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Chemical Reactivity within NO/Ethanol Cluster Ions

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Abstract: The direct influence of hydrogen-bonding on chemical reactivity within $[\{NO\}_n\{CH_3CH_2OH\}_m]^+$ ions is presented in this study. At high ethanol concentrations in the ethanol/NO gas mixture, the primary ion−molecule reaction generates CH_3CH_2ONO and HNO via loss of a hydrogen solely from the hydroxy group of the ethanol. This behavior continues without regard to the ethanol concentration until a certain critical value of the ethanol concentration is reached. Further decreasing the ethanol composition gives rise to a change in the position of the hydrogen atom loss, from the hydroxyl group to the methylene group. These results, we believe, originate from structural changes in the hydrogen-bonding network of the ethanols. We propose a model to account for this distinctive chemistry within NO/ethanol clusters and have interpreted the difference in the chemical reactivity between NO/ethanol and NO/methanol in terms of geometrical versus energetic factors.

Introduction

Recently, a number of investigations have been performed to better understand the chemical reactivity of the nitric oxide molecule (NO) in clusters, due to its central role in many global problems.[1] NO is found to exhibit reactive behavior within ionic clusters containing molecules having a hydroxyl group such as water and methanol.[2−5] For example, in the D region of the atmosphere NO^+ is involved in a series of ion−molecule reactions with water clusters.[2] In the presence of trace amounts of water and methane, it is also known that ionic clusters of NO generate dinitrogen trioxide (N_2O_3).[3] Very recently, Shin et al. have reported the generation of methyl nitrite (CD_3ONO) molecules, within NO/CD_3OH mixed cluster ions, again mediated by the cluster environment.[4]

Particular attention has been paid to the effect of clusters on nonthermal plasma processes in flue gas treatment, in part due to investigations which concluded that the formation of ionic clusters enhances the efficiency of removal of air pollutants such as NO_x and SO_x.[6] Alcohols are now also being studied as an additive to further increase the removal efficiency of air pollutants.[7] Because of the importance of NO, we therefore carried out the present investigation of heterogeneous clusters of NO with ethanol.

In the present study, we have investigated heterogeneous clusters of NO with three partially deuterated isotopomers of ethanol, CD_3CH_2OH, CH_3CD_2OH, and CH_3CH_2OD, utilizing nonresonant multiphoton ionization time-of-flight mass spectrometry (MPI-TOF). The purpose of this present work is to study the chemical reactivity occurring in ionic clusters as a function of the composition of ethanol in the gas mixture and to elucidate the possibility of the generation of unfavorable byproducts when, for example, ethanol is used as an additive to improve the removal efficiency of NO_x. In our previous work on the NO/CD_3OH cluster system,[4] it was found that the mixed cluster ions lose hydrogen atoms only from the hydroxyl group, not from the methyl group, over a wide range of the concentration of CD_3OH in the gas mixture. In contrast, we now note in the present study of CH_3CD_2OH, that the mixed cluster ions lose hydrogens from the methylene group as well as from the hydroxyl group. In addition, we have also observed that the relative intensity between these two processes depends strongly on the concentration of ethanol in the gas mixture prior to ionization.

Experimental Section

Cluster mass spectra were produced using a reflectron time-of-flight mass spectrometer (RTOFMS, Jordan Co.) that has been previously

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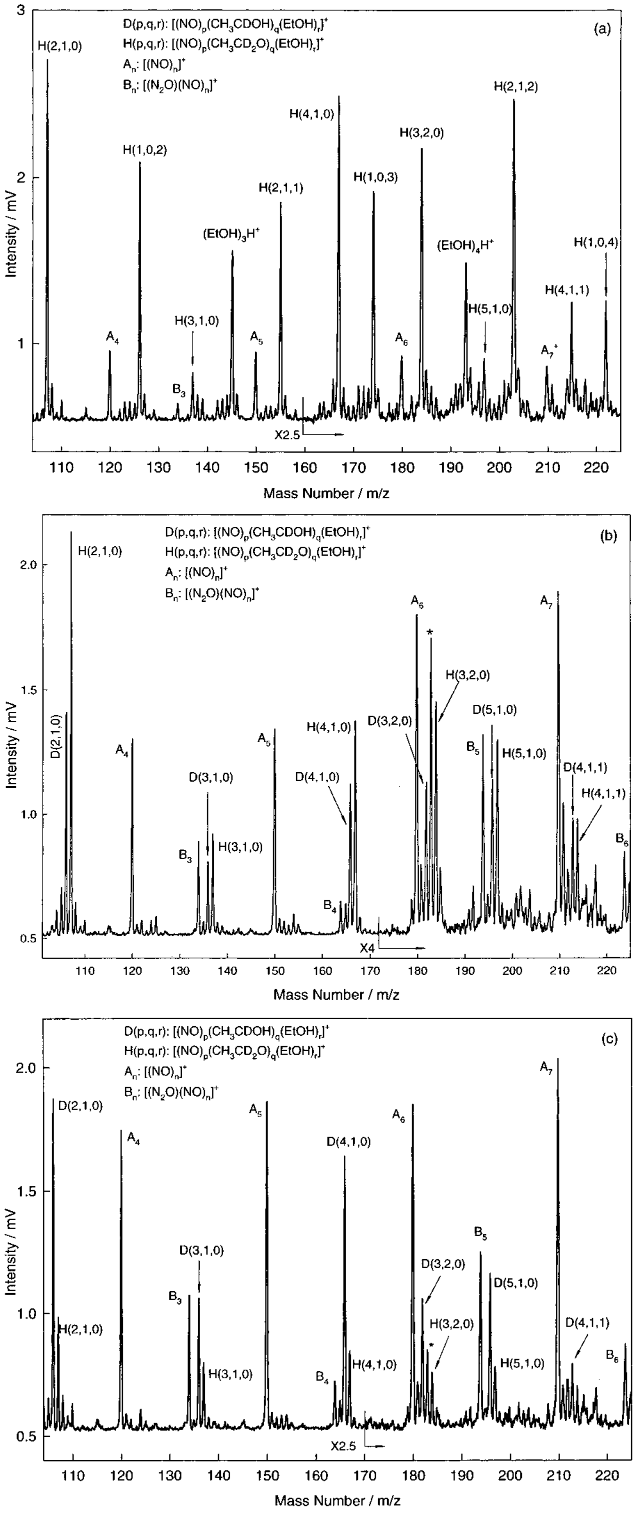

Figure 1. Time-of-flight mass spectra of heterogeneous NO/CH_3CD_2OH cluster ions taken at the different mixture concentrations: (a) 0.49% CH_3CD_2OH and 5% NO, (b) 0.07% CH_3CD_2OH and 5% NO, and (c) 0.02% CH_3CD_2OH and 5% NO in 3.0 atm of Ar carrier gas. A_n and B_n designate the $(NO)_n^+$ and the $[\{N_2O\}\{NO\}_n]^+$ cluster ion series, respectively. The mixed cluster ion series, $[\{NO\}_p\{CH_3CDOH\}_q\{CH_3CD_2OH\}_r]^+$ and $[\{NO\}_p\{CH_3CD_2O\}_q\{CH_3CD_2OH\}_r]^+$, are denoted by D(*p*,*q*,*r*) and H(*p*,*q*,*r*), respectively. In (b) and (c), * designates a peak losing one D atom and one H atom, $[\{NO\}_3\{CH_3CD_2O\}\{CH_3CDOH\}]^+$.

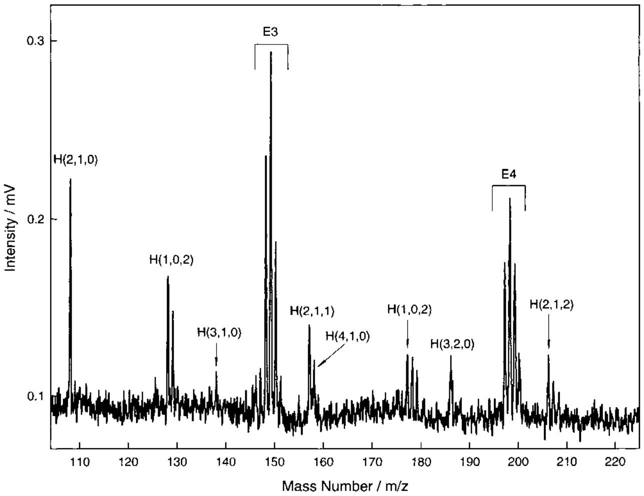

Figure 2. Time-of-flight mass spectrum of 0.7% CD_3CH_2OH and 5% NO in 3.0 atm of Ar carrier gas. The mixed cluster ion series, $[\{NO\}_p\{CD_3CH_2O\}_q\{CD_3CH_2OH\}_r]^+$, are denoted by H(*p*,*q*,*r*). E_n designates the group of the homogeneous ethanol cluster ions.

described in detail.[8] Neutral heterogeneous clusters are generated by the supersonic expansion of a gas mixture of 5% NO (premixed 5% NO gas in Ar, Matheson Gas Co.) and 0.49−0.02% CH_3CD_2OH (Cambridge Isotope Laboratories, D 99%) or 0.7% CD_3CH_2OH or CH_3CH_2OD (Aldrich Chemical Co., D 99%) seeded in 3.0 atm of Ar through an 800 μm diameter pulsed nozzle (General Valve Co., IOTA ONE). Ions generated by an unfocused 248 nm laser beam (Lambda Physik, EMG101 or EMG150), with typical laser energy below 3.5 mJ $pulse^{-1}$, are accelerated by a double-stage electric field toward the reflectron through a 1.4 m long flight tube. The reflected ions are then detected by a dual micro channel plate, and the resulting ion species are recorded by a transient digitizer (LeCroy 9310A).

Results

Figure 1 displays representative mass spectra taken at three different ethanol compositions: (a) 0.49% CH_3CD_2OH and 5% NO, (b) 0.07% CH_3CD_2OH and 5% NO, and (c) 0.02% CH_3CD_2OH and 5% NO, seeded in 3.0 atm of Ar carrier gas. As shown in Figure 1a, the spectrum reveals a series of homogeneous cluster ions that can be readily assigned to $\{NO\}_n^+$ and $\{CH_3CD_2OH\}_nH^+$ clusters. However, mixed cluster ions are observed to be much more intense than the homogeneous peaks at the high concentration of ethanol in Figure 1a. The heterogeneous cluster ion series appears to have undergone intracluster reactions losing hydrogen atoms from either the hydroxyl group or the methyl group of the CH_3CD_2OH molecule. For a definitive characterization of the position of H atom loss, it was necessary to employ another isotopically substituted species that would allow the correct identification of the hydrogen atom loss either from the hydroxyl group or from the methyl group. Figure 2 shows the mass spectrum resulting from nonresonant MPI of 0.7% CD_3CH_2OH and 5% NO in 3.0 atm of Ar carrier gas. The heterogeneous cluster ion series losing H atoms from the hydroxyl group are dominantly detected. Peaks related to the loss of D atoms from the methyl group of the CD_3CH_2OH molecule are not observed under these conditions. A brief study of NO/CH_3CH_2OD further confirms these conclusions. Therefore, a comparison of the experimental results, obtained from three different isotopomers, provides definitive proof that the reaction of H atom loss within NO/ethanol cluster ions takes place mainly on the hydroxyl group when a relatively high concentration of ethanol exists in the gas mixture. The hetero-

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geneous cluster ion series in Figure 1a is therefore assigned as $[\{NO\}_p\{CH_3CD_2O\}_q\{CH_3CD_2OH\}_r]^+$, which is designated as H(p,q,r). This result is consistent with our previous work on the NO/CD_3OH system[4] in which it was observed that the hydrogen atom loss reaction generates species of the type $[\{NO\}_p\{CD_3O\}_q\{CD_3OH\}_r]^+$ with cluster ions possessing an even number of electrons being clearly favored.

When the ethanol concentration in the expansion gas mixture is decreased, the D atom loss from the methylene group is enhanced as displayed in Figure 1b. Upon further decrease of the ethanol concentration in the gas mixture, the D atom loss from the methylene group dominates over the H atom loss, as shown in Figure 1c. This ion series has the form $[\{NO\}_p\{CH_3CDOH\}_q\{CH_3CD_2OH\}_r]^+$ and is designated as D(p,q,r). For example, the following prominent feature is readily discerned from a comparison of the spectral peaks of mixed cluster ions containing three NO molecules. At a relatively high concentration of ethanol, it has been observed that mixed cluster ions undergo the loss of H atoms to produce peaks such as H(3,1,0) and H(3,2,0) as shown in Figure 1a. As the composition of ethanol decreases, the intensities of the mixed cluster ions losing D atoms such as D(3,1,0) and D(3,2,0) increase, while those losing H atoms decrease, as shown in parts b and c of Figure 1. In the case of the three-NO-two-ethanol species, three types of mixed cluster ions have been observed: losing two D atoms, D(3,2,0), losing two H atoms, H(3,2,0) and losing one H and one D atom, denoted by a *. As shown in Figure 1c, at the lowest ethanol concentration, the intra-cluster reaction that leads to loss of two D atoms, D(3,2,0), is favored over the other two reaction channels.

These results lead us to conclude that three competitive intra-cluster reaction pathways are operational in the formation of the mixed cluster ions, either hydrogen loss from the hydroxy group (eq 1), the methylene group (eq 3), or both (eq 2).

$$[\{NO\}_p\{CH_3CD_2OH\}_q]^+ \rightarrow [\{NO\}_n\{CH_3CD_2O\}_x\{CH_3CD_2OH\}_m]^+ + (p-n)NO + xHNO + (q-x-m)CH_3CD_2OH \tag{1}$$

$$\rightarrow [\{NO\}_n\{CH_3CD_2O\}_a\{CH_3CDOH\}_b\{CH_3CD_2OH\}_m]^+ + (p-n)NO + aHNO + bDNO + (q-a-b-m)CH_3CD_2OH \tag{2}$$

$$\rightarrow [\{NO\}_n\{CH_3CDOH\}_x\{CH_3CD_2OH\}_m]^+ + (p-n)NO + xDNO + (q-x-m)CH_3CD_2OH \tag{3}$$

The formation of the neutral species HNO and/or DNO is proposed as products of the intra-cluster ion−molecule reactions.[4,5] Which of these three pathways predominates depends explicitly on the ethanol concentration in the gas mixture prior to the beam expansion and cluster formation.

It is quite common for cluster mass spectra obtained from species having an unpaired electron, such as NO, to exhibit even−odd alternation in intensity according to the number of molecules in the cluster ions. The presence of even−odd alternation in intensity can be interpreted as an increased stability of cluster ions containing an odd number of species of an unpaired electron (which produces an even electron configuration) as compared to the cluster ions containing an even number of species of an unpaired electron (which produces an odd electron configuration). In pure NO clusters, the degree of the even−odd alternation is observed to decrease with increasing cluster sizes. In the present study, however, an increased predominance of even electron configuration cluster ions is observed with increasing cluster size. Even though mixed cluster ions such as $[\{NO\}_3\{CH_3CDOH\}]^+$, $[\{NO\}_3\{CH_3CD_2O\}]^+$, $[\{NO\}_5\{CH_3CDOH\}]^+$, and $[\{NO\}_5\{CH_3CD_2O\}]^+$ have an odd electron configuration, they are observed in surprisingly significant quantities. At larger cluster sizes, however, there is a selective generation of clusters possessing an even electron configuration, while mixed cluster ions containing an odd electron configuration are nearly suppressed, as shown in Figure 3. For example $[\{NO\}_{17}\{CH_3CDOH\}_2]^+$ and $[\{NO\}_{19}\{CH_3CDOH\}_2]^+$ at 602 and 662 amu, respectively, are much more intense than $[\{NO\}_{18}\{CH_3CDOH\}_2]^+$, the odd-electron species nominally at 632 amu. Similarly, the even electron species $[\{NO\}_{18}\{CH_3CDOH\}]^+$ and $[\{NO\}_{20}\{CH_3CDOH\}]^+$ are more intense than the odd electron species$[\{NO\}_{19}\{CH_3CDOH\}]^+$. In addition to this odd−even electron configuration effect, the selective intra-cluster reaction leading to D atom loss from the methylene group, dominates in generating $[\{NO\}_{even}\{CH_3CDOH\}]^+$ plus DNO or $[\{NO\}_{odd}\{CH_3CDOH\}_2]^+$ plus two DNO species. The enhanced abundance of the even electron configuration clusters with increasing cluster size may be due to the nature of the evaporation process that preferentially generates clusters with an even electron configuration.[9] The selective cleavage of the C−D bond of the CH_3CD_2OH molecule within the cluster ions will be rationalized later in terms of a competition between factors that selects either the geometrically or the energetically favored reaction products.

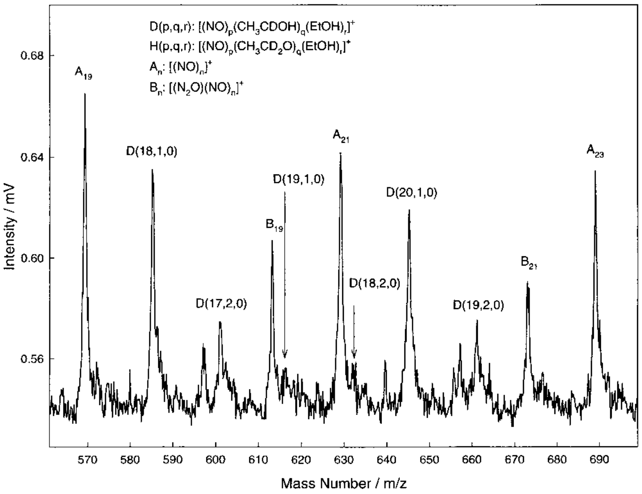

Figure 3. High mass region of time-of-flight mass spectrum taken at 0.02% CH_3CD_2OH and 5% NO in 3.0 atm of Ar carrier gas. The notations used are the same as those in Figure 1.

The loss of a D atom from the methylene group starts to be drastically enhanced as the concentration of ethanol in the gas mixture decreases below a critical value as shown in Figure 4. At high ethanol concentrations, the intensity ratios of the D/H loss remain nearly constant as the concentration of ethanol is gradually decreased up to the point where the critical value of the ethanol concentration is reached. Below the critical value, the relative intensity of the D loss channels is greatly increased with further decrease in the ethanol concentration. We feel that this finding is indicative that a significant change in the microscopic cluster structure is occurring near the critical value of the ethanol concentration that determines whether the D or H atom loss channel will predominant.

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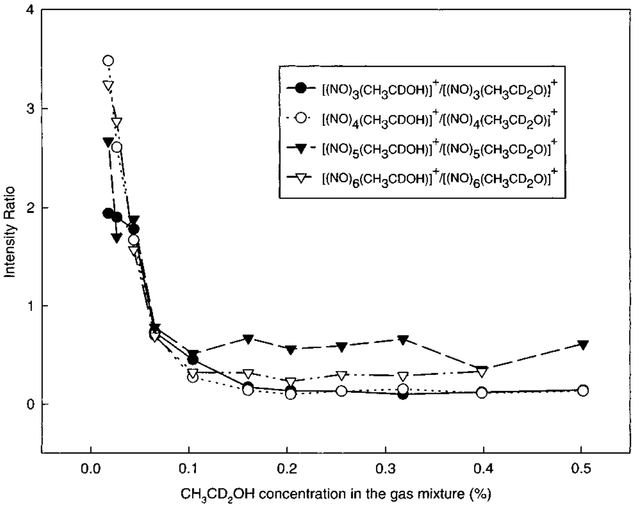

Figure 4. The relative intensity ratios of the mixed cluster ions losing D atoms to those losing H atoms as a function of the ethanol concentration in the gas mixture.

Table 1. Table of Bond Dissociation Enthalpies[a] (in kcal mol^{-1}) and Ionization Potentials[b] (in eV)

	ethanol	methanol
O−H	103.9 ± 1	103.6 ± 1
C_α−H	93.0 ± 1	94.0 ± 1
IP	10.48	10.84

[a] *Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Ed. CRC Press, Boca Raton, FL, 1980−1981. [b] Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST WebBook*. http://webbook.nist.gov.

Discussion

Since both methanol and ethanol molecules have not only the same functional group but also similar chemical properties such as bond strength and ionization potential (see Table 1), they might have been expected to exhibit similar behavior in intra-cluster reactions with the NO molecule. However, the pattern of the mass spectra between the two cluster systems is found to be remarkably different at low concentrations of ethanol in the gas mixture. Over the entire range of methanol compositions in the gas mixture of NO/CD_3OH cluster system,[4] we observed mixed cluster ions produced only by hydroxy H atom loss. We did not observe mixed cluster ions losing any D atoms from the methyl group of the CD_3OH molecule.

For the NO/methanol or NO/ethanol cluster ions, little structural or energetic information is known about the detailed mechanisms that lead to the loss of hydrogen atoms from the mixed cluster ions. A related study that provides some information on structures and reaction mechanisms is an experimental investigation of the fragmentation of $NO^+\{CH_3OH\}_n$ cluster ions.[5] In this study it was found that $NO^+\{CH_3OH\}_n$ cluster ions are of the form $\{CH_3OH\}_{n-1}H^+\cdots CH_3ONO$ since the separate loss of neither NO nor CH_3O was observed. Recently, Aschi and Grandinetti have reported that the structure of the protonated methyl nitrite ion can be considered as an ion−dipole complex between the NO^+ and the CH_3OH species.[10] This suggests that there is a preference for the O atom of the methanol molecule to be bound to the nitrogen rather than the oxygen atom in NO^+. In our previous study,[4] we have found that mixed cluster ions can lose several H atoms leading to the generation of $[\{NO\}_p\{CD_3O\}_q\{CD_3OH\}_r]^+$ plus qHNO species, where the structure of the resulting cluster ions is assigned tentatively to be $[\{NO\}_{p-q}\{CD_3ONO\}_q\{CD_3OH\}_r]^+$.

Table 2. Estimated Heats of Formation (in kcal mol^{-1}) for Major Potential Products from the Intra-Cluster Ion−Molecule Reactions of CH_3OH/NO and CH_3CH_2OH/NO Systems[a]

CH_3OH/NO		CH_3CH_2OH/NO	
species	energies[b]	species	energies[b]
$CH_3ONOLNO^+$	220.1 (−28.1)	$CH_3CH_2ONOLNO^+$	211.0 (−29.8)
$CH_2OH^+L(NO)_2$	209.6 (−)	$CH_3CHOH^+L(NO)_2$	179.5 (−)

[a] The enthalpies of formation of all species are taken from ref 15. In case of $(NO)_2$, the heat of formation is calculated to be 41.6 kcalmol^{-1} (see ref 16). [b] Heat of formation for $A^+\cdots B$ complex was estimated to be $\text{ÄH}^0_{f298}(A^+\cdots B) = \text{ÄH}^0_{f298}(A^+) + \text{ÄH}^0_{f298}(B)$, where values in parentheses are binding energies between A^+ and B species which can be estimated by a linear relation correlating the bond energy (BE) with the proton affinities (PA). The relation parameters for $NO^+\cdots X$ were found to be BE = −36.38 + 0.338 PA (see ref 17).

To establish a more quantitative understanding of the hydrogen loss reactions within NO/methanol and NO/ethanol clusters, we present the estimated heats of formation for major potential products as representative species from the ion−molecule reaction of the NO/methanol and the NO/ethanol cluster systems. Two representative products are considered for each cluster system, where the charge is assumed to always reside on the species having the lower ionization potential. As illustrated in Table 2, the formation of $CH_3CHOH^+\cdots\{NO\}_2$ ions is expected to be energetically favored over that of CH_3CH_2-$ONO\cdots NO^+$ for the NO/ethanol system by more than 30 kcal mol^{-1}, without considering the binding energies between the ion and the neutral species. In the case of the NO/methanol system, the difference in the heats of formation between the two ion−neutral complexes is around 10 kcal mol^{-1}, again without consideration of the binding energies between the ion and the neutral species. Therefore, it is of interest to note that the relative energy differences between the two possible ion−neutral complexes in the NO/ethanol system is much larger than those in the NO/methanol system.

Two possible mechanisms explaining the origin of the formation of cluster ions under MPI conditions have been proposed:[11] (1) MPI occurs first, followed then by the subsequent intra-cluster ion−molecule reactions, or (2) photochemical reactions within clusters, forming neutral products, precede the ionization. Since the NO molecule has an unpaired electron, it should exhibit a preference for the formation of neutral clusters containing an even number of NOs due to the enhanced electronic stability of such clusters. Moreover, if the photochemical reaction occurs before the ionization, it will give rise to the formation of even-number NO clusters since evaporation of NO monomers will accompany excitation. Therefore, under nanosecond laser pulse width conditions, the even−odd intensity alternation in homogeneous $\{NO\}_n^+$ cluster ions will be deteriorated if the second mechanism is operative in the generation of such cluster ions. However, Smith and Miller[12] have reported that, under the condition of nonresonant MPI, there is no fundamental difference in the mass spectra obtained with nanosecond and picosecond lasers. In our experiment using 5% NO in Ar carrier gas, we have observed mass spectra showing a nearly identical degree of the even−odd intensity alternation in the $(NO)_n^+$ cluster ions as compared to those of

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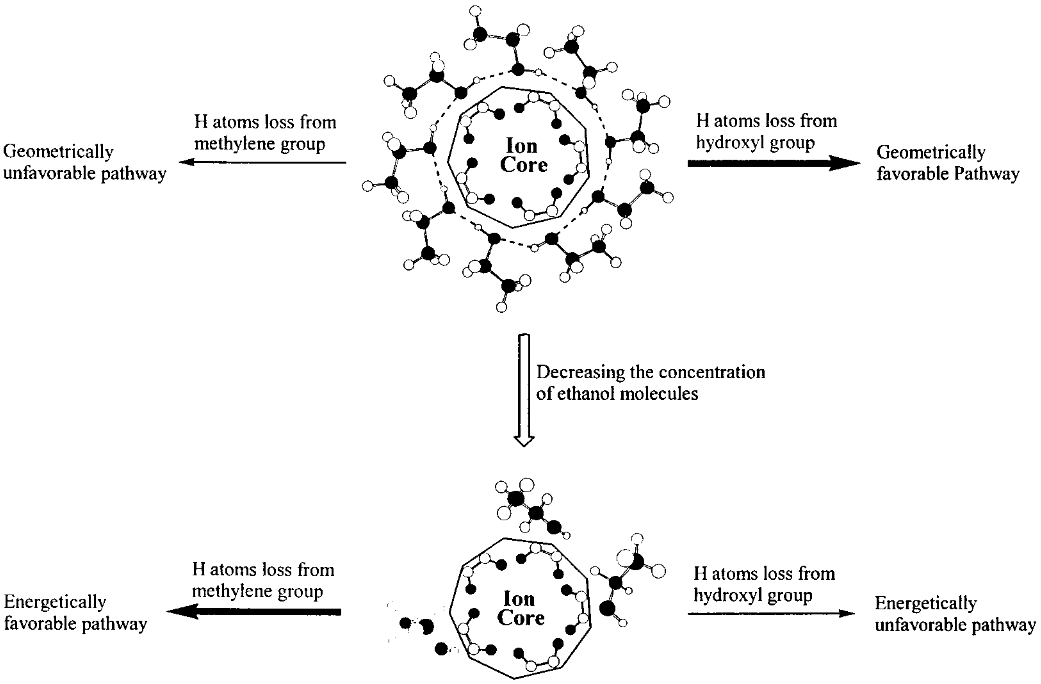

Figure 5. Schematic picture illustrating the effect of the hydrogen-bonding network on the reaction pathways leading to the generation of mixed cluster ions in the NO/ethanol cluster system. The open, black, and gray circles represent hydrogen, carbon, and oxygen atoms of the ethanol molecule, respectively. In the ion core, the open and gray circles designate nitrogen and oxygen atoms, respectively. Within the cluster ions, we assume that the NO moiety exists as dimeric units and the charge is located on the species having the lowest ionization potential.

Castleman's[13] and Miller's[14] groups which utilized femtosecond and picosecond lasers, respectively. The generation of the heterogeneous cluster ions in the present study has exhibited an enhanced preference for even-electron configurations that is exactly the same as that seen in our previous study of the NO/CD_3OH cluster system.[4] Although the present study employing a nanosecond laser pulse width cannot provide direct evidence of which mechanism is predominantly operative, these complimentary experimental findings support the mechanism that nonresonant MPI takes place first, followed subsequently by intra-cluster ion−molecule reaction. However, the proposed reaction model, discussed below, can be applied to either mechanism.

On the basis of our results, we have constructed a schematic drawing in Figure 5 where the H/D loss exhibited by the mixed cluster ions of the NO/ethanol cluster system is qualitatively rationalized in terms of geometric and energetic effects. The modeling efforts herein account for the characteristic intra-cluster reactions within the NO/ethanol cluster ions by applying two key assumptions. First, it is assumed that the initially generated positive charge in the mixed clusters will reside on the NO moiety, since it has the lowest ionization potential. This is analogous to the structure of alcohol−water ionic clusters in which an ionic central core of water is observed to be surrounded by a solvation shell of alcohol.[18] This is also supported by the lack of hydrogenated species of the form $[(NO)_m(ROH)_nH]^+$ that are rapidly formed in pure alcohol ionic clusters.[8b] Second, that the relative composition of ethanol to NO species within the heterogeneous neutral cluster may be changed by varying the composition of ethanol in the gas mixture. That is, when the concentration of ethanol in the gas mixture decreases, the available number of ethanols within the heterogeneous cluster ions is likewise diminished. As shown in Figure 1c for low ethanol concentrations, heterogeneous cluster ions containing only one or two ethanols are observed. It is not unreasonable then to suggest that higher ethanol compositions form heterogeneous neutral clusters containing more ethanols and fewer NOs, while lower ethanol compositions form heterogeneous neutral clusters with relatively fewer ethanols and more NOs.

At relatively high ethanol concentrations, we expect that the ethanol molecules would act as a solvation shell, surrounding the ion core of NOs. As shown in the upper part of Figure 5, the O atoms of individual ethanol molecules are preferentially oriented toward the N atoms of the ion core, stabilizing the positive ion. The hydrogen-bonding network among the solvating ethanol molecules should restrict the movement of the ethanol molecules on the ion core surface. This structural rigidity will give rise to a low probability that the hydrogen atoms of the methylene group can react with the NO moiety. This results in a geometrically unfavorable path for the loss of hydrogen atoms from the methylene group of ethanol. At relatively high ethanol compositions in the gas mixture, therefore, the reaction in which the mixed cluster ions lose H atoms from the hydroxyl group is the more favorable pathway, since the exposed hydroxyl hydrogens have a greater opportunity to react with the exposed NO moiety. Below the critical value of the ethanol concentrations, the hydrogen-bonding network is destroyed because there are fewer ethanol molecules surrounding the ion core. This situation is illustrated on the bottom portion of Figure 5. Breaking the hydrogen-bonding solvation network gives rise to an enhanced chance that the ethanol molecules may freely arrange in a favorable configuration to generate the more

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energetically stable products. This results in the generation of heterogeneous cluster ions losing D atoms from the methylene group of the CH_3CD_2OH molecules. Therefore, the influence of the relative concentration of the gas mixture on the product mass spectrum suggests that changes in the hydrogen-bonding network of the ethanol species within the mixed cluster ions play a critical role in deciding the intra-cluster reaction pathways.

We note in Figures 1 and 4 that the same final products, without regard to the ethanol concentration in the gas mixture, are generated, but with a different intensity ratio of D/H loss channels. As noted above, the origin of the differences in the intensity ratios of D/H loss of the heterogeneous cluster ions must be ultimately attributed to the differences in the neutral precursor distribution, that eventually gives rise to the different microscopic structures of the cluster ions upon ionization. We therefore propose the following possible model. The heterogeneous neutral clusters, produced at different ethanol concentrations, are first rapidly ionized by nonresonant MPI. Upon ionization, ion−molecule reactions and rearrangement would ensue within the initially generated cluster ions to accommodate the newly formed NO cluster ions. Following ionization, evaporation and fragmentation/reaction will be influenced by the relative composition of the cluster ions. At high and at low ethanol concentrations the predominant evaporations of ethanol and NO species would be different, consistent with the availability of ethanol. These overall processes should be incorporated to generate the same final product ions, but with different intensity ratios of D/H loss channels due to the different microscopic structure of the initially generated cluster ions. As already presented, there is little change in the intensity ratios of D/H loss channels when the ethanol concentrations in the gas mixture are larger than the critical value of the ethanol concentration. Below the critical value of the ethanol concentration, however, the intensity ratio of D/H loss channels becomes a strong function of the ethanol composition in the gas mixture.

As mentioned previously, attempts to detect the mixed cluster ion losing D atoms from the methyl group of the CD_3OH molecule were unsuccessful in all ranges of methanol composition in the gas mixture. In the case of the NO/CH_3CD_2OH cluster, however, we have observed that the mixed cluster ions can undergo loss of D atoms from methylene. This difference in the behavior of the intra-cluster reactions between the NO/methanol and the NO/ethanol cluster systems can be explained by means of the interplay between the cluster geometry and energetics. In the case of NO/methanol, formation of the mixed cluster ions containing methyl nitrite molecules is the most favorable reaction channel both energetically and geometrically, regardless of the methanol composition in the gas mixture. In contrast to the NO/methanol cluster system, the formation of mixed cluster ions containing ethyl nitrite molecules is the geometrically favorable reaction channel above the critical value of the ethanol composition, while the generation of the cluster ions losing H atoms from the methylene group is the energetically favored reaction channel below the critical value.

Conclusions

We have observed in the case of NO/ethanol ion clusters a hydrogen abstraction reaction such that hydrogen loss can occur from either the hydroxy group or the methylene group of the ethanol. We further note that the branching ratio of these two processes is directly altered by changing the ethanol concentration in the gas mixture, prior to the beam expansion, which produces the neutral clusters. That is, in ethanol-rich expansions only hydroxy loss is observed while in ethanol-lean expansions both processes can be observed. This, we believe, is direct evidence that hydrogen bonding can restrict reaction dynamics. We have proposed a mechanism to account for these observations invoking ethanols acting as a solvent shell surrounding a central NO ion core. Further work is planned to attempt to utilize tandem mass spectrometry to probe these reactions as a function of cluster size.

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