Structures of NO_3^- Formed via Glow Discharge in Atmospheric Gases

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Tandem mass spectrometry experiments using both ion-molecule reactions and collision-induced dissociation (CID) in an ion trap mass spectrometer have been performed to characterize the structures of the NO_3^- ions that issue from an atmospheric sampling glow discharge ionization source. The experimental evidence suggests that significant abundances of at least two stable forms of NO_3^- can be obtained from an air-sustained glow discharge. Ab initio calculations have been performed to identify the structures of the likely isomers. Rate constants have been measured for the reaction of the less thermodynamically stable isomer(s) with carbon dioxide, and evidence is given for a new reaction, $(\text{OO}-\text{NO})^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{O}_2 + \text{NO}^\cdot$. The combination of CID with a kinetic study is shown to be a useful approach for obtaining rate constant information when a mixture of reactive and unreactive isomers is present in the reactant population. (*J Am Soc Mass Spectrom* 1990, 1, 217-224)

The nitrogen-centered NO_3^- ion is a relatively common gas-phase anion, and it is particularly important for several reasons. For example, it is known to play an important role in the D region of the earth's ionosphere as well as in the stratosphere [1-3]. The high electron affinity of the D_{3h} symmetry structure of NO_3 (3.9 eV [4]) and the stability, with respect to fragmentation, of the resulting NO_3^- ion (dissociation threshold ≈ 3.8 eV, as determined from literature enthalpy values [4]) result in low rates for destruction of this form of NO_3^- . This ion, among others, is therefore important in modeling the photochemistry and ion/molecule chemistry in particular regions of the earth's atmosphere. The gas-phase NO_3^- anion is also important analytically in that its peak is frequently the base peak in negative ion mass spectra of nitrate esters and nitric acid. This is the case for a variety of means for forming anions such as low-pressure electron capture [5], negative ion chemical ionization [6], and atmospheric pressure ionization [7]. The NO_3^- ions formed from these compounds are all likely to have the structure of D_{3h} symmetry. A second stable form of NO_3^- , however, was postulated by Fehsenfeld and co-workers [8, 9] following rate measurements of NO_3^- anions formed in reactions with various neutral atmospheric species. Further support for the existence of this anion, referred to as the peroxy form with the structure $(\text{OO}-\text{NO})^-$, was later provided by photodissociation and photodetachment studies [10].

We observe intense signals in the negative ion mass

spectra of nitrate esters and nitric acid at m/z 62 when an atmospheric sampling glow discharge ionization (ASGDI) source is used [11]. However, an anion peak at m/z 62 is always present under normal ASGDI conditions. This is hardly surprising because a discharge current of several milliamperes in the ion source is sustained in a mixture of nitrogen and oxygen. A variety of reactive species, including O_3 , NO_2 , $\text{NO}^\cdot$, and others, are formed under these conditions. We recently coupled an ASGDI source to an ion trap mass spectrometer (ITMS) [12] and are using the tandem mass spectrometry (MS/MS) and ion storage capabilities of the ITMS to study the reactive species formed in the ASGDI source. During the course of this work, results have been obtained that indicate that at least two structurally different anions of m/z 62 can be formed in the ASGDI source. One of these structures is clearly the nitrogen-centered D_{3h} symmetry structure, while the other is likely to be the peroxy $(\text{O}_2-\text{NO})^-$ structure. This paper relates the experimental evidence that indicates the presence of two or more NO_3^- structures, ab initio calculations made to determine the structures and relative stabilities of the possible isomers, and studies performed to determine the reactivity of the less stable structures with background gases in the vacuum system.

Experimental

Details of the ASGDI source/ITMS combination can be found elsewhere [12]. Briefly, air is drawn into the ASGDI source via a 200- μm diameter aperture at a rate of 5 mL/s. The ionization region is typically held at a pressure of ~ 0.7 torr, and a glow discharge is established

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between the 200- μm aperture plate and a parallel aperture plate separated by ~ 19 mm. For anion analysis, a glow discharge is typically induced by applying a negative voltage of 350–400 V to the plate containing the 200- μm aperture while the second aperture plate is held at or near ground potential. The discharge current is determined by the voltage applied to the 200- μm aperture plate [11] and is variable over the range of 1.5–20 mA, the upper limit being determined by the current output capability of the power supply. The discharge current is an important variable in the relative contributions of the two structures (see below). The second aperture plate, which separates the ionization region from the high-vacuum region of the mass spectrometer, contains an 800- μm diameter aperture. Ions that enter the vacuum system through the 800- μm aperture are gated into the ion trap by a three-element lens system. The base pressure in the ion trap region is $\sim 1 \times 10^{-4}$ torr, which consists primarily of air and the reactive species formed in the discharge such as NO^+ , NO_2^+ , and O_3^+ . A bath gas (helium) is typically added to bring the total pressure in the ITMS vacuum system to ~ 2 mtorr.

Two types of MS/MS experiments were performed in this study, those that employed collision-induced dissociation (CID) between stages of mass analysis and those that relied on exothermic ion-molecule reactions between stages of mass analysis. The former made use of a supplementary radio-frequency (rf) voltage applied to the end caps to kinetically excite the anions of interest [13], and the latter employed trapping time as a variable [14]. One set of experiments used both types of reactions. The application of a dc voltage to the ring electrode for parent ion isolation was typically unnecessary for the MS/MS experiments involving CID. Ions of $m/z < 62$ were eliminated from the ion trap simply via an appropriate rf ramp applied to the ring electrode, and parent ions were mass-selectively excited by the use of a supplementary rf voltage of the appropriate frequency applied to the end caps. Parent ion isolation for the experiments involving ion-molecule reactions employed the application of a dc voltage to the ring electrode to remove all ions other than those at m/z 62 prior to the reaction period. The experiment that employed CID in conjunction with a kinetic experiment included a kinetic excitation step that followed a variable time delay after the parent ion isolation step.

Method of Computation

Full-geometry optimizations were carried out on various structures of NO_3^- . A 6-311+G(2d) basis set was used for all calculations. The 6-311G part of the basis set is from Krishnan et al. [15], and the polarization functions and diffuse functions are from Frisch et al. [16] and ref. 13 cited therein. Single-point energy calculations at the MP2 level of theory were then carried out on each structure with the same basis set. All MP2 calculations were carried out by using the frozen

Table 1. Calculated geometries, relative total energies, and bond indices for the NO_3^- structures (bond lengths in angstroms)

Geometry	Parameter	Value	Relative total MP2 energy (kJ/mol)	Bond index	Bond angle
NO_3 (D_{3h})	r_{NO}	1.22	0.0	1.51	120°
					(ONO)
ON-O_2 ($C_{\infty v}$)	r_{ON}	1.20	613.8	1.18	180°
	r_{NO}	2.62		0.21	(ONO)
	r_{OO}	1.17		1.80	
NO-O_2 ($C_{\infty v}$)	r_{NO}	1.21	658.1	1.15	180°
	r_{OO}	2.80		0.07	(NOO)
	r_{OO}	1.16		1.46	

core approximation. Also, a force constant matrix calculation was performed on each optimized structure to verify that each was indeed a true minimum on the potential energy surface, that is, that all nontrivial vibrational frequencies are real. Version 7 of the HONDO program of Dupuis was used for all computations [17].

Results and Discussion

The theoretical calculations indicate that two linear NO_3^- structures of similar energy are bound, although they are less stable than the structure with D_{3h} symmetry. Calculated energies, bond lengths, and bond indices are given in Table 1 for the three stable geometries. In each linear geometry the central bond linking the NO and OO groups is long and weak, particularly for the (NO–OO) $^-$ isomer. The central bond in (NO–OO) $^-$ is 0.18 Å longer than the central bond in (OO–NO) $^-$. Interestingly, the Mulliken population analysis, which gives the charge distribution (see Table 2), reveals that nearly all of the negative charge is localized on the NO subunit in both linear isomers. The CID results described below and photodissociation studies [10] both show, however, that the charge

Table 2. Population analysis for NO_3^- species

Geometry	Atom	Net charge
NO_3 (D_{3h})	N	+0.597
	O	–0.532
$\text{O}_1\text{–N}_2\text{–O}_3\text{–O}_4$	O_1	–0.372
	N_2	–0.577
	O_3	–0.168
	O_4	+0.117
$\text{N}_1\text{–O}_2\text{–O}_3\text{–O}_4$	N_1	–0.621
	O_2	–0.368
	O_3	+0.067
	O_4	–0.077

goes with the oxygen molecule upon dissociation. This result is expected because of the relative electron affinities of O_2 and NO^+ [4].

Throughout this discussion it is assumed that the most commonly observed anion at m/z 62 is the most stable form of NO_3^- , the ion structure of D_{3h} symmetry. For example, it is assumed that the nitrate esters give NO_3^- anions of the D_{3h} structure because the NO_3 groups are already in the proper geometry within the molecule and because the NO_3^- anions fragment to NO_2^- (see below). The peroxy structure referred to throughout is generally written as $(\text{OO}-\text{NO})^-$. However, the calculations show that $(\text{NO}-\text{OO})^-$ is also stable and only slightly less so than $(\text{OO}-\text{NO})^-$. None of the data obtained in this work can be used to definitively distinguish between the two linear forms of the anion. Neither can it be determined if free interconversion can occur. Therefore, the peroxy form of the anion sampled in these studies may actually be a mixture of structures. It is also assumed throughout the discussion that the more reactive and less stable NO_3^- anions observed in these studies have peroxy structure(s). The participation of some other form of NO_3^- cannot be precluded. However, the relatively long time frame and multiple collision nature of the ion trap experiment would tend to minimize the participation of any electronically excited species, and the calculations did not indicate any other thermodynamically stable forms of NO_3^- (see below).

Figure 1 shows an energy diagram based on the literature values for the heats of formation and electron affinities of the appropriate species [4, 18]. The diagram is incomplete in that the heat of formation of the peroxy form of NO_3^- has not been reported and the barrier to isomerization is unknown. However, some conclusions regarding the magnitudes of these quantities can be drawn from experimental results described below. Note that the relative energies obtained by cal-

culation listed in Table 1 are inconsistent with the experimentally derived literature values (compare Table 1 with Figure 1). The theoretical values for the differences in energy between the D_{3h} structure and the linear structures are clearly too high. The reason for the poor accuracy of the calculations with respect to the energy differences between the structures is not clear. It is possible that perturbation theory at the MP2 level is not adequate for the accurate determination of the relative energies of these structures or that a structure exists that is intermediate in stability between the D_{3h} and linear forms. However, we have tested a variety of structures that might be expected to be stable and have found none to be more stable than the linear forms. We are therefore confident that one (or both) of the linear forms is the less stable NO_3^- isomer observed in these studies despite the fact that the calculations give rather high values for the relative energies.

CID Results

Figure 2a shows the background negative ion mass spectrum normally observed when the ASGDI source samples laboratory air and operates at a discharge current of 3 mA. Figure 2b shows the MS/MS daughter ion spectrum of the anions at m/z 62 that appear in the mass spectrum. Daughter ions appear at m/z 46 and at m/z 32 and are presumably due to NO_2^- and O_2^- , respectively. The NO_2^- anion would be expected by loss of an oxygen atom from the D_{3h} form of NO_3^- , but the loss of NO , although favorable thermodynamically, might be precluded if the isomerization barrier were greater than the threshold for loss of $\text{O}^\cdot$ (see Figure 1). When compounds that contain one or more nitrate groups, such as nitric acid, nitroglycerin, or other nitrate esters, are admitted into the ion source, the NO_2^- anion in the MS/MS daughter ion spectrum of the anions at m/z 62 increases in abundance with the

Figure 2. (a) ASGDI negative ion mass spectrum obtained from laboratory air. (b) CID spectrum of the anions at m/z 62 formed from laboratory air.

m/z 62 signal whereas the m/z 32 daughter ion does not. This can be seen by comparing Figure 2b with the MS/MS spectrum obtained from the m/z 62 anions formed when nitroglycerin was admitted into the ion source (Figure 3) operated under the same conditions as were used to obtain the data in Figure 2. Sufficient nitroglycerin was admitted to the ion source that the signals at both m/z 46 and m/z 62 were driven off scale to show that even when a large excess of the ion that leads to the m/z 46 daughter ion is present in the ion source, no effect is observed on the signal at m/z 32. This is also observed when much smaller quantities of nitroglycerin are admitted into the ion source such that the O₂⁻ and NO₂⁻ signals remain on the same scale and are not broadened by space charge. Furthermore, reactions between the daughter ions and neutral nitroglycerin that enters the vacuum system cannot play a significant role in the appearance of the MS/MS spectrum. The maximum nitroglycerin pressure that can be generated within the vacuum system when nitroglycerin at room temperature is held near the sampling aperture of the ASGDI source is roughly 3×10^{-11} torr, and the time over which a reaction can proceed after O₂⁻ daughter ions are formed is about 15 ms. Under these conditions, even a reaction with a large rate constant, for example, 1×10^{-9} cm³/(molecule·s), can de-

Figure 3. CID spectrum of the anions of m/z 62 with nitroglycerin present.

plete the population of O₂⁻ by only about 0.001%. We conclude from these observations, therefore, that the daughter ions at m/z 32 and m/z 46 do not share the same parent.

Collision-induced dissociation of the anion at m/z 62 clearly reveals when a compound with a nitrate group is drawn into the ion source via the change in intensity of the characteristic NO₂⁻ daughter anion. When a mixture of *D*_{3h} and peroxy structures of NO₃⁻ is present, changes in the relative intensities of the O₂⁻ and NO₂⁻ daughter anions can indicate changes in the relative proportions of the two isomers. For example, CID experiments reveal that discharge current strongly influences the relative proportions of the isomeric NO₃⁻ anions. This is illustrated in Figure 4, which summarizes CID spectra acquired as a function of discharge current under MS/MS conditions where both daughter ions are readily formed (see below). Figure 4 indicates the general tendency for the relative and absolute quantities of the peroxy form to be maximized at low discharge currents. Furthermore, the absolute number of peroxy structure anions tends to level off above a discharge current of a few milliamperes, whereas the total signal due to NO₃⁻ continues to increase. Other ion source operating parameters also affect the absolute and relative contributions of the peroxy structure. For example, the relative and absolute contributions of the peroxy form decrease as the outer aperture plate temperature is elevated. However, we have not been successful at significantly increasing the number of peroxy ions formed in the ion source over that obtained under normal operating conditions using a low discharge current and an unheated outer aperture plate.

Qualitative information regarding the relative stabilities to dissociation of the two structures can also be obtained from CID experiments with the ITMS. It has been demonstrated that the amount of internal energy deposited into an ion in the collisional excitation stage of an MS/MS experiment using an ITMS with a He bath gas pressure of 1–3 mtorr can be influenced by a number of variables. These include the amplitude of the rf voltage applied to the ring electrode, the amplitude of the supplementary rf voltage applied to the

Figure 4. Daughter ion abundances from the CID of anions at m/z 62 as a function of the discharge current in the ASGDI source.

end caps, and the duration of the application of the supplementary rf voltage [13]. Under fixed conditions of ring electrode voltage and duration of application of the supplementary rf voltage, the amplitude of the supplementary rf voltage is effective at increasing the average velocity of the parent ions. The collision energy can therefore be increased by increasing the amplitude of the supplementary rf voltage. Figure 5 summarizes MS/MS spectra acquired for the anion mixture at m/z 62 formed at a discharge current of about 2 mA using a 10-ms application of supplementary rf voltage at a fixed ring electrode voltage amplitude of 148 V 0-p. The fact that the supplementary voltage threshold for the observation of O₂⁻ is lower than for NO₂⁻ is consistent with photodissociation results for these anions [10] and Figure 1 and reflects the lower stability of the peroxy form of NO₃⁻.

It is clear from Figure 5 that at relatively high supplementary rf voltage amplitudes, the daughter ion signals do not quantitatively account for the loss of parent ion signal. Two major loss mechanisms can come into play under these conditions. First, as the supplementary rf amplitude increases, the likelihood grows that an ion can attain a displacement from the center of the ion trap greater than the dimensions of the device and can therefore be ejected from the ion trap prior to CID. Second, electron detachment upon collision, a process that frequently competes with CID for anions, can occur, resulting in a loss in anion signal. The net effect for both mechanisms is a loss in signal that, with the normal ion trap experiment, makes the contributions from the two loss mechanisms difficult to separate. It is likely that the different NO₃⁻ structures are characterized by different cross sections for elec-

Figure 5. Daughter ion abundances from the CID of anions at m/z 62 as a function of the amplitude of the supplementary rf voltage applied to the end caps.

Figure 6. Abundances of $[\text{CO}_3^-]$, $[\text{NO}_3^-]$, and $[\text{NO}_2^-]$ obtained as a function of storage time.

tron detachment and could therefore be distinguished on this basis. We have not pursued this possibility in this case, because the different ion structures give distinct daughter ions and clearly show different reactivities (see below). However, in cases where isomeric anion structures fragment to a common daughter ion, experiments could be devised to measure the relative propensity for electron detachment that are less prone to have errors introduced by ejection of the parent ions from the ion trap. These experiments might include, for example, the detection of anions ejected from the ion trap during the period when the supplementary rf voltage is applied to the end caps.

It is, perhaps, noteworthy that no isomerization of the peroxy form to the D_{3h} form was evident in any of these experiments. The major loss mechanisms for the peroxy form, in the absence of kinetic excitation, was reaction with CO_2 , which diffused into the vacuum system through the ASGDI source, and, to a lesser extent, reaction with NO and NO_2 , which were formed in the glow discharge and diffused into the vacuum system (see below). These loss mechanisms accounted for essentially 100% of the loss of the peroxy form when no supplementary rf voltage was applied to the end caps. Therefore, isomerization of the peroxy form to the D_{3h} structure, if it occurs, must be characterized by a half-life significantly longer than 0.2–0.4 s, the half-life associated with peroxy NO_3^- depletion due to ion-molecule reactions. Furthermore, the CID experiments indicate that the D_{3h} structure fragments before it isomerizes. This is observed despite the multiple collision nature of collisional activation in the ITMS and the relatively long time between collisions (10^{-4} s). This indicates that the barrier for isomerization is greater than the threshold for D_{3h} NO_3^- to fragment to NO_2^- and O^- and is therefore also greater than the threshold for the peroxy form to fragment to O_2^- and NO (see Figure 1).

Kinetic Studies

The ion-trapping capability of the ITMS can also be used to study the peroxy form of NO_3^- . It was observed that the peroxy form was depleted in the vacuum system by reactions with background neutrals that diffused into the vacuum system from the ASGDI source. The principal reactions are presumed to be

and possibly

This is determined from the appearance of anions at m/z 60 and m/z 46 as m/z 62 is allowed to react with background gas in the vacuum system. Figure 6 shows the abundances of the NO_3^- , CO_3^- , and NO_2^- ions observed as a function of time after NO_3^- , formed from air at a discharge current of 2.7 mA, was injected into the ITMS and mass-selected. No nitrate-containing species were intentionally admitted into the ion source. The total NO_3^- abundance decreases with time, and the abundances of CO_3^- and NO_2^- increase with time until about 1 s, when they each tend to level off. The population of NO_3^- anions comprises both ion structures, and only the peroxy form is known to be reactive. If it is assumed that after 1.5 s the peroxy form of the anion has been essentially depleted, then the fraction of D_{3h} NO_3^- in the original population was about 54%.

Both reactions 1 and 2 have been reported previously [8, 9] and are deemed to be exoergic. The fact that these product ions are observed provides evidence complementary to the CID results for the presence of the peroxy form of NO_3^- . Reaction 3 has not been re-

ported but, on the basis of the minimum heat of formation of (OO-NO)⁻ necessary for reaction 1 to be exoergic (-74 kJ/mol), is expected to be exoergic. Reactions 2 and 3 cannot be distinguished in these experiments. Reaction 2 alone, however, cannot account for all of the NO₂⁻ formed by ion-molecule reactions of peroxy NO₃⁻ if it proceeds with the reported rate constant of $\approx 1.5 \times 10^{-11}$ cm³/(molecule-s) [8]. The number density of NO[•] that is present in the vacuum system under typical ion source operating conditions is about 2×10^9 cm⁻³ [19]. The product of the rate constant and number density (0.03) is too small a fraction of the experimentally obtained values for the sum of all ion-molecule reactions (1.4-1.7, see below) to fully account for the NO₂⁻ that is formed. Reaction 3 appears to be the likely source for the bulk of the NO₂⁻ formed in ion-molecule reactions, because the number density of NO₂ in the vacuum system, under typical ion source operating conditions, is $\sim 1 \times 10^8$ cm⁻³ [19], and the reaction is expected to be exoergic.

Correcting the measured NO₃⁻ abundance for the contribution from the unreactive form and plotting $-\ln[(\text{OO}-\text{NO})^-]_t/[(\text{OO}-\text{NO})^-]_0$ vs. time gives a slope of 1.6 (correlation coefficient = 0.99). This value is the sum of the products of the rate constants and relevant number densities for the ion-molecule reactions of (OO-NO)⁻. If reactions 1-3 are the only major ion-molecule reactions in these studies, then

$$k_1[\text{CO}_2] + k_2[\text{NO}^\bullet] + k_3[\text{NO}_2] = 1.6 \quad (4)$$

where k_1 , k_2 , and k_3 are the rate constants for reactions 1, 2, and 3, respectively. Only k_2 has been reported, but approximate values for k_1 and k_3 can be determined from the approximate number densities of the relevant neutral reactants and the following relationships:

$$[(\text{NO}_2^-)_a]_t = k_2[\text{NO}^\bullet][(\text{OO}-\text{NO})^-]_0(1 - e^{-\alpha t})\alpha^{-1} \quad (5)$$

$$[(\text{NO}_2^-)_b]_t = [\text{NO}_2^-]_t - [(\text{NO}_2^-)_a]_t \quad (6)$$

$$k_3 = [(\text{NO}_2^-)_b]_t \alpha [[\text{NO}_2] [(\text{OO}-\text{NO})^-]_0 (1 - e^{-\alpha t})]^{-1} \quad (7)$$

$$k_1 = [\text{CO}_3^-]_t \alpha [[\text{CO}_2] [(\text{OO}-\text{NO})^-]_0 (1 - e^{-\alpha t})]^{-1} \quad (8)$$

where $[(\text{NO}_2^-)_a]$ and $[(\text{NO}_2^-)_b]$ are the abundances of the NO₂⁻ ions formed from reaction of (OO-NO)⁻ with NO[•] and NO₂ (reactions 2 and 3), respectively, and $\alpha = k_1[\text{CO}_2] + k_2[\text{NO}^\bullet] + k_3[\text{NO}_2]$. For $t = 1.4$ s and $\alpha = 1.6$, $k_1 = 4.9 \times 10^{-10}$ cm³/(molecule-s) and $k_3 = 3.5 \times 10^{-11}$ cm³/(molecule-s).

Given the uncertainties in the number densities and in the percentage of the *D*_{3h} structure, these rate constants are only accurate to within $\pm 70\%$. The major source of error in this measurement lies in the un-

certainty in the value of α , which, in turn, is determined primarily by the uncertainty in the percentage of (OO-NO)⁻ taken to be in the original population of NO₃⁻.

Combined Kinetic/CID Experiment

The fact that the population of NO₃⁻ anions initially accumulated for a kinetic study is a mixture of reactive and unreactive forms compromises somewhat the measurement of the rate constants for reactions of (OO-NO)⁻. A combination of CID with a kinetic study, however, can improve the measurement by eliminating the uncertainty associated with the relative abundances of the unreactive and reactive forms in the measurement of α . As shown above, CID of (OO-NO)⁻ gives O₂⁻, whereas the *D*_{3h} form of the ion gives NO₂⁻. Therefore, subjecting the NO₃⁻ anions that remain after each reaction period to collisional activation and monitoring the O₂⁻ daughter ion signal as a function of reaction time permits α to be determined directly from the slope of the plot of $-\ln[\text{O}_2^-]_t/[\text{O}_2^-]_0$ vs. time. Such an experiment was performed using a discharge current of 3 mA and yielded a value of α of 1.48. This α value, when used with the data mentioned in the previous section, yields a value for k_1 of 4.6×10^{-10} cm³/(molecule-s) and a value for k_3 of 3.4×10^{-11} cm³/(molecule-s). These values are accurate to within $\pm 25\%$, with the largest source of uncertainty arising from the uncertainty in the values of the number densities of the neutral reactants.

An advantage of the use of CID in conjunction with the kinetic measurement is that the accuracy with which α can be measured is independent of the relative abundance of the unreactive form of NO₃⁻ initially present. With the kinetic method alone, the uncertainty in α increases as the proportion of unreactive NO₃⁻ increases. In cases where only one reaction occurs, the kinetic/CID method can be used directly to obtain the rate constant for the reactive isomer. In cases such as the one just described, where several competing reactions occur, however, some estimate of the initial abundance of the reactive form of the isomer must be made to obtain the rate constants (see, for example, eqs 5-8). This can be done either by allowing the reactive form to be depleted and measuring the unreacted ions, as was done here, or by measuring the CID efficiency of the reactive isomer.

Summary

This study has demonstrated that at least two structures of NO₃⁻ are formed in the glow discharge in air and that their relative abundances are sensitive to such parameters as discharge current and temperature. One is clearly the *D*_{3h} symmetry structure, and another is likely to be the peroxy structure proposed and confirmed previously [9, 10]. The results of the first ab initio treatment of the NO₃⁻ system that is described here,

however, indicate that two structures less stable than the D_{3h} form may exist. One or both of these structures may be present in the glow discharge. Collision-induced dissociation experiments, like previous photodissociation studies [10], show that the less stable form fragments to O_2^- whereas the D_{3h} form fragments to NO_2^- . Furthermore, the dissociation threshold for the former is significantly less than that for the latter, as expected. Ion-molecule reaction studies also indicate the presence of at least two structures of NO_3^- in the glow discharge and establish the rate constant for the reaction of the less stable form of NO_3^- with CO_2 to be $\sim 4.6 \times 10^{-10} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ under ion storage conditions in the ITMS. Evidence is given for a previously unreported reaction of peroxy NO_3^- with NO_2 to give NO_2^- , O_2 , and NO , which has a rate constant $\sim 3.4 \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$. A useful approach to kinetic measurements for impure reactant ion populations that incorporates CID is also illustrated.

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