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Mass Spectrometric Study of the Negative Ion Formation of Nitroethylene at High Electron Energies

By

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The formation of the molecular and the dimer negative ions of nitroethylene at high electron energies was studied. The intensity of the molecular negative ion showed a second order dependence on the pressure below 10^{-4} torr and a higher than second order dependence above 10^{-4} torr. The intensity of the dimer negative ion showed a second order dependence greater than that of the molecular negative ion. The intensity of the molecular negative ion was found to be dependent on the pressure of additional rare gases. This suggests that the collisional stabilization of excited ions is very important at high electron energies.

Introduction

The chemical interaction of high-energy radiation with gases or condensed phases features the initial formation of transient intermediates. A technique appropriate to the investigation of these transient intermediates in the gas phase is that of mass spectrometry. This technique is particularly useful for the study of ion-molecule reactions important in radiation-induced reactions.¹⁾ This method is also expected to yield valuable information about the initiation process of radiation-induced ionic polymerization, even in condensed phases. The basic differences between a gas and a condensed phase, however, lead to differences in the primary physical and chemical processes of energy absorption and thus in the nature and distribution of products.

In a previous paper on the mass spectrometric study of nitroethylene²⁾, it was found that the non-dissociative resonance electron capture of a nitroethylene molecule led to the formation of the molecular negative ion and that the dimer negative ion was formed by the ion-molecule reaction between the

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molecular negative ion and a neutral nitroethylene molecule. The observed nature of the nitroethylene molecule as a strong electron acceptor was in reasonable agreement with data obtained from the electron spin resonance^{3,4)} and the optical investigations.⁵⁾ These findings support the concept that the precursor of the radiation-induced polymerization of nitroethylene is the molecular negative ion.

It was also found in a previous study²⁾ that the intensities of the molecular and the dimer negative ions of nitroethylene increased markedly with increasing source pressure at high electron energies.

In the present study, experiments have been carried out at high electron energies under high source pressures in order to elucidate this phenomenon.

Experimental

The apparatus used in the present study was a 90° single-focusing Hitachi RMU-6 mass spectrometer as previously described in detail⁶⁾. The ion acceleration voltage and the supplied voltage to the conversion dynode of the electron multiplier were adjusted to -3.5 and -1.5 kV, respectively. The repeller potential was always kept at 0 V.

The experimental procedures were the same as in the previous study²⁾. Neon, argon, krypton, and xenon (Takachiho Chemical Ind.) were used without further purification.

Results and Discussion

The intensities of the principal negative ions obtained from nitroethylene are shown in Figure 1 as a function of the electron energy above 20 eV. Special attention was paid to the formation of the molecular and the dimer negative ions from the viewpoint of the initiation process in radiation-induced polymerization.

Figure 2 shows the dependence on source pressure of the molecular negative ion formation produced with electron energies of 25, 50 and 100 eV. At pressures of less than 10^{-4} torr, there appeared to be a second order dependence of the intensity of the molecular negative ion on the pressure at all the electron energies. A three-body process obviously occurred under the present conditions, indicating that the molecular negative ion is stabilized by collision.

At source pressures above 10^{-4} torr, the intensity of the molecular negative ions was observed to attain a dependence on the pressure higher than second order. In order to obtain further information about the formation of negative ions at higher pressure, experiments in which rare gases were introduced into

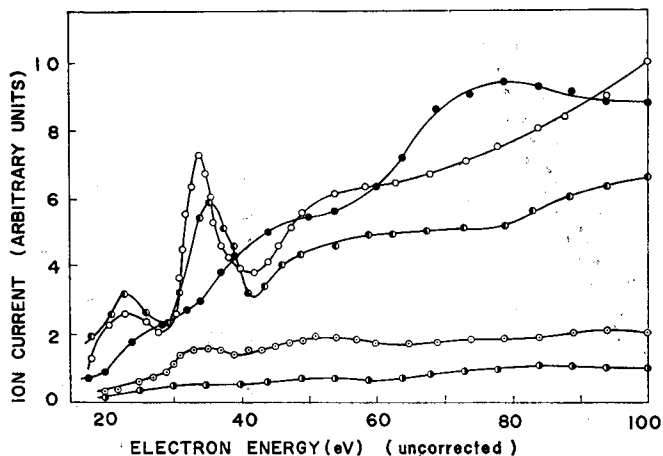


Fig. 1. Ionization efficiency curves of the principal negative ions from nitroethylene.

\ominus —: O^- ($\times 3$), \bullet —: C_2H^- ($\times 3$), \circ —: NO_2^- ($\times 1$),
 \bullet —: $C_2H_5NO_2^-$ ($\times 1$), \bullet —: $(C_2H_5NO_2)_2^-$ ($\times 100$)

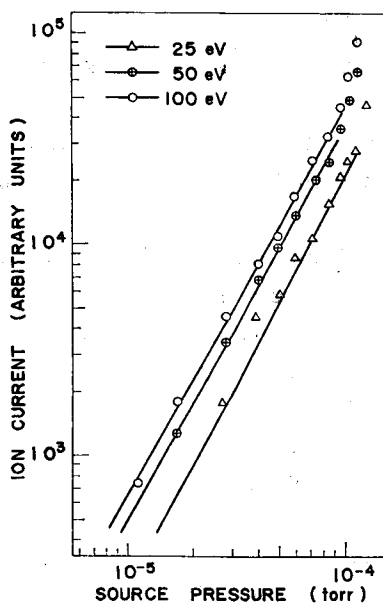


Fig. 2. Source pressure dependence of the parent negative ion produced by high energy electrons.

the ionization chamber were carried out at an electron energy of 100 eV. At nitroethylene constant pressure (10^{-5} torr), the intensities of the molecular negative ions as a function of added rare gas pressure are shown in Figure 3, for neon, argon, krypton, and xenon. In all cases, a second order dependence of the ion intensity on added gas pressure was observed, and the relative intensities were found to increase in the order: Ne, Ar, Kr, and Xe. At rare

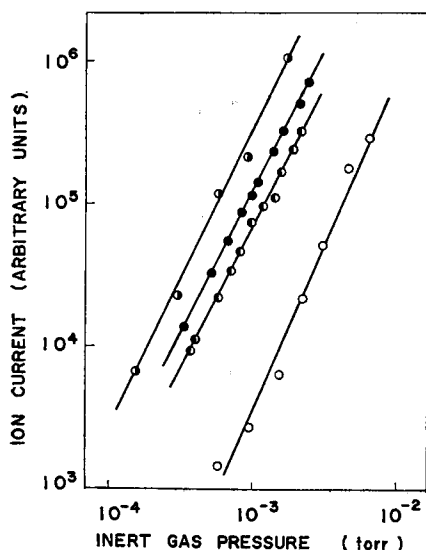


Fig. 3. Dependence of the parent negative ion intensity on rare gas pressure. Electron energy: 100 eV, nitroethylene pressure: 10^{-3} torr. Rare gas: \circ —: neon, \ominus —: argon, \bullet —: krypton, \bullet —: xenon.

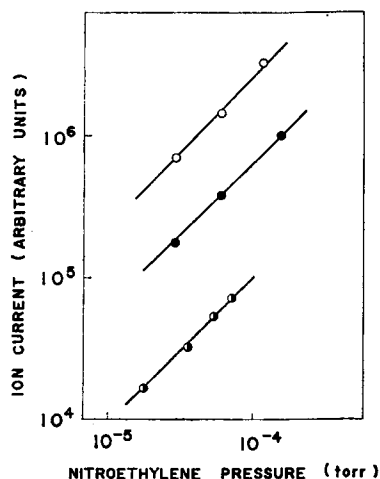


Fig. 4. Dependence of the parent negative ion intensity on nitroethylene pressure. Electron energy: 100 eV. Rare gas: \ominus —: neon, \bullet —: argon, \circ —: xenon.

gas constant pressure (10^{-3} torr), the intensity of the molecular negative ion was linearly proportional to the pressure of nitroethylene in the pressure range examined, as seen in Figure 4.

The results thus obtained may be explained as follows: The molecular negative ion is formed by the capture of secondary electrons which are released predominantly by rare gas atoms. The process requires that the molecular negative ion formed is further stabilized by the collision with rare gas atoms. In such cases, the efficiency of collisional stabilization may be expected to be larger for heavy gas atoms than for light gas atoms. Thus, the relative intensities of the molecular negative ion formation shown in Figure 3 seem to be qualitatively correlated with the order of the rare gas atom mass number. An alternative explanation is provided by considering the existence of rare gas atoms in long-lived highly excited states. The significance of collisions between electronically excited particles and other neutral particles leading to ionization of the particles has been clearly recognized since the discovery of Penning ionization⁷⁾.

For the negative ion formation, Hotop and Niehaus⁸⁾ found that the molecular negative ion of sulfur hexafluoride was produced in collisions of highly excited atoms (X) with certain ground-state molecules of sulfur hexafluoride

where X refers to rare gas atoms. In a recent study of the molecular negative ion formation of deuterated acetonitrile (CD_3CN), Sugiura and Arakawa⁹⁾ reported that the molecular negative ion formed in a binary mixture of CD_3CN and rare gases appeared at electron energies which were close to the ionization potentials of corresponding rare gas atoms, and that the contribution of long-lived highly excited rare gas atoms was very important for the process. Similar effects may also be anticipated for rare gas atoms in the present system. In order to discuss the contribution of highly excited atoms, however, more exact measurements of the effects of ionizing electron energy and of rare gas pressure would be necessary.

Uncertainty remains about many of the factors involved in the formation process of molecular negative ions at high electron energies. But it can be tentatively concluded that the vibrationally excited molecular negative ion of nitroethylene is first produced by the capture of secondary electrons or by the interaction with highly excited molecules. It is then stabilized by collision with other neutral molecules.

For the dimer negative ion at an electron energy of 100 eV, the ion intensity was found to have a fourth order dependence on the nitroethylene pressure in the ionization chamber at pressures below 10^{-4} and a higher than fourth order

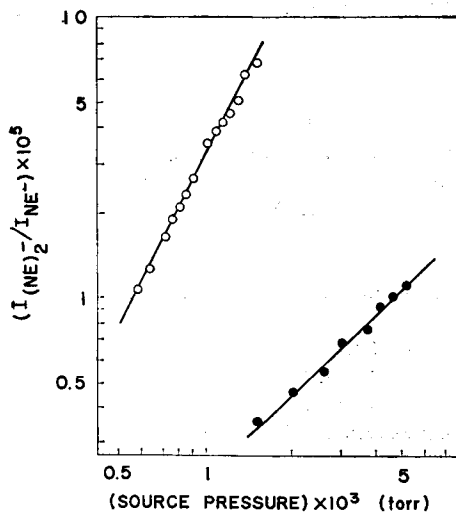


Fig. 5. Relationships between the intensity ratio $(\text{C}_2\text{H}_3\text{NO}_2^-)_2/\text{C}_2\text{H}_3\text{NO}_2^-$ and the source pressure.
 -○-: electron energy 100 eV,
 -●-: electron energy 0 eV.

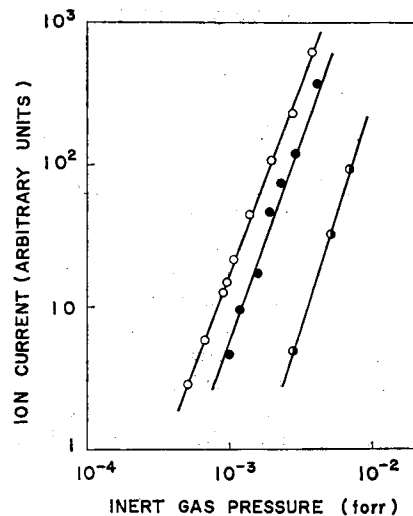


Fig. 6. Dependence of the dimer negative ion intensity on rare gas pressure. Electron energy: 100 eV, nitroethylene pressure: 10^{-5} torr. Rare gas: -○-: neon, -●-: argon, -○-: krypton.

dependence at pressures above 10^{-4} torr. As seen in Figure 5, however, the intensity ratio of the dimer ion to the molecular ion exhibits second order dependence on the nitroethylene pressure in the whole pressure range examined. By comparison, a linear dependence was observed at 0 eV energy, as mentioned in the previous paper.²⁾ In the experiment using binary mixtures of nitroethylene and rare gas, there appeared to be a third order dependence of the intensity of the dimer negative ion on the pressure of rare gas introduced into the ionization chamber, as shown in Figure 6.

Although the reaction mechanism leading to the dimer negative ion at high electron energies is not yet clear, it can reasonably be assumed that the precursor of the dimer negative ion at high electron energies is the molecular negative ion, as it is at 0 eV, and that the dimer ion is therefore formed by the ion-molecule reaction between the molecular ion and the neutral molecule. The experimental evidence that the intensity ratio of the dimer ion to the molecular ion is proportional to the square of nitroethylene pressure may indicate that such a process requires collisional stabilization of the initially formed, vibrationally excited, dimer negative ion. The effect of added rare gases might be similarly explained by the supposition that rare gas atoms act as colliding particles to stabilize the excited dimer ion produced by the ion-molecule reaction. The process of collisional stabilization of the product ions appears to be very important at high electron energies.

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