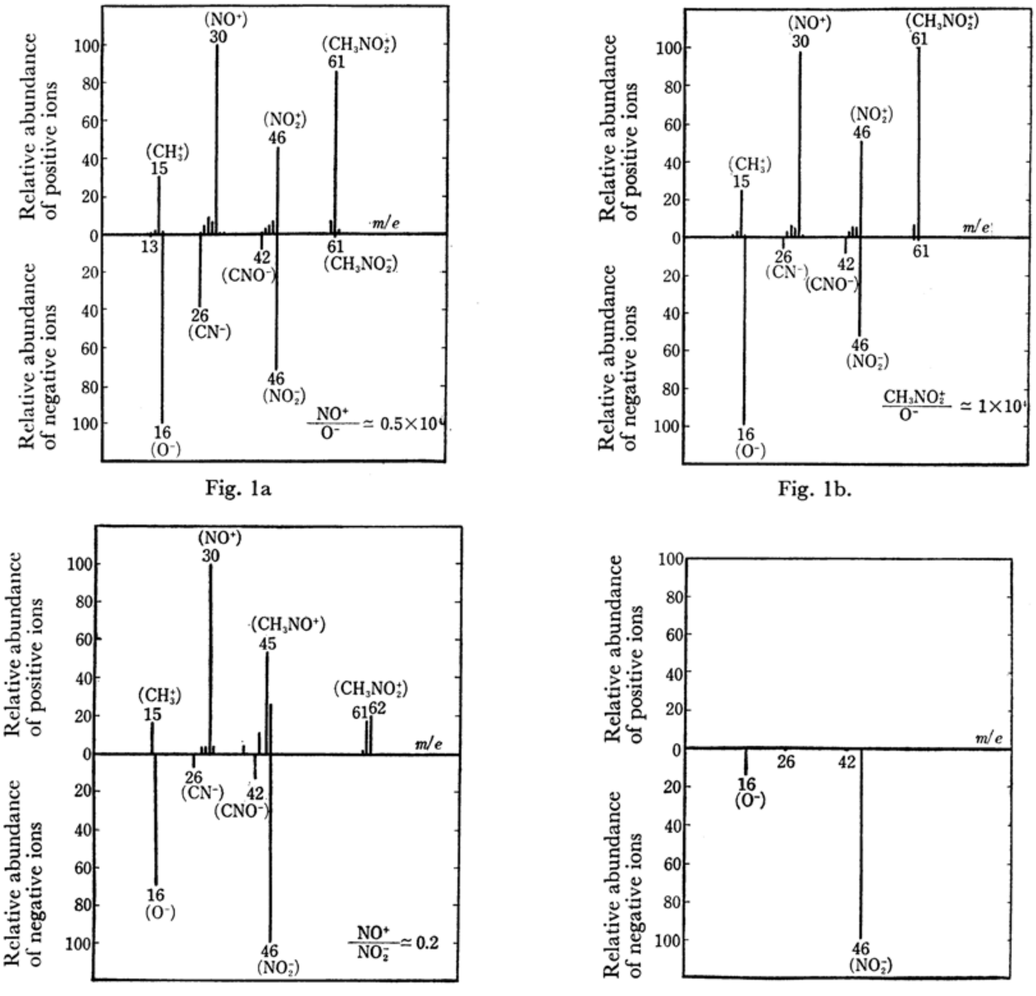

Fig. 1a

Fig. 1b.

Fig. 1c.

Fig. 1d.

Fig. 1. Positive and negative ion mass spectra of nitromethane (source pressure: ~10^{-6} mmHg).
a 80 eV b 40 eV c 15 eV for positive ions, 9.5 eV for negative ions d 4.5 eV

pressure and in the geometry of the ion source are responsible for this discrepancy, which emphasizes the much greater sensibility of negative ion mass spectrometry toward the change in experimental conditions as compared with positive ion mass spectrometry.

As in alcohols[2)] the most intense peak was the *m/e* 16 (O^-) ion. Also, it might be mentioned that it is one of the characteristics found frequently in the compounds containing oxygen atoms. When the yield of O^- ion was compared with that of positive ion of *m/e* 30 (NO^+) (the most intense peak among the positive ions), NO^+/O^- was $\sim 0.5\times10^4$.

For 40 eV electrons (Fig. 1b), the pattern of the negative ions did not differ so much from that for 80 eV electrons except the decrement in the intensity of *m/e* 26 (CN^-) ion, and the ratio of $CH_3NO_2^+$ to O^- was $\sim 1\times10^4$.

The comparison of the yield of *m/e* 46 (NO_2^-) ion obtained with 9.5 eV electrons with that of positive ion of *m/e* 30 (NO^+) obtained with 15 eV electrons*[3] (Fig. 1c; C condition) gave a value

TABLE 1. MINOR NEGATIVE IONS FROM CH_3NO_2

m/e	Relative intensities for electron energies of		
	80 eV*	9.5 eV**	4.5 eV**
12	0.2		
13	1.1	0.2	
26			1.2
42			2.5
60	0.7		
61	1.8		

* Normalized to O^- (yield=100)
** Normalized to NO_2^- (yield=100)

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*[3] Since the species of positive ions produced by the impact of 9.5 eV electrons are very limited, the data for 15 eV electrons were conveniently used for comparison.

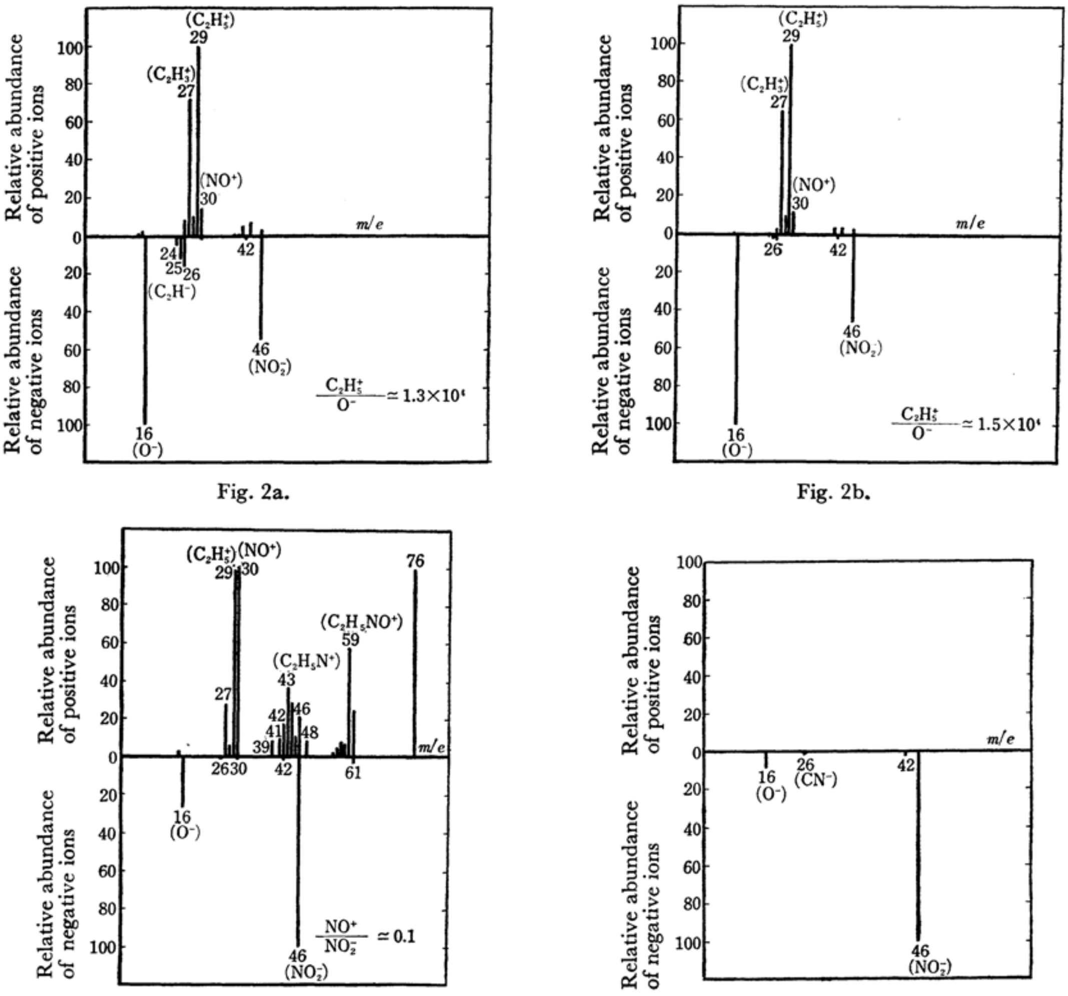

Fig. 2a.

Fig. 2b.

Fig. 2c.

Fig. 2d

Fig. 2. Positive and negative ion mass spectra of nitroethane (source pressure: $\sim 10^{-6}$ mmHg).
a 80 eV b 40 eV c 15 eV for positive ions, 9.5 eV for negative ions d 4.5 eV

of ~ 0.2 for NO^+/NO_2^-. It should be noted that under this condition the yield of NO_2^- is somewhat higher than NO^+.

For 4.5 eV electrons (Fig. 1d) *m/e* 46 (NO_2^-) ions predominated over other negative ions.

Table 1 shows the yields of the minor negative ions for 80 eV, 9.5 eV and 4.5 eV. For 80 eV, a relatively high yield of *m/e* 13 (CH^-) among the negative ions arising from the methyl group is consistent with that in methyl alcohol.[2] It is also of interest that the *m/e* 61 ($CH_3NO_2^-$) ion has been observed.

Nitroethane. For the impact of 80 eV electrons (Fig. 2a) negative ions of *m/e* 16 (O^-), 46 (NO_2^-), 26 (probably, CN^-), 25 (C_2H^-), 24 (C_2^-) and 42 (probably, CNO^- or $C_2H_4N^-$) have been observed. The peak of parent ion ($C_2H_5NO_2^-$) has not been found. When the yield of O^- ion was compared with that of $C_2H_5^+$ (the most intense peak among the positive ions), $C_2H_5^+/O^-$ was $\sim 1.3\times10^4$. A relatively large peak of *m/e* 25 (C_2H^-) among the negative ions arising from the ethyl group is quite similar to the situations in ethane or ethyl alcohol.[2]

TABLE 2. MINOR NEGATIVE IONS FROM $C_2H_5NO_2$

m/e	Relative intensities for electron energies of		
	80 eV*	9.5 eV**	4.5 eV**
25		0.1	
26		1.1	1.0
30	1.2	0.8	0.4
40		0.1	
42	1.6	1.9	0.4
47		0.2	
48		0.2	

* Normalized to O^- (yield=100)
** Normalized to NO_2^- (yield=100)

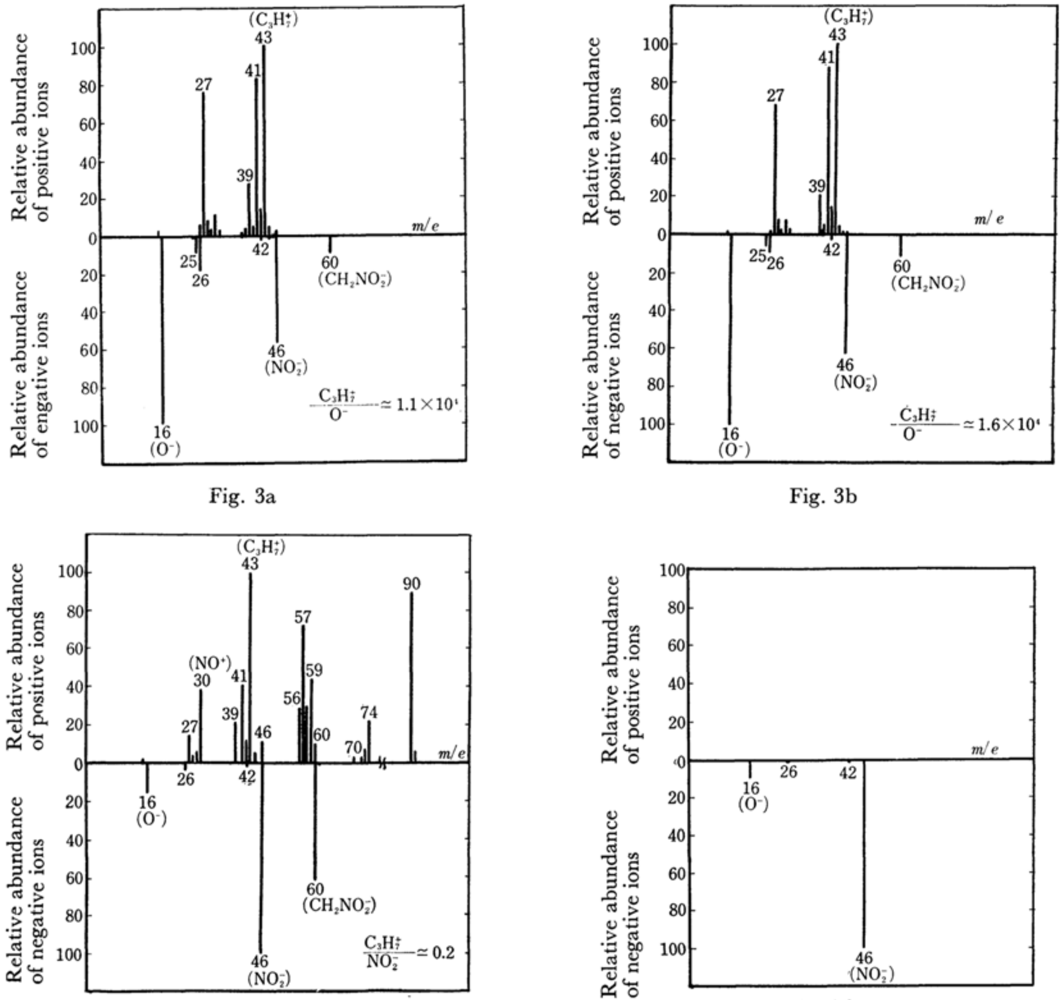

Fig. 3a

Fig. 3b

Fig. 3c

Fig. 3d.

Fig. 3. Positive and negative ion mass spectra of 1-nitropropane (source pressure: ~10^{-6} mmHg).
a 80 eV b 40 eV c 15 eV for positive ions, 9.5 eV for negative ions d 4.5 eV

Mass spectra for 40 eV (Fig. 2b) were not so different from those of 80 eV except the decrement of peaks of *m/e* 26 (CN^-), 25 (C_2H^-) and 24 (C_2^-) ions. The ratio $C_2H_5^+/O^-$ was ~1.5×10^4.

For 9.5 eV and 4.5 eV (Figs. 2c and 2d), the *m/e* 46 (NO_2^-) ion predominated over other negative ions. Under C condition NO^+/NO_2^- was ~0.1.

Table 2 shows the yields of the minor negative ions in relation to the electron energy. It can be seen that the ions formed extend over the range of *m/e* 25 to 48 and their variety is relatively small in both cases of 80 eV and 4.5 eV.

1-Nitropropane and 2-Nitropropane. For the impact of 80 eV and 40 eV electrons (Figs. 3a, 4a and 3b, 4b), 1-nitropropane and 2-nitropropane gave almost the same negative ions; *m/e* 16 (O^-), 46 (NO_2^-), 26 (CN^-) and 25 (C_2H^-), except for the appearance of *m/e* 60 ($CH_2NO_2^-$) in 1-nitropropane.

It is of great interest that in 1-nitropropane a relatively strong peak of *m/e* 25 (C_2H^-) ion has been observed as one of negative ions arising from the propyl group. This was consistent with the situation in *n*-propyl alcohol.[2]

The comparison of the yield of O^- ion with that of $C_3H_7^+$ (the most intense peak among the positive ions) gave the following values for $C_3H_7^+/O^-$; ~1.1×10^4 at 80 eV and 1.6×10^4 at 40 eV for 1-nitropropane, ~1.0×10^4 and ~1.4×10^4 for 2-nitropropane, respectively.

Patterns obtained for 9.5 eV and for 4.5 eV (Figs. 3c, 4c and 3d, 4d) were similar respectively for the two samples, except a large peak of *m/e* 60 ($CH_2NO_2^-$) for electron impact of 9.5 eV on 1-nitropropane.

The ratio of the yield of $C_3H_7^+$ to O^- under the C condition; $C_3H_7^+/O^-$ were ~0.2 for 1-nitropropane and ~0.3 for 2-nitropropane.

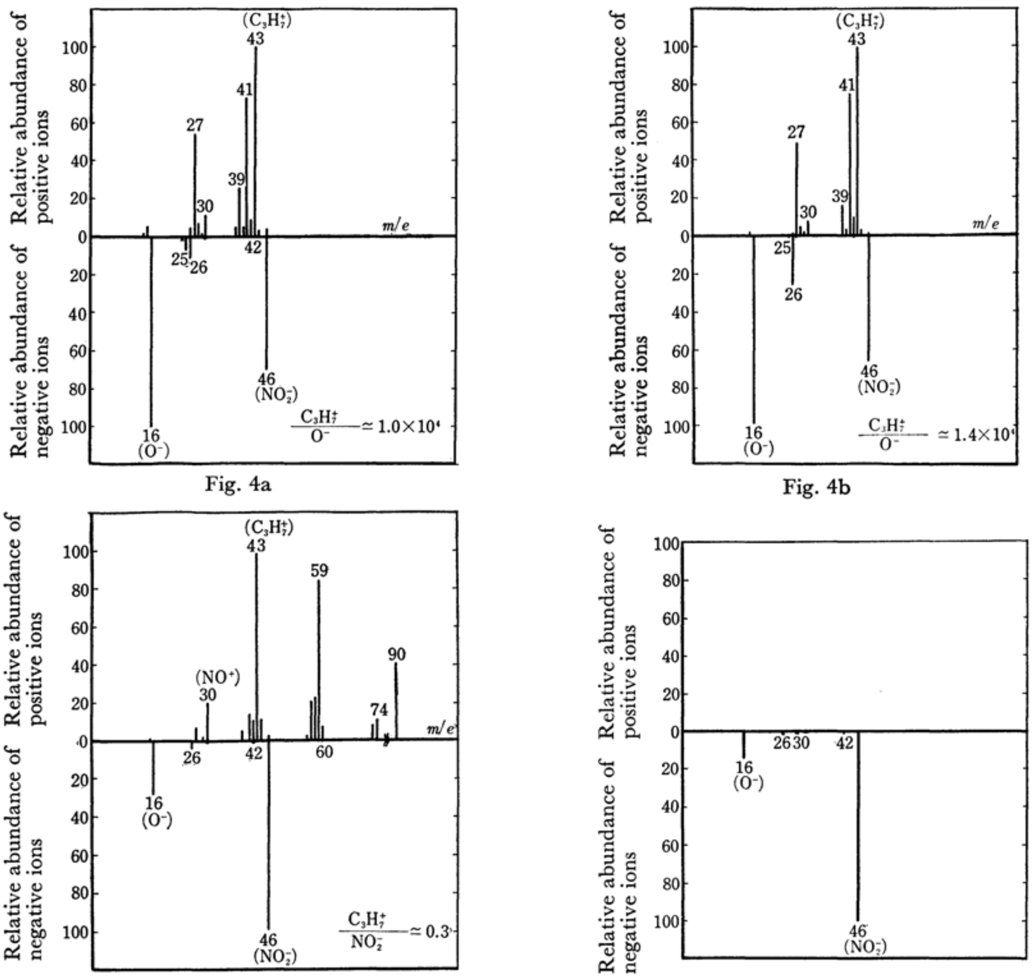

Fig. 4a

Fig. 4b

Fig. 4c

Fig. 4d

Fig. 4. Positive and negative mass spectra of 2-nitropropane (source pressure: ~10^{-6} mmHg).
a 80 eV b 40 eV c 15 eV for positive ions, 9.5 eV for negative ions d 4.5 eV

TABLE 3. MINOR NEGATIVE IONS FROM 1-$C_3H_7NO_2$

m/e	Relative intensities for electron energies of		
	80 eV*	9.5 eV**	4.5 eV**
12	0.2		
13	0.4		
14	0.2		
24	1.1		
26			0.2
27		0.1	
30	0.7	0.5	
36	0.2		
37	0.2		
42		2.1	0.4
44		0.4	
47		0.4	
48		0.2	
58		0.2	
61		0.8	
62		0.1	

* Normalized to O^- (yield=100)
** Normalized to NO_2^- (yield=100)

Tables 3 and 4 show the yields of minor negative ions for 1-nitropropane and 2-nitropropane respectively in relation to the electron energy.

Effect of Pressure. Figure 5 shows the relation between yields of *m/e* 46 (NO_2^-), 16 (O^-), 26 probably CN^-) and 42 (probably, CNO^- or $C_2H_4N^-$) ions and the pressure for each sample (5a for *m/e* 46 ion, 5b for *m/e* 16 ion, 5c for *m/e* 26 ion and 5d for *m/e* 42 ion) under the electron energy of 80 eV.

All the results showed good linearity against the pressure under a given experimental condition. Also, this linear relationship was independent of the electron energy as shown in Fig. 6 where the yields of *m/e* 46 (NO_2^-) ion from nitromethane are shown as an example. A similar linear relationship had been reported for *m/e* 1 (H^-) ion produced from hydrogen[13] under the electron energies of 6.8 eV, 10.0 eV and 14.2 eV in the range of pressure

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

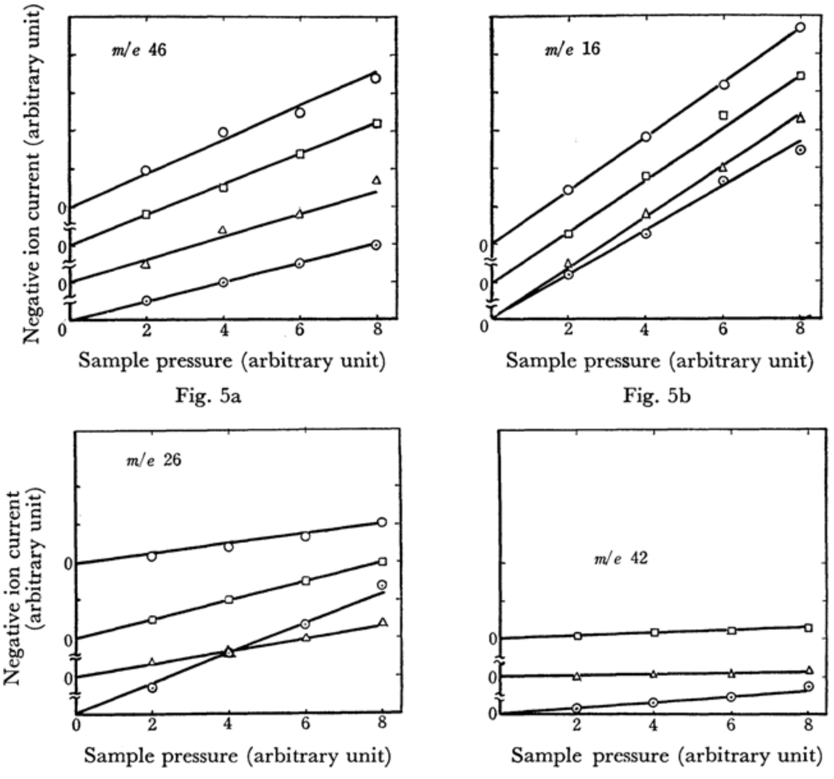

Fig. 5a

Fig. 5b

Fig. 5c

Fig. 5d

Fig. 5. Plot of negative ion current against pressure (Electron energy: 80 eV).
○ 2-$C_3H_7NO_2$ □ 1-$C_3H_7NO_2$ △ $C_2H_5NO_2$ ⊙ CH_3NO_2

TABLE 4. MINOR NEGATIVE IONS FROM 2-$C_3H_7NO_2$

m/e	Relative intensities for electron energies of		
	80 eV*	9.5 eV**	4.5 eV**
14	0.3		
24	0.9		
26			0.2
30	1.1	1.1	
36	0.4		
37	0.4		
38	0.4		
39	0.4		
40		0.1	0.1
41	0.2		0.4
42		0.4	<0.1
47		0.2	
48		0.3	

* Normalized to O^- (yield=100)
** Normalized to NO_2^- (yield=100)

from 1×10^{-4} mmHg to 4×10^{-4} mmHg and for *m/e* 39 (CH_3CC^-) ion from methylacetylene in the range of pressure[14] up to about 5×10^{-5} mmHg. Of course, the pressure dependency may become complicated at higher pressures because of the occurrence of ion-molecule reactions. In the

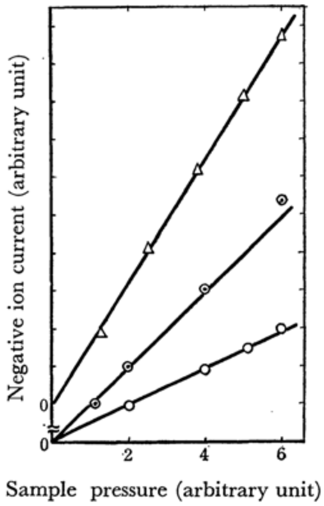

Fig. 6. Plot of negative ion current (NO_2^-) against pressure in CH_3NO_2.
△ 4.5 eV ⊙ 9.5 eV ○ 40 eV

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

present work, however, such a study was not made because of instrumental difficulties.

Role of Negative Ions in Radiolysis. The results obtained in this work suggest clearly the importance of the role of negative ions in the radiolysis of these compounds, at least in the primary process.

Indeed, in the radiolysis of nitromethane, the importance of the following reactions has been pointed out.[7]

$$CH_3NO_2 + e \longrightarrow CH_3 + NO_2^- \quad (1)$$
$$\longrightarrow CH_3^- + NO_2 \quad (2)$$
$$\longrightarrow CH_3NO + O^- \quad (3)$$
$$\longrightarrow CH_3NO^- + O \quad (4)$$

The finding that neither CH_3^- nor CH_3NO^- ions can be found, however, shows that the reactions (2) and (4) are to be rejected. Instead, the reaction (5) is to be taken into consideration, as presumed from the measurement of appearance potential of O^- ion from nitromethane.[*4]

$$CH_3NO_2 + e \longrightarrow CH_3N + O + O^- \quad (5)$$

Besides the above reactions, the reactions (6) and (7) accompanied with the formation of CN^- and CNO^- should be also added.[*5]

$$CH_3NO_2 + e \longrightarrow H_2O + OH + CN^- \quad (6)$$
$$CH_3NO_2 + e \longrightarrow H_2O + H + CNO^- \quad (7)$$

Furthermore, in 1-nitropropane the reaction (8) accompanied with the formation of $CH_2NO_2^-$ ion appears to be significant.[*4]

$$C_3H_7NO_2 + e \longrightarrow H + C_2H_4 + CH_2NO_2^- \quad (8)$$

Also, a relatively strong peak of $CH_2NO_2^-$ ion might provide an useful method for the identification of 1-nitropropane.

[*4] to be discussed in the 2nd report of this series.

[*5] to be published.