A Negative Ion-molecule Reaction in Nitroethylene

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The formation of negative ions and the negative ion-molecule reaction in nitroethylene by electron impact have been studied. The nondissociative resonance electron capture of the nitroethylene molecule led to the formation of the molecular negative ion. The ionization efficiency curves and the appearance potentials of several fragment negative ions and the molecular negative ion were measured. The dimer negative ion of nitroethylene was found to be formed by the ion-molecule reaction between the molecular negative ion and a neutral nitroethylene molecule, and the rate constant of this ion-molecule reaction was estimated to be approximately 3.2×10^{-13} cc molecule^{-1}sec^{-1}.

A number of studies of ion-molecule reactions for positive ions done by the use of a mass spectrometer have been reported in recent years. Such investigations have provided useful information on those radiation-induced chemical reactions where more than one-half of the product formation usually results from the reactions of intermediate ions. For negative ion-molecule reactions, however, detailed studies have been limited to reactions which occur in oxygen and other gases of ionospheric interest,[1–6] although negative ions have also been considered to play an important role as active species in radiation-induced reactions.

In the course of investigations of radiation-induced polymerizations, it has been elucidated on the basis of the results of kinetic experiments[7] that the polymerization of nitroethylene proceeds by a free anionic mechanism through negative intermediates. An ESR study[8] and preliminary mass spectrometric observations[9] of nitroethylene have indicated that the polymerization was initiated by anion radicals of nitroethylene formed by the capture of electrons.

In the present study done by the use of a mass spectrometer, the formation of negative ions from nitroethylene and the dimer-negative-ion formation of nitroethylene by the ion-molecule reaction were investigated in order to obtain some information on the initial process of the radiation-induced polymerization of nitroethylene.

Experimental

The apparatus used for this study was a 90° single-focusing Hitachi RMU-6D mass spectrometer which had been modified to measure negative ions as described in a previous paper.[10] A conventional-type electron gun was used without paying any attention to the energy spread of the impact electrons. A 10-stage Ag–Mg electron multiplier combined with a DC amplifier was used as the ion detector, and the output current was recorded by means of a Rikadenki B-34 three-pen recorder. The minimum detectable ion current was 5×10^{-19}A. During the experiments, except when studying the effect of the ion-accelerating potential, the ion-acceleration voltage and the voltage supplied to the conversion dynode of the electron multiplier were kept at -3.5 and -1.5 kV respectively. The electron-trap voltage was maintained at the same potential as the ionization chamber. The repeller potential was always adjusted to 0 V in order to obtain the molecular negative ions of nitroethylene with thermal velocity. A source magnet, which had a flux intensity of 150 gausses, was also used for the collimation of the electron beam. The total emission was maintained at 100 μA throughout the energy range of the electron impact, and then the 40% trap current was obtained above 10 eV electron energies. The electron-accelerating potentials were read at each 1/50 V by means of a 10-turn precision Helipot variable resister in the range from 0 to 20 V; the resister had previously been well calibrated by means of a Yokokawa DC Voltage Standard GOS-11.

Sulfur hexafluoride and oxygen were used to calibrate the electron-energy scale. The appearance potentials of the SF_6^- ion from sulfur hexafluoride and the O^- ion from oxygen were taken as 0.03 eV[11] and 4.53 eV[12] respectively. The appearance potentials of the negative ions formed by the resonance-capture process were determined by the linear extraporation method.

The pressure in the ionization chamber was determined indirectly from the pressure in the sample reservoir, which was measured by means of a manometer, a McLeod gauge, and a CEC 23-105 Micro-Manometer. The ratio of the

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sample pressure of the steady state in the ionization chamber to that in the reservoir was determined by the static operation of the inert gases (He, Ne, and Ar[13]) in the energy range in which the ion intensity of the resonance-electron capture was linearly proportional to the pressure.

Nitroethylene was prepared by the dehydration of 2-nitroethanol and purified as has been described previously.[7b] Sulfur hexafluoride (Allied Chemical Co.) was purified by trap-to-trap distillation in a vacuum. Oxygen and methane (Takachiho Chemical Ind.) were used without further purification.

Results

Formation of Negative Ions. A large number of negative ions were observed to be formed from nitroethylene by an electron impact of 100 eV. The relative abundance of the main negative ions, which were normalized to the intensity of NO_2^-, is shown in Table 1.

TABLE 1. RELATIVE ABUNDANCE OF THE MAIN NEGATIVE IONS PRODUCED FROM NITROETHYLENE BY ELECTRON IMPACT OF 100 eV

m/e	Ion	Source pressure (mmHg)	
		2.6×10^{-6}	9×10^{-3}
16	O^-	7.4	6.8
17	OH^-	6.8	9.1
25	C_2H^-	19	22
30	NO^-	0.93	0.96
42	CNO^-	3.4	7.3
46	NO_2^-	100	100
55	C_2HNO^-	0.62	0.85
72	$C_2H_2NO_2^-$	0.03	5.8
73	$C_2H_3NO_2^-$	0.27	88
98	$C_2H_3NO_2C_2H^-$	—	0.2
99	$C_2H_3NO_2C_2H_2^-$	—	0.6
146	$(C_2H_3NO_2)_2^-$	—	0.1
219	$(C_2H_3NO_2)_3^-$	—	2×10^{-4}

The molecular negative ion of nitroethylene, $C_2H_3NO_2^-$, was found at a pressure of 2.6×10^{-6} mmHg, and the relative abundance of $C_2H_3NO_2^-$ increased remarkably with the increase in the source pressure. At a pressure of 9×10^{-3} mmHg, the dimer negative ion of nitroethylene, $(C_2H_3NO_2)_2^-$, and the trimer negative ion, $(C_2H_3NO_2)_3^-$, were also observed, although the intensity of the trimer ion was very low.

The ionization efficiency curves of the main negative ions from nitroethylene, such as O^-, C_2H^-, NO_2^-, and $C_2H_3NO_2^-$, and that of SF_6^- from sulfur hexafluoride are shown in Fig. 1. The intensity of these negative ions in the electron-energy region less than 10 eV was proportional to the pressure of nitroethylene in the ionization chamber. From these curves, the appearance potentials and the apparent energy widths of the resonance-electron-capture processes from the molecular and fragment ions were obtained. The main results are summarized in Table 2. The appearance potential of NO_2^- in this study is higher than that of the NO_2^- from nitroalkanes (below 1 eV[14]).

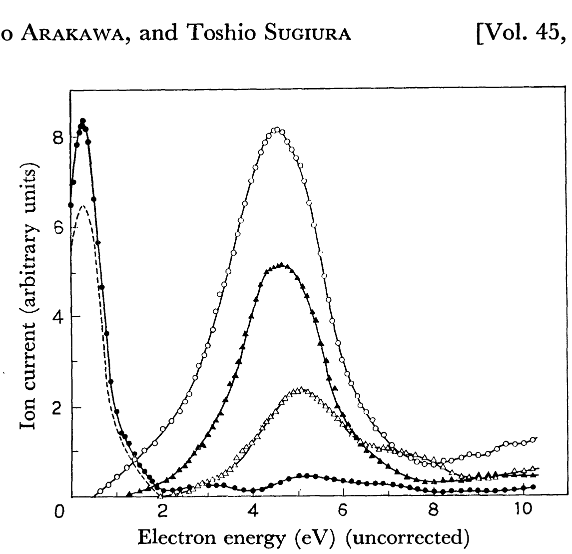

Fig. 1. Ionization efficiency curves of the main negative ions from nitroethylene.
-△-: O^- (×10), -▲-: C_2H^- (×2), -○-: NO_2^- (×1), -●-: $C_2H_3NO_2^-$ (×4), ----: SF_6^-.

TABLE 2. APPEARANCE POTENTIALS AND APPARENT ENERGY WIDTHS OF THE MAIN NEGATIVE IONS FORMED BY THE RESONANCE ELECTRON CAPTURE PROCESSES FROM NITROETHYLENE

m/e	Ion	1st Appearance potential (eV)	Half width (eV)
16	O^-	2.5 ± 0.2	1.5
17	OH^-	2.8 ± 0.2	1.6
25	C_2H^-	2.2 ± 0.2	1.4
26	$C_2H_2^-$	2.8 ± 0.2	1.5
30	NO^-	2.8 ± 0.2	1.4
46	NO_2^-	1.5 ± 0.2	1.8
55	C_2HNO^-	2.5 ± 0.2	1.3
72	$C_2H_2NO_2^-$	2.1 ± 0.2	1.5
73	$C_2H_3NO_2^-$	0	0.7

From the ionization efficiency curve of $C_2H_3NO_2^-$ shown in Fig. 1, it is clear that the appearance potential is about 0 eV and that the width of the resonance capture is very narrow; both of those properties are also exhibited in the molecular negative ion of sulfur hexafluoride. These facts indicate that the nitroethylene molecule has the ability to capture thermal electrons easily by means of nondissociative process. Similar results in the cases of nitrocompounds of benzene derivatives have been reported by Christophorou *et al.*[15] and Jäger and Henglein.[16] The width of the nondissociative resonance capture of nitroethylene seems to be due to the energy spread of the impact electrons used, since the energy spread of the resonance-electron-capture process of SF_6 has been considered to be narrower than 0.05 eV.[11]

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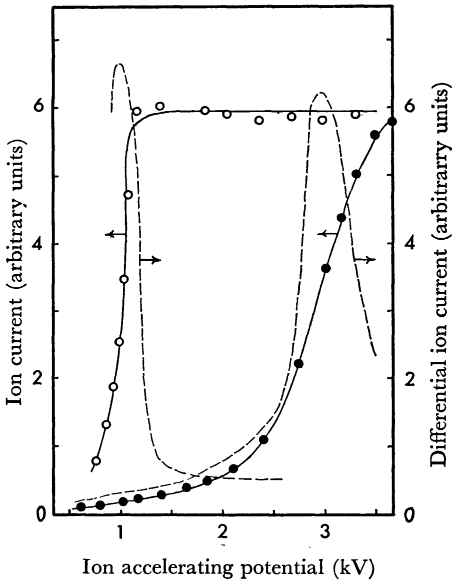

Fig. 2. Dependences of the ion accelerating potential on the ion intensity for $C_2H_3NO_2^-$ and SF_6^-.
-●-: $C_2H_3NO_2^-$. -○-: SF_6^-.

Compton *et al.*17) measured the lifetimes of the molecular negative ions for SF_6, $C_6H_5NO_2$ and $(CH_3CO)_2$ by the use of a time-of-flight mass spectrometer. For the molecular negative ion of nitroethylene, an attempt to estimate the mean lifetime was made using the following procedures. The ion intensity of $C_2H_3NO_2^-$ was remarkably dependent upon the ion-accelerating potential. As is shown in Fig. 2, the dependence of the ion-accelerating potential on the ion intensity was measured for $C_2H_3NO_2^-$ and SF_6^- by using a Faraday cage as the ion detector. The dotted lines in Fig. 2 are the first differential curves obtained from the relations between the ion intensity and the ion-accelerating potential. Neglecting the change in the ion-collection efficiency with the variation in the accelerating potential, the sum of the residence time of the ions in the ionization chamber and the flight time of the ions at the peak of the first differential curve can be approximately considered as the mean lifetime of the ions. From the results of Fig. 2 and the estimated residence times in the ionization chamber to be described in the next section, the mean lifetimes for $C_2H_3NO_2^-$ and SF_6^- were calculated to be 14 μ sec and 28 μ sec respectively. The value for SF_6^- shows a close agreement with the result obtained by Compton *et al.* (25 μ sec17)).

Dimer-negative-ion Formation by Ion-molecule Reaction. In the case of an electron impact of 100 eV, many secondary products of ion-molecule reactions were observed. However, at an electron energy of less than 1 eV, the secondary ions were the only products obtained by the reaction with $C_2H_3NO_2^-$; the mass numbers of the main secondary ions were 99, 119, and 146.

From the viewpoint of studying the initial process of the polymerization, special attention was paid to the formation process of the dimer negative ion. The ionization efficiency curves of $C_2H_3NO_2^-$ and $(C_2H_3NO_2)_2^-$ are shown in Fig. 3. The close agreement of the shapes of the two peaks indicates that the precursor of $(C_2H_3NO_2)_2^-$ is $C_2H_3NO_2^-$. The intensity of $(C_2H_3NO_2)_2^-$ at the peak in Fig. 3 was proportional to the square of the pressure of nitroethylene, whereas that of $C_2H_3NO_2^-$ was linear to the pressure, as is shown in Fig. 4. The plots of the $(C_2H_3NO_2)_2^-/C_2H_3NO_2^-$ ratio *vs.* the pressure of nitroethylene give a linear relation, as is shown in Fig. 5. From these results, it is evident that $(C_2H_3$-

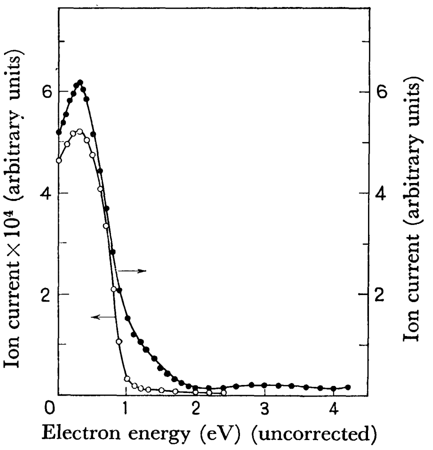

Fig. 3. Ionization efficiency curves of $C_2H_3NO_2^-$ and $(C_2H_3NO_2)_2^-$. Source pressure: 4.4 × 10^{-4} mmHg.
-●-: $C_2H_3NO_2^-$, -○-: $(C_2H_3NO_2)_2^-$.

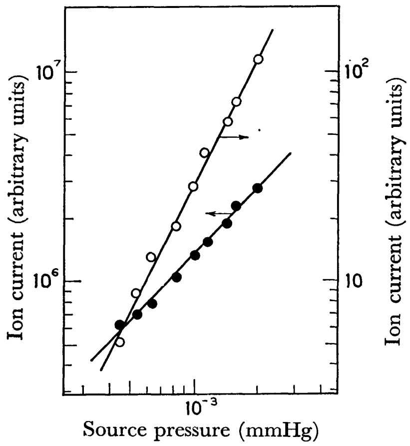

Fig. 4. Dependences of the pressure in the ionization chamber on the ion intensity for $C_2H_3NO_2^-$ and $(C_2H_3NO_2)_2^-$.
-●-: $C_2H_3NO_2^-$, -○-: $(C_2H_3NO_2)_2^-$.

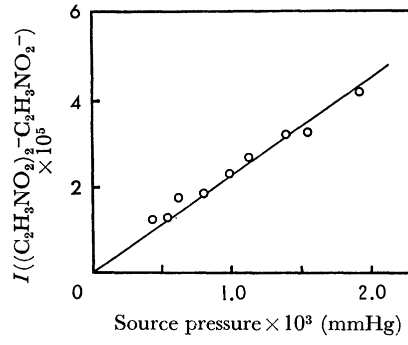

Fig. 5. Relation between the intensity ratio $(C_2H_3NO_2)_2^-/C_2H_3NO_2^-$ and the pressure in the ionization chamber.

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$NO_2)_2^-$ is produced by the ion-molecule reaction of the molecular ion with a neutral nitroethylene molecule, which can be demonstrated as follows:

$$C_2H_3NO_2^- + C_2H_3NO_2 \xrightarrow{k} (C_2H_3NO_2)_2^- \qquad \text{(a)}$$

The rate constant of the (a) reaction was estimated by the following procedures. Assuming that the source pressure is low and that the fraction of the molecular ion which reacts is very small, Eq. (1) is obtained by introducing a treatment similar to that developed by Koyano *et al.*[18] for a reaction cross section:

$$g\left(\frac{I_D}{I_P}\right) = k[C_2H_3NO_2]\tau_N \qquad (1)$$

where I_D/I_P is the ratio of the intensities of the dimer ion and the molecular ion, $[C_2H_3NO_2]$ is the concentration of nitroethylene, τ_N is the residence time of the molecular ion in the ionization chamber, and g is the ratio of the electron-multiplier gain of I_D to that of I_P. g was experimentally obtained as $1/\sqrt{2}$. For the estimation of τ_N, the ion-molecule reaction of the methane positive ions, represented by the (b) formula, was taken as a standard:

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad \text{(b)}$$

Using the published value of the rate constant for this reaction (1.1×10^{-9} cc mol^{-1}sec^{-1} [19]), the residence time of CH_4^+ in this apparatus ($\tau_{CH_4^+}$) was determined to be 2.1 μ sec from the slope of the linear relation between $I_{CH_5^+}/I_{CH_4^+}$ and the pressure of methane in the ionization chamber. It is generally known that the residence time of ions in the ionization chamber is a function of the mass of ions, the field strength in the chamber, and the distance from the electron beam to the exit slit of the chamber. In both the (a) and (b) reactions, the distance from the electron beam to the exit slit is the same, and the field strength is considered to be equal for positive and negative ions, although the signs of the gradients are the opposite. Consequently, the residence time of ions in this study is only a function of the mass of ions. By multiplying $\tau_{CH_4^+}$ by the square root of the mass ratio of $C_2H_3NO_2^-$ and CH_4^+, τ_N was estimated as 4.6 μ sec. Since $k\tau_N$ in Eq. (1) was obtained from the slope of Fig. 5, the rate constant of Reaction (a) was determined to be 3.2×10^{-13} cc mol^{-1}sec^{-1}.

Discussion

The results presented in Table 2 clearly show that many of the fragment ions from nitroethylene have appearance potentials which are almost identical. It might be expected that some of them result from ion-molecule reactions. However, the experimental evidence that the intensities of the ions increase linearly with the increase in the pressure in the ionization chamber indicates that these fragment ions are not produced by ion-molecule reactions, but are formed by the dissociative-resonance-capture processes.

It is interesting that the molecular negative ion of nitroethylene is observed at a lower pressure in the ionization chamber. The formation of molecular negative ions is generally classified into two different processes as has been pointed out by Compton *et al.*[17]: (i) metastable molecular negative ion formation, and (ii) molecular negative ion formation, in which the ion is stabilized by collision or radiation.

In the present study, the intensity of the molecular negative ion of nitroethylene is also proportional to the pressure by an electron impact of less than 1 eV. This fact indicates that the molecular negative ion is predominantly formed by the (i) process, in which the molecule is able to capture thermal electrons while maintaining its interatomic distances. The exact cross section of the electron capture can not be determined by the apparatus used. However, the relative intensity of the molecular ion of nitroethylene in the energy range of the resonance capture was about 1/200 of that for SF_6^- at a normalized pressure. Several values for the cross section of SF_6^- formation by nondissociative electron attachment have been reported.[11,17,20-24] Among them, the value of 2.6×10^{-14} cm^2 determined by Mahan and Young[24] was chosen as the most reliable one. Consequently the cross section of the nondissociative resonance capture of nitroethylene was estimated to be approximately 1.3×10^{-16} cm^2.

Now, the technique used in the present study for determining the ion lifetime should be discussed, since it has not been clearly established. As is well known, there is a strong tendency toward defocusing as the ion accelerating potential is reduced, and, of course, the beam will tend to spread as the retention time in the analyzer tube is increased. It is, therefore, necessary to obtain some information on the effect of the ion-accelerating voltage upon the collected current of several positive ions. In an attempt to correct some uncertain effects, the dependence of the accelerating voltage on the ion intensities of Ar^+ and SF_6^- was measured by changing the sign of the supplied voltage. The ion-intensity ratio of SF_6^-/Ar^+ changed in almost the same manner as is shown in Fig. 2 with the variation in the accelerating voltage. This fact, and the close agreement of the lifetime for SF_6^- between the values obtained by Compton[17] and by ourselves seem to imply that the method in the present study is still valid despite the limitations imposed by the obvious oversimplification.

The lifetime of the molecular negative ion thus formed is closely related to the electron affinity of the molecule.[17] Kamiyama *et al.*[25] calculated the electronic configurations, matrix elements, and energy levels for the molecular negative ion of nitroethylene by a semi-empirical MO method; they also gave the value of

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1.53 eV as the electron affinity of nitroethylene. The observed long lifetime of the molecular negative ion of nitroethylene may be given by this positive electron affinity and the stable molecular configuration in the electron attachment.[25] The nature of the nitroethylene molecule as a strong electron acceptor shown in this study is in reasonable agreement with those suggested by the ESR[8] and the optical investigations.[25] On the other hand, in the case of the electron impact with 100 eV, the remarkable increase in the molecular negative ion at higher pressures shown in Table 1 seems to be caused by the (ii) process or by other processes.

It is clear from the results shown in Figs. 2 and 3 that the precursor of the dimer negative ion is the molecular negative ion of nitroethylene, and that the dimer negative ion is formed by the ion-molecule reaction of the molecular ion with a neutral nitroethylene molecule. The theoretical kinetic equation of ion-molecule reactions was first derived by Gioumousis and Stevenson[26] on the basis of an ion-induced-dipole model. Moran and Hamill[27] have considered the interaction of an ion with a molecule possessing a permanent dipole. Using a similar model, Harridon *et al.*[28] have proposed a modified collision theory including the effect of ion-dipole interaction. They have shown that the mean rate constant for collisions where both an ion and a neutral molecule have thermal velocities is given by the following equation:

$$\bar{k}_{\text{therm}} = 2\pi e\left(\frac{\alpha}{\mu}\right)^{1/2} + \frac{2\pi e\mu_{\text{D}}}{\mu}\left(\frac{2\mu}{\pi kT}\right)^{1/2}$$

where e is the electron charge, μ is the reduced mass of the colliding pair, α is the polarizability of the molecule, μ_{D} is the dipole moment of the molecule, and kT is the thermal kinetic energy.

According to this theory, the rate constant for the dimerization reaction of nitroethylene was calculated. Although the polarizability and the dipole moment of the nitroethylene molecule are unknown, it can be assumed that they are in the same order as those of nitroethane. The calculated values are 6.2×10^{-9} and 5.9×10^{-9} cc mol^{-1}sec^{-1} at 323°K and 373°K respectively. The rate constant measured experimentally (3.2×10^{-13} cc mol^{-1}sec^{-1}) is several orders of magnitude smaller than that predicted by the theory. This may indicate that a great portion of collisions do not give rise to dimerization reactions. The reasons for the apparent low rate constant of the dimerization reaction are not clear. One possible explanation is that the collisions lead to other ion-molecule reactions. However, the secondary ions observed at an electron energy of less than 1 eV are not abundant, as has already been mentioned. It would appear, therefore, that the contribution of other ion-molecule reactions is not very large. Alternatively, the apparent low rate constant could be explained by the occurrence of a charge transfer or a collision-induced electron detachment from the molecular negative ion which was not detected in the present study. A more likely explanation is that the model used does not adequately describe the ion-molecule collision since it contains no consideration of the electronic structures of the interacting species. Recently, Schaefer and Henis[29] have presented a qualitative description of low-energy ion-molecule reactions based on the assumption that the probability of reaction can be described by the change in the electron density around the nulcear centers involved. For the dimerization reaction of nitroethylene, however, this description cannot be applied because of the difficulty in calculating the detailed electron density distribution in complicated reaction systems.

In general, the mass-discrimination effect must be considered in determining the rate constants of ion-molecule reactions. However, this effect, caused by the repeller potential, was not present in the present study, where the repeller potential was always kept at 0 V. Other factors in the mass-discrimination effect, such as the space charge, the surface potential, and the source magnet in the ionization chamber, were not taken into consideration.

No experiment on the polymerization in the gas phase has yet been carried out, since the vapor pressure of nitroethylene is extremely low at room temperature. The rate constant of the polymerization in the liquid phase was determined from the kinetic experiments to be 6.7×10^{-14} cc mol^{-1}sec^{-1} at 20°C.[7b]

For the trimer negative ion, the measurements of the ionization efficiency curve and the dependence of the source pressure were difficult because of the low intensity of the trimer ion. In the positive-ion mass spectra, however, neither dimer nor trimer positive ions were observed in the pressure range examined. This fact also indicates that neither the dimer nor the trimer negative ions are produced by a direct electron capture process of a neutral nitroethylene dimer or trimer; rather, both are formed as secondary products. Consequently, the formation process of the trimer negative ion can involve only a consecutive reaction:

$$(C_2H_3NO_2)_2^- + C_2H_3NO_2 \longrightarrow (C_2H_3NO_2)_3^- \qquad \text{(c)}$$

Although only a limited range of the pressure was examined, the mass spectrometric observation mentioned above supports the concept that the precursor of the radiation-induced polymerization of nitroethylene is the molecular negative ion.

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