Formation of Positive and Negative Ions in CH_3NO_2

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Absolute dissociative ionization cross-sections from threshold to 200 eV have been measured using Fourier transform mass spectrometry (FTMS). In the production of positive ions by electron impact ionization, 13 ions are detected, including the parent ion $CH_3NO_2^+$ and the four most important fragment ions CH_3NO^+, NO_2^+, NO^+, and CH_3^+. Kinetic energies of some selected positive ions are determined using the technique of trapping potential dependency study in FTMS experiments. In the production of negative ions by dissociative electron attachment to nitromethane, three anions were detected: $CH_2NO_2^-$, NO_2^-, and CN^-. The high sensitivity of the FTMS permits the subsequent time-resolved reactions of these anions to be studied at very low pressure.

I. Introduction

Nitromethane (CH_3NO_2) has been of great research interest because of its use as a fuel and as a prototype molecule for a class of high-energy materials. At high altitudes, uninhabited air vehicles (UAVs) and other aircraft have had problems with flameout and reignition. Solutions have included silane that is pyrophoric, but it also produces abrasive silicon dioxide. Recent approaches have used plasma igniters and fuels that contain oxygen such as nitromethane. Plasma-assisted ignition is also an approach being explored for scramjet flame holding.[1] To design such systems, one needs a database for the ionization cross-sections of the fuel compounds. As a fuel, nitromethane and other NO_2 containing hydrocarbons have much shorter ignition delays at a given temperature compared to the corresponding hydrocarbon without an NO_2 group. This result is believed to be due to the production of alkyl radicals that facilitate the ignition processes.[2] In a parallel study, the formation of negative ions in nitromethane has been measured. It has been well-known for decades that nitromethane can be sensitized significantly toward detonation by amines, but the sensitization mechanism is not well-understood. A comprehensive review of the mechanism of the amine sensitization of shocked nitromethane can be found in recent studies by Gruzdkov et al.[3] and by Woods et al.[4] In brief, a central issue of the mechanism is whether and how an anion from nitromethane, $CH_2NO_2^-$, is involved in the early stages of the decomposition of the detonating nitromethane.

In this paper, we report our study on the positive and negative ion chemistries in nitromethane using Fourier transform mass spectrometry (FTMS). The cross-sections for electron impact ionization of nitromethane and some measurements of the energies of the ions fragments are presented. The ion−molecule reactions involving $CH_2NO_2^-$ are discussed.

II. Experimental Section

All of the experiments are performed using a modified Extrel FTMS equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and a 2 T superconducting magnet.[5] The theory and methodology of FTMS have been well-documented in the literature.[6−8] CH_3NO_2 was purchased (96+%, Aldrich), and in addition we applied multiple liquid N_2 freeze−pump−thaw cycles to remove noncondensable gases. For the specific lot of CH_3NO_2 used in our experiments (Lot No. DO 0086PI), the purity is 99.1% as determined by Aldrich using gas chromatography, with the major impurity noted as H_2O. Our FTMS data indicate no impurities other than H_2O at an estimated 0.2%. CH_3NO_2 is mixed with argon (99.999%, Matheson) with a ratio about 1:1 to a total pressure of ∼10 Torr, as determined by capacitance manometry. The mixture is then admitted through a precision leak valve into the FTMS system. Ions are formed by electron impact in the trapping cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiates the cell with a few hundred picocoulombs of low-energy electrons. The motion of the ions is constrained radially by the superconducting magnetic field and axially by an electrostatic potential (trapping potential) applied to the trap faces that are perpendicular to the magnetic field. The trapping potential is usually set to 10 V unless stated otherwise (see below). Ions of all mass-to-charge ratios are simultaneously and coherently excited into cyclotron orbits using stored waveform inverse Fourier transform (SWIFT)[9−11] applied to two opposing trap faces which are parallel to the magnetic field. Following the cyclotron excitation, the image currents induced on the two remaining faces of the trap are amplified, digitized, and Fourier analyzed to yield a mass spectrum.

FTMS is an established technique for studying the kinetics of charged particle reactions, in which the signal peak heights are used to evaluate the number of ions in the cell.[12] In this study, the intensity ratios of the ions from CH_3NO_2 to Ar^+ give cross-sections relative to those for argon ionization[13] since the pressure ratio of CH_3NO_2 to Ar is known.

A modification has been made recently to the trapping cell of the Extrel FTMS, which consists of adding a pair of screen electrodes in front of the trapping plates. A significant improvement to the quality of the cross-section data has been achieved by this modification: holding the screens to ground potential produces the particle-in-a-box potential (rather than the harmonic

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oscillator potential) along the *z*-axis of the trapping cell.[14] Thus, we can apply high trapping potentials to entrap more kinetically energetic ions, while in most of the volume of the cell the potential drop is small enough to avoid the broadening of the electron energy distribution. Wang and Marshall[15] have a cell geometry similar to the one in our FTMS instrument and give a detailed description of the design of the screen electrodes. Each screen electrode was constructed from 0.0010 in. diameter tungsten 50 × 50 mesh (Unique Wire Weaving Co., Inc., Hillside, NJ); two out of every three wires were then removed to give a final mesh of 16/in. The mesh was held in place by spot-welds to a 314 stainless steel frame that was positioned 1/8 in. inside of the adjoining trapping plate. When the trapping potential is set to 10 V, as mentioned above, the potential drop within the screen electrode region along the *z*-axis is estimated to be 0.3 V.

For studies of the kinetic energy of ions generated by electron impact ionization, the trapping potential dependence (harmonic oscillator potential) of the ion intensity is determined, as described previously.[16] In these experiments, the screen electrodes are connected to their adjoining trapping plates and the trapping potential is varied from 0.40 to 10 V. Because of the shape of the harmonic oscillator potential, this corresponds to an actual well depth of the trap, V_{eff}, varying from 0.26 to 6.6 V. If the ions are kinetically energetic, increasing V_{eff} results in a greater number of ions trapped in the cell and the plots of the fraction of the ions trapped, *f*, versus the square root of V_{eff} are expected to show two distinct linear regions described by

$$V_{\mathrm{eff}} \geq E_{\mathrm{k}}, \quad f = 1$$

$$V_{\mathrm{eff}} < E_{\mathrm{k}}, \quad f = (V_{\mathrm{eff}}/E_{\mathrm{k}})^{1/2}$$

where E_{k} is the kinetic energy of the ions (a single value isotropic kinetic energy distribution is assumed although the method can also be applied to more complicated situations).[17−19] The break between these two linear regions defines the kinetic energy of the ions.

III. Results and Discussion

Thirteen positive ions are generated with cross-sections above 10^{-18} cm^2 from the electron impact ionization of nitromethane. The partial cross-sections as functions of the electron energy are shown in Figure 1. There are mass spectral data at 70 eV compiled by the National Institute of Standards and Technology (NIST) Mass Spec Data Center published in the NIST Webbook,[20] which are shown in Table 1 for comparison with our current FTMS data. In general the two sets of data show similar major fragmentation patterns; the relative intensities of fragment ions are similar, except that we observe significantly less of the parent ion than ref 20. Our data show the total ionization cross-section reaches a maximum of 6.8 × 10^{-16} cm^2 at 60 eV. The parent ion, $CH_3NO_2^+$, remains one of the more significant ions within the studied energy range of 10−200 eV, and the most important fragment ions include NO^+, NO_2^+, CH_3^+, and CH_2NO^+. The neutral partners of interest cannot be determined experimentally using FTMS but are briefly discussed here on the basis of results from the literature. For NO^+, the neutral partner is expected to be the radical CH_3O, and the formation of the ion/neutral pair proceeds through an isomerization of the parent ion $CH_3NO_2^+$ followed by dissociation, which has been studied by several groups in the past:[21−25]

$$CH_3NO_2^+ \rightarrow [H_3CONO]^+ \rightarrow NO^+ + CH_3O \qquad (1)$$

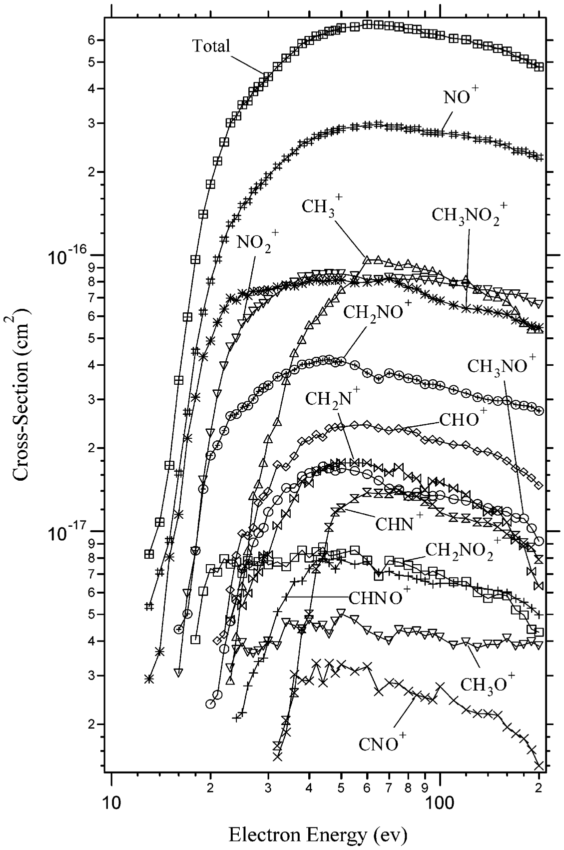

Figure 1. Absolute cross-sections for ionization of nitromethane by electron impact shown in log−log plot. Errors are estimated at ±15% for the total ionization cross-section.

TABLE 1: Comparison of Relative Ion Intensities[a] (Normalized to NO^+) from Our FTMS Experiments and from the NIST Webbook[20]

m/z	ion	rel intens FTMS	 NIST Webbook
12			2
13			8
14			8
15	CH_3^+	32	48
16			6
17			1
18			1
26			2
27	CHN^+	5	10
28	CH_2N^+	6	7
29	CH_3N^+	8	11
30	NO^+	100	100
31	CH_3O^+	1	2
32			1
41			1
42	CNO^+	1	2
43	$CHNO^+$	2	5
44	CH_2NO^+	13	5
45	CH_3NO^+	5	7
46	NO_2^+	28	37
60	$CH_2NO_2^+$	3	4
61	$CH_3NO_2^+$	28	57
62			1

[a] The electron energy is 70 eV. The ion formulas for the specific *m/z* are shown only as the current authors' suggestions. Ions with low intensities (i.e., with cross-sections < 10^{-18} cm^2 at 70 eV) are not included in the FTMS results.

Similarly, CH_2NO^+ is formed via another isomerization of the parent ion followed by dissociation resulting in OH as the neutral

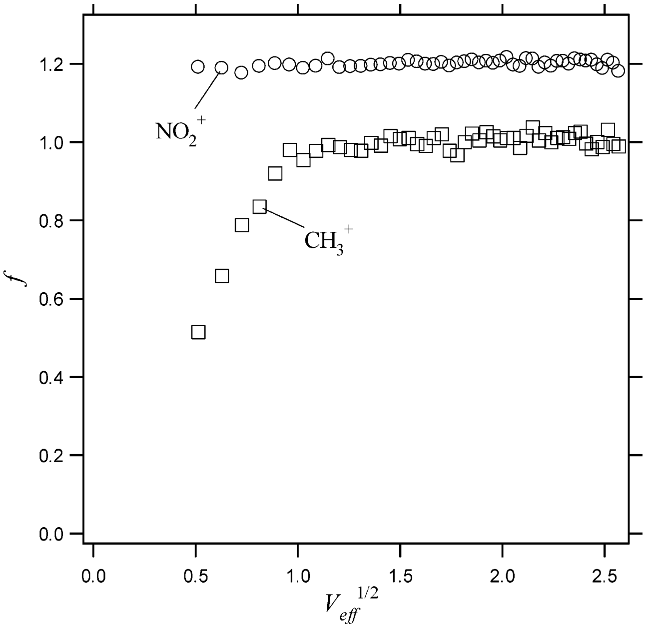

Figure 2. Fraction of NO_2^+ and CH_3^+ ions trapped in the cell vs the square root of the effective trapping voltage. Data for NO_2^+ are displayed so that f is offset by 0.2.

radical partner:[23−25]

$$CH_3NO_2^+ \rightarrow [H_2C{=}N(O)OH]^+ \rightarrow CH_2NO^+ + OH \quad (2)$$

On the other hand, NO_2^+ and CH_3^+ are thought to result from, respectively, a direct bond cleavage of $H_3C{-}NO_2^+$:[22,23]

$$CH_3NO_2^+ \rightarrow NO_2^+ + CH_3 \quad (3)$$

$$CH_3NO_2^+ \rightarrow CH_3^+ + NO_2 \quad (4)$$

In the mid 1950s, Kandel[26] in an electron impact ionization study of nitromethane found that the product ion CH_3^+ had 1.1 ± 0.2 eV kinetic energy while many other product ions including NO_2^+ were essentially kinetically thermal. In our FTMS experiments we have probed the kinetic energy of the ions by the technique that is described in detail in a previous paper[16] and briefly outlined in the Experimental Section. Figure 2 shows the trapping potential dependence of the ion intensities for NO_2^+ and CH_3^+. While the data for NO_2^+ show no changes of the fraction of trapped ions as V_{eff} varies, the data for CH_3^+ show a slope break at $V_{eff} = 1.0 \pm 0.2$ V, which indicates a 1.0 ± 0.2 eV kinetic energy for CH_3^+ and for NO_2^+ insignificant kinetic energy. Our FTMS results thus agree with the observation in ref 26.

We have studied the formation of anions by electron attachment to nitromethane and by the subsequent ion/molecule reactions. For the attachment experiments we use the secondary electrons that are generated by irradiating nitromethane gas molecules with primary electrons of 100 eV energy for 50 ms. With the trapping potential set to −5 V, the secondary electrons trapped in the cell are estimated to have energies ranging from thermal to 3.3 eV (the actual potential depth in the cell). We eject all anions formed during the time in which the primary electron beam is on, and then, after 100 ms collision time to allow the trapped electrons to collide with nitromethane gas molecules, we observe $CH_2NO_2^-$, NO_2^-, and CN^- in roughly equal intensities. This ion population appears to result from the attachment of the electrons with energies of thermal to 3.3 eV and is unlikely to have been substantially disturbed by ion/molecule reactions because they are rather slow, as will be discussed below.

We focus our attention on $CH_2NO_2^-$ because it is considered to be the product of the first step of amine sensitization of nitromethane.[3,4] It has been generally accepted that cleavage of the C−N bond in nitromethane is a key step in the decomposition of the molecule.[27−31] However, the details of the decomposition remain unclear. Engelke et al.[32] suggested that $CH_2NO_2^-$ plays an important role in the rate-limiting step of the detonation. Constantinou et al.[29] and Cook et al.[30] questioned the importance of $CH_2NO_2^-$ and proposed different sensitization mechanisms through a charge-transfer complex between nitromethane and the amine, or a hydrogen-bonded complex, respectively. Politzer et al.[31] revisited the $CH_2NO_2^-$ hypothesis and pursued it further by suggesting the most energetically favorable reaction involving $CH_2NO_2^-$:

$$CH_2NO_2^- + NH_3 \rightarrow CH_3NH_2 + NO_2^- \quad (5)$$

Recently, Gruzdkov et al.[3] proposed another mechanism for the amine sensitization as outlined below:

$$CH_3NO_2 + RNH_2 \rightarrow CH_2NO_2^- + RNH_3^+ \quad (6)$$

$$CH_2NO_2^- + CH_3NO_2 \rightarrow CH_3NO_2^{\bullet-} + CH_2NO_2 \quad (7)$$

$$CH_3NO_2^{\bullet-} \rightarrow CH_3 + NO_2^- \quad (8)$$

To offer more experimental evidence of the above mechanism, Woods et al.[4] used laser-initiated decomposition of single aerosol particles and a time-of-flight mass spectrometer to study the decomposition in nitromethane/amine mixtures. Only under large amine concentration conditions did they observe $CH_2NO_2^-$ and at very low intensity; they correctly attributed the very low intensity to the high reactivity of this anion. By comparing the anion mass spectra in pure nitromethane and nitromethane/amine mixture they found larger intensity of the NO_2^- in the latter, suggesting NO_2^- as the product of the reaction $CH_2NO_2^-$ (reactions 7 and 8). In discussing the reaction thermochemistry, they found that the proposed reaction pathway (reactions 6−8) was considerably endothermic but suggested that solvation energies could greatly reduce the reaction enthalpy.[4]

We have examined the reactions involving $CH_2NO_2^-$ using FTMS under gas pressures in the range of $\sim 10^{-7}$ to 10^{-6} Torr so that any intermediate product ions such as $CH_3NO_2^{\bullet-}$ can be detected if they have lifetimes of a few milliseconds or longer. To prevent interference from the trapped electrons in the cell, we eject the electrons by dropping the trapping voltage to ground to allow the charged particles to diffuse out of the trapping cell. Both ions and electrons are lost during this field-free period, but because at low ion density the Debye length is large and the electrons diffuse much faster than the ions, the length of the field-free duration can be adjusted so that almost all of the electrons have left the trap while there are still sufficient ions remaining in the cell for the reaction studies. Among the ions generated from the electron attachment mentioned above, we select $CH_2NO_2^-$ for reactions by ejecting all other ions out of the cell using large amplitude radio frequency (rf) excitation that contains the cyclotron frequencies of all of the ions except $CH_2NO_2^-$. Typical reaction mass spectra are shown in Figure 3. Three product anions are observed from the reaction of $CH_2NO_2^-$ with nitromethane: NO_2^- (73%), CN^- (15%), and CNO^- (12%), with the branching ratios shown in

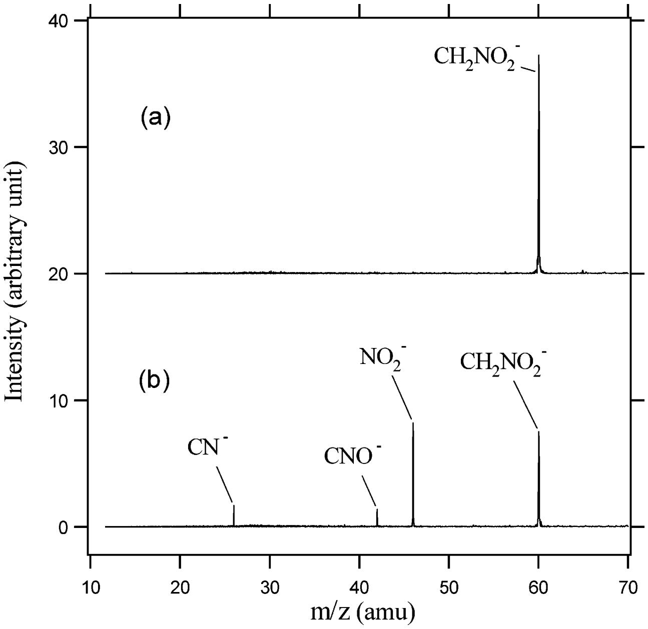

Figure 3. Mass spectrum of the isolated $CH_2NO_2^-$ acquired (a) without delay after isolation and (b) with a delay of 300 ms to react with CH_3NO_2 (~10^{-6} Torr) after isolation.

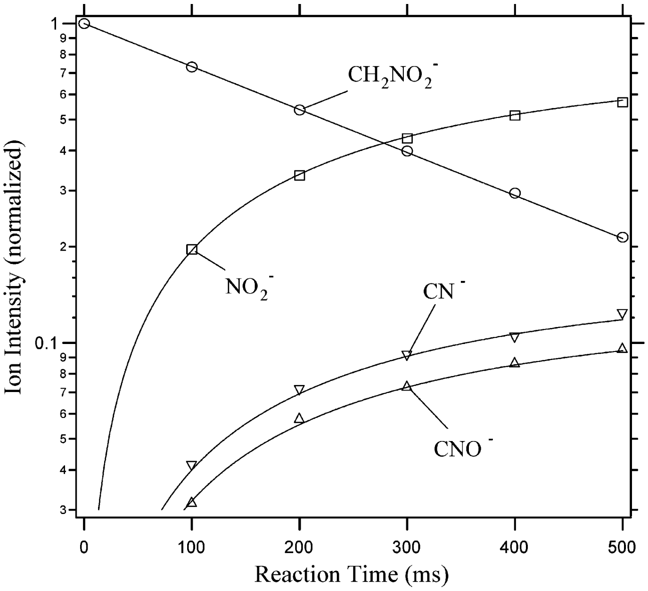

Figure 4. Semilogarithmic plot of the anion intensities vs reaction time. The solid lines are the curve fittings assuming the rate constant as 3.1 s^{-1} and the branching ratios to generate NO_2^-, CN^-, and CNO^- as 73, 15, and 12%, respectively.

parentheses. There are two possible explanations for the observed gas-phase reaction of $CH_2NO_2^-$: (a) the reaction is exothermic or (b) the reaction is a “hot ion” reaction. To probe the possibility of the hot ion reaction, the reactant intensity as a function of the reaction time is measured, and the resultant kinetics plot is presented in Figure 4. The data show a single-exponential behavior of the $CH_2NO_2^-$ decay, suggesting it is an exothermic reaction rather than a hot ion reaction. On the basis of this result we propose the reaction of $CH_2NO_2^-$ forming NO_2^- as

$$CH_2NO_2^- + CH_3NO_2 \rightarrow NO_2^- + CH_3CH_2NO_2 \qquad (9)$$

because it has a reaction enthalpy of −102 kJ/mol.[33] The composition of the neutral product in the above equation presents the authors’ suggestion only and has not been proved experimentally or theoretically. The neutral products of the minor reaction channels that form CN^- and CNO^-, respectively, cannot be uniquely identified. The overall reaction rate producing these three anions is rather small. In the above anion reaction experiments, the CH_3NO_2 pressure is raised 10 times higher (on the order of 10^{-6} Torr) than in the electron impact or attachment experiments, so that we can measure a significant change of the ion population within the given reaction time. The absolute reaction rate has not been measured because the vapor pressure of CH_3NO_2 is too low for an accurate pressure calibration procedure using a pulsed valve and a spinning rotor friction gauge.[34] However, we can compare the rate of $CH_2NO_2^-$ reaction with that of Ar^+ reaction under the same reactant pressure. Ar^+ is found to react with neutral nitromethane molecule producing NO_2^+ (41%), NO^+ (32%), CH_3NO^+ (14%), CH_3^+ (10%), CH_2NO^+ (2%), and CH_3N^+ (1%), with a decay rate approximately 80 times faster than the reaction rate of $CH_2NO_2^-$. Given that the Langevin collision rate for the Ar^+ reaction is calculated to be 1.3×10^{-9} cm^3/s using the polarizability of nitromethane to be 7.37×10^{-24} cm^3,[35] the NO_2^- reaction rate should be $\leq 1.6 \times 10^{-11}$ cm^3/s. Such a low reaction rate probably reflects a poor steric factor of reaction 9. The low reaction rate raises the question of the possibility that the observed reaction is due to the 0.9% (maximum value) of the impurity in the CH_3NO_2 sample. Although the impurity concentration appears to be too small to account for the observed reaction rate (shorter by ~40%), this possibility cannot be completely excluded at this point.

The measurements of the reaction kinetics have identified a possible reaction pathway for $CH_2NO_2^-$ to form NO_2^- in the gas phase that is thermochemically allowed. Whether this reaction actually takes place in the process of amine sensitization of nitromethane is not known, and further investigation into this question is desirable. The reaction rate in the gas phase is low, but in the condensed phase it should be quite rapid.

In the early 1980s, Domenico et al.[36] studied negative ions in the mass spectrum of nitromethane, and on the basis of the pressure dependence of the ion intensity, they identified the primary ions (ions formed by the electron attachment) and the secondary ions (ions resulted from the ion/molecule reactions). They suggested the following reaction produces some of the $CH_2NO_2^-$ ions they detected:

$$NO_2^- + CH_3NO_2 \rightarrow CH_2NO_2^- + HNO_2$$

However, this reaction is not observed in our experiments. We have isolated NO_2^- from other ions to observe its reactivity with the parent gas unambiguously, but even after a considerable time delay no detectable product ions are seen.

IV. Summary

Electron impact ionization of nitromethane in the energy range from threshold to 200 eV produces 13 positive ions, with $CH_3NO_2^+$, CH_3NO^+, NO_2^+, NO^+, and CH_3^+ as the most abundant ions. The total ionization cross-section peaks at 60 eV with the value of 6.8×10^{-16} cm^2. The estimated error of the partial ionization cross-sections is ±15%. CH_3^+ is found to have 1.0 ± 0.2 eV kinetic energy, while other fragment ions have insignificant kinetic energies, in a good agreement with the findings reported in the literature.[26]

Dissociative electron attachment of nitromethane in the energy range of 0−3.3 eV is found to produce three detectable anions, $CH_2NO_2^-$, NO_2^-, and CN^-. $CH_2NO_2^-$ is observed to react with the parent molecule to form NO_2^-. We find the following: (1) at low pressures no intermediate product ion such as $CH_3NO_2^{\bullet -}$ is formed ($CH_2NO_2^-$ produces NO_2^- directly, along with minor product ions CN^- and CNO^-); (2) the reaction is exothermic and yet slow, with the rate $\leq 1.6 \times 10^{-11}$ cm^3/s; (3) no other anions are found to be reactive with the parent molecule. Due to the time resolution of the FTMS, observation 1 does not rule out the possibility of $CH_3NO_2^{\bullet -}$ as an intermediate product that undergoes unimolecular dissociation with a lifetime shorter than milliseconds. If this was the case, we could not observe such an intermediate. Referring to the previously proposed amine sensitization mechanism of nitromethane, which includes an endothermic reaction pathway from $CH_2NO_2^-$ to form NO_2^-,[3,4] the current FTMS results point out another possible reaction pathway (reaction 9) which is exothermic. Whether this reaction pathway makes a significant contribution to amine sensitization in the condensed phase is a question which warrants further investigation.

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Note Added in Proof. W. Sailer et al.[37] have reported recently on absolute partial cross sections for dissociative electron attachment (DEA) to nitromethane. They used a crossed electron beam−molecular beam interacting system whose products were measured using a quadrupole mass spectrometer. The data as a function of electron energy over the range 0 to 9.5 eV show various resonances. They explain the detection of O^- and CNO^- at low electron energies in terms of DEA to multimode energy transfer from vibrationally excited molecules.

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