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Chemical Reactivity of $[(NO)_n(ROH)_m]^+$ Cluster Ions

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Mixed clusters of nitric oxide and various alcohols (ethanol, *n*-propanol, 2-propanol, *n*-butanol, 2-butanol, and *tert*-butyl alcohol) were generated via a continuous molecular beam expansion and analyzed using an electron impact tandem triple quadrupole mass spectrometer. The unique chemistry of the $[(NO)_n(ROH)_m]^+$ cluster ions was investigated employing collision induced dissociation (CID). Formation of product cluster ions containing alkyl nitrites $[(NO)_n(RONO)]^+$ and the subsequent loss of neutral HNO (when $n = 1$) are the most prominent features of this chemistry.

Introduction

The atmospheric chemistry of nitrogen oxides is extremely complex. The interconversion of the various nitrogen compounds in the atmosphere involves either directly or indirectly OH radicals, ozone, peroxides, and a variety of volatile organic hydrocarbons.[1−3] To further complicate the issue, heterogeneous and multiphase chemical reactions are certainly involved in this rich chemistry.[4] The study of chemistry in clusters containing NO with one or more additional components can play an important role in understanding the frequently novel types of chemical reactions which can occur in the atmosphere. In the D region of the atmosphere, trace amounts of NO are known to be ionized by solar radiation. The newly generated NO cation can then combine with water and other atmospheric molecules forming complex cluster ions.[1−8] This complex ion chemistry of NO has been the subject of a great deal of study in recent years.[1−8]

In a recent study, performed in a multiphoton ionization time-of-flight mass spectrometer, we reported the generation of methyl nitrite (CH_3ONO) within heterogeneous clusters of nitric oxide and methanol.[9] It was found that heterogeneous clusters of the type $[(NO)_n(CD_3O)_x(CD_3OH)_m]^+$ were generated when $n \geq x + 1$. The cluster ion structure, $[(NO)(CH_3ONO)]^+$, was postulated and a mechanism involving loss of HNO from the parent cluster ion was proposed. It was also found that there was no correlation between the number of alcohol molecules present and the generation of methyl nitrite within the cluster. The present electron impact CID studies have been undertaken to test the hypothesis of the formation of alkyl nitrite and the proposed HNO loss mechanism. In this paper we report similar generation of alkyl nitrites of the form $[(NO)_n(RONO)_m]^+$, generated from $[(NO)_n(ROH)_m]^+$ cluster ions, where ROH is either ethanol, *n*-propanol, 2-propanol, *n*-butanol, 2-butanol, or *tert*-butyl alcohol. We also report a cluster size specific reaction in which a heterogeneous cluster of the type $[(NO)_2(RO)]^+$ reacts to generate a neutral HNO after undergoing CID.

Experiment

The molecular beam apparatus used for these experiments has previously been described in detail.[10,11] It consists of a Campargue-type source pumped by a high throughput roots blower package.[12] The neutral cluster beam was generated by bubbling 5.0% NO in argon (Matheson) through a reservoir containing one of the six selected alcohols (JT Baker, Aldrich). The NO/ROH vapor mixture is then adiabatically expanded through a 250 μm temperature controlled nozzle. The nozzle temperature maintained in each experiment is noted for the various alcohol mixtures. The stagnation pressure of the expansion varied from 1 to 2.6 atm and was varied as necessary in order to optimize the formation of NO/ROH heterogeneous clusters. The neutral cluster beam was collimated by a 0.5 mm skimmer, 7.0 mm distant from the nozzle. The cluster beam then enters a differentially pumped chamber, passes through a second skimmer and finally into the differentially pumped tandem mass spectrometer chamber.

The mass spectrometer employed is an Extrel C-50 triple quadrupole mass spectrometer with collinear ion optics which employs electron impact ionization. The energy of the ionizing electrons was 65 eV, and an emission current of 1.0 mA was maintained in all experiments. For all survey scans, the first quadrupole was operated as a conventional mass spectrometer and the second and third quadrupoles were operated in the RF only mode. For the CID experiments, the first quadrupole was used as a fixed mass filter to select out only the reactant cluster ion of interest. The second quadrupole was operated in RF only mode (to act as an ion guide), effectively creating a collision cell for the mass selected cluster ions exiting from the first quadrupole. The final quadrupole mass filter was then scanned in order to analyze any and all ions which exited from the collision cell. The output signal, provided by an off-axis channeltron, was passed through a 1.5 kHz low pass filter and averaged on a LeCroy 9300 digital osciloscope. Scan rates of 50 AMU/s were used for 100 AMU wide scans and 100 AMU/s were used for 200 AMU wide scans. For all the CID spectra performed, the expansion condition were the following: for all butanol spectra, the stagnation pressure was kept between 1 and 1.2 atm and the nozzle temperature was kept at 255−257 K; for *n*-propanol, stagnation pressure = 2.5 atm, nozzle temperature = 277 K; for 2-propanol, stagnation pressure = 2.6 atm, nozzle temperature = 261 K; for ethanol, stagnation pressure = 2.5 atm, nozzle temperature = 258 K.

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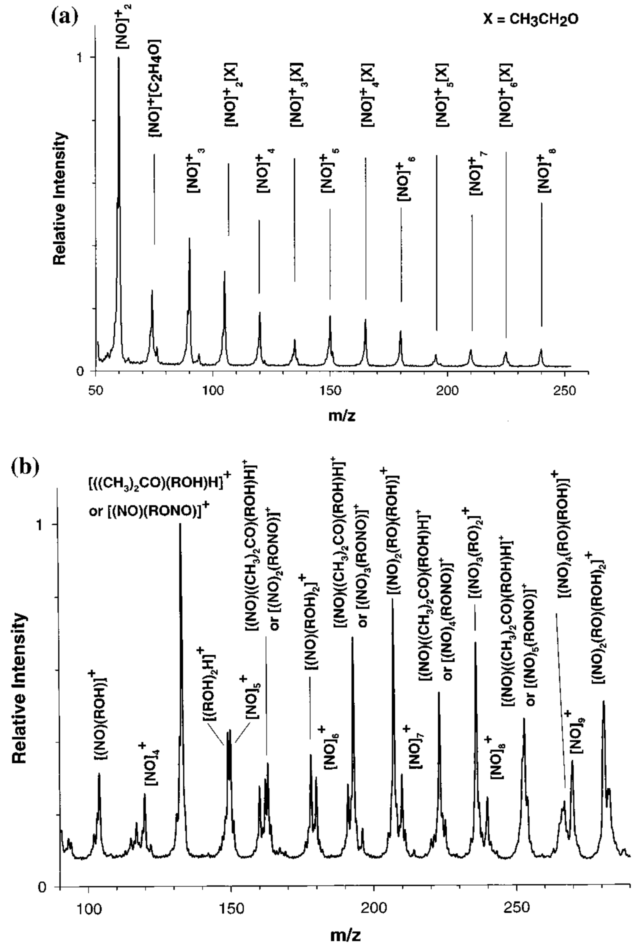

Figure 1. (a and b) EI mass spectrum of the NO/ethanol and NO/*tert*-butyl alcohol cluster beam expansions using 5% NO in Ar. The experimental conditions for ethanol were: electron energy 65.1 eV, nozzle temperature 257 K, and stagnation pressure 2.5 atm. The experimental conditions for *tert*-butyl alcohol were: electron energy 65.2 eV, nozzle temperature 256 K, and stagnation pressure 2.5 atm.

Results

Heterogeneous cluster expansions of alcohol with NO are observed to generate cluster ion series that are very different from those of the pure alcohol. Typically for pure alcohol expansions, the dominant series is hydrogenated cluster ions of the form $[(ROH)_nH]^+$. In the heterogeneous clusters of primary and secondary alcohols, we observe the complete dehydrogenation of the alcohol to form an ion series having the stoichiometry $[(NO)_n\ (RO)]^+$. A second ion series observed in the cluster mass spectrum of the tertiary alcohol 2-methyl, 2-propanol, hereafter referred to as *tert*-butyl alcohol, has the stoichiometry $[(NO)_n((CH_3)_2CO)(ROH)H]^+$. Notably absent from the cluster mass spectra are clusters of the pure alcohol or clusters of the hydrogenated alcohol. Of all the alcohols which we studied, it is only for the expansion of *tert*-butyl alcohol with NO that ion clusters containing the pure alcohol or clusters of the pure alcohol are ever detected in significant quantities. The complete dehydrogenation of the heterogeneous clusters may be partly dependent on the experimental conditions. In our previous work on the time-of-flight mass spectrometer using photoionization,[9] it was found that the mixing ratio of NO to methanol could greatly affect the composition of the cluster beam generated. In the present continuous beam apparatus, such fine control of the mixing ratio was not possible.

Figure 1a shows the typical EI cluster mass spectrum of the NO/ethanol expansion. The ethanol was seeded into the gas by bubbling 5% nitric oxide in argon through a reservoir containing pure ethanol.[13] Note that there are virtually no clusters containing the pure alcohol or clusters of the form $(ROH)_nH^+$.

There are two major cluster series observed in the spectrum. The dominant homogeneous cluster series is the pure NO cluster series and exhibits the even/odd intensity alternation commonly seen with NO cluster ions. This enhanced stability of the clusters containing an odd number of NO molecules is the result of the even electron configuration possessed by these cluster cations.[15−17]

The dominant heterogeneous cluster series is the cluster series $[(NO)_n(RO)]^+$. This cluster series displays an intensity alternation similar to that observed in pure NO clusters in which the clusters containing an even number of nitric oxide molecules are the more stable, even electron species. This we feel is due to a reaction of the type

$$(NO)_{n+1}(ROH) \rightarrow [(NO)_n(RO)]^+ + HNO \qquad (1)$$

The cluster mass spectrum shown in Figure 1a is representative of the observed mass spectra for *all* of the alcohols with the exception *tert*-butyl alcohol. The t- butanol was seeded into the gas by bubbling the nitric oxide through a reservoir containing pure *tert*-butyl alcohol.[13] Figure 1b shows the mass spectrum for the NO/*tert*-butyl alcohol clusters where several different cluster ion series are present in the spectrum.[14] The dominant homogeneous cluster series consists of clusters of pure nitric oxide. This series again displays an even/odd intensity alternation in which the clusters containing an odd number of nitric oxide molecules are more intense due to the enhanced stability of the even electron configuration possessed by these cluster cations. There is also a homogeneous series of pure hydrogenated *tert*-butyl alcohol clusters of the type $(ROH)_nH^+$. This cluster series is very weak and virtually terminates after the hydrogenated trimer. As has been mentioned, in all other NO/alcohol expansions clusters, the pure alcohol or hydrogenated alcohol are greatly suppressed or nonexistent. The dominant heterogeneous cluster series is either $[(NO)_n(RONO)]^+$ cluster series or $[(NO)_n((CH_3)_2CO)(ROH)H]^+$ and displays a similar intensity alternation in which the clusters containing an even number of nitric oxide molecules are the more intense. These two cluster series both have the same nominal masses and are discussed in detail elsewhere in this paper. The cluster series $[(NO)_n((CH_3)_2CO)(ROH)H]^+$ begins with $n = 0$ and subsequently adds NO monomers to the $[((CH_3)_2CO)(ROH)H]^+$ core. The origins of the $[((CH_3)_2CO)(ROH)H]^+$ cluster ion in clusters of *tert*-butyl alcohol have been previously studied.[18,19,20]

Other heterogeneous cluster ions visible in the spectrum and their mass-to-charge ratio are, in order of increasing mass, $[(NO)(ROH)]^+$, 104; $[ROH]_2H^+$, 149; $[(NO)(ROH)_2]^+$, 178; $[(NO)_2(RO)(ROH)]^+$, 207; $[(NO)_3(RO)_2]^+$, 236; $[(NO)_4(RO)(ROH)]^+$, 267; and $[(NO)_2(RO)(ROH)_2]^+$, 281.

For all of the other NO/alcohol expansions investigated, similar heterogeneous clusters were directly detected in the survey mass spectrum. As in the previous work with methanol, the dehydrogenation of the alcohol appears to depend solely on the nitric oxide and not on the alcohol present in the cluster. In heterogeneous clusters containing only one nitric oxide molecule the alcohol is never dehydrogenated; however, in clusters containing two or more nitric oxide molecules, some or all of the alcohol in the cluster has been dehydrogenated. Thus, for the intracluster dehydrogenation of the alcohol to occur, we believe there must be at least two nitric oxide molecules present in the cluster for the reaction to be initiated.

Figure 2 is the CID spectrum of the $[(NO)_2(RO)]^+$ cluster cation, where $RO = CH_3CH_2O$. There are two major loss

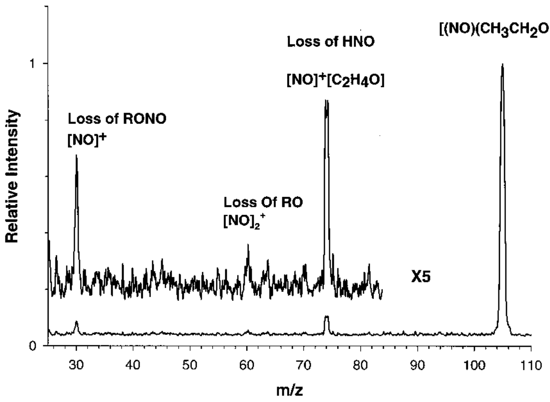

Figure 2. CID spectrum of the $[(NO)(RONO)]^+$ cluster ion for NO/ethanol expansion. Experimental conditions are: electron energy 65.1 eV, nozzle temperature 258 K, collision cell pressure 9×10^{-4} Torr argon, and stagnation pressure 2.5 atm.

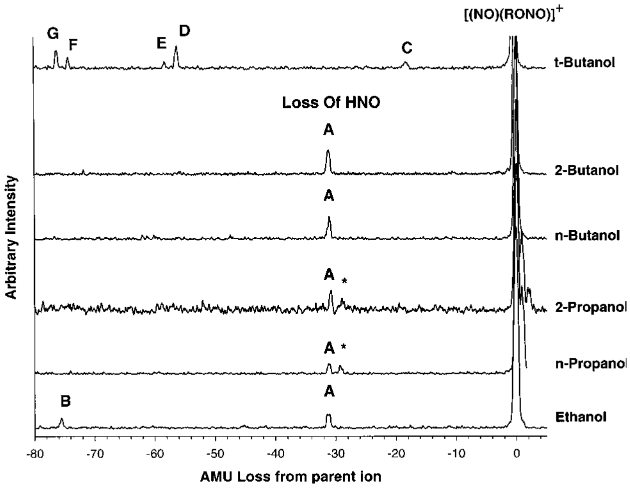

Figure 3. Composite plot showing the CID spectra for the mass selected $[(NO)\,(RONO)]^+$ cluster ion, for all six alcohols studied. The product ions labeled are identified as follows: **A**, $[(NO)(R{=}O)]^+$; **B**, NO^+; **C**, $[((CH_3)_2CO)((CH_3)_3C)]^+$; **D**, $[((CH_3)_2COH)(H_2O)]^+$; **E**, $[(CH_3)_3COH_2]^+$; **F**, $[(CH_3)_2COH]^+$; **G**, $[(CH_3)_3C)]^+$. For all spectra electron energy was between 65 and 65.5 eV and collision cell pressure ranged from 9.0×10^{-4} Torr -1.0×10^{-3} Torr of argon. The ions labeled with an asterisk (*) in the NO/2-propanol and NO/*n*-propanol spectra are the loss of a single NO molecule from the $[NO]_4^+$ ion.[26]

channels that are the result of intracluster reactions and one minor loss channel that is the result of simple evaporation of monomer units observed in this spectrum. The first major reaction channel is loss of single neutral HNO from the parent ion to generate $[(NO)(C_2H_4O)]^+$. This loss of neutral HNO is specific for cluster ions of the type $[(NO)_2(RO)]^+$ where RO is a dehydrogenated alcohol. The second loss channel is the sequential loss of neutral ethyl nitrite to leave the lone NO^+ cation. A final minor loss channel is observed in the spectrum which is the direct loss of the RO moiety from the parent cluster leaving behind $[NO]_2^+$ dimer. Based on this evidence, we believe the $[(NO)_2(RO)]^+$ cluster ion to be primarily composed of a nitric oxide molecule and an alkyl nitrite, having the general formula $[(NO)(RONO)]^+$. Both loss channels indicate that the charge resides on the NO molecule and not on the alkyl nitrite and is consistent with the ionization potentials (IPs) of the two species (i.e., NO has an IP of 9.26 eV and ethyl nitrite has an IP of 10.53 eV).[21]

Figure 3 shows a comparison of the CID spectra of the $[(NO)(RONO)]^+$ cluster ion for all six NO/alcohol expansions studied. The intensities of each individual spectrum have been normalized with respect to the intensity of the parent peak, which is set to an arbitrary intensity of 1.0. In all of the CID spectra shown in Figure 3, there are common features which are described below.

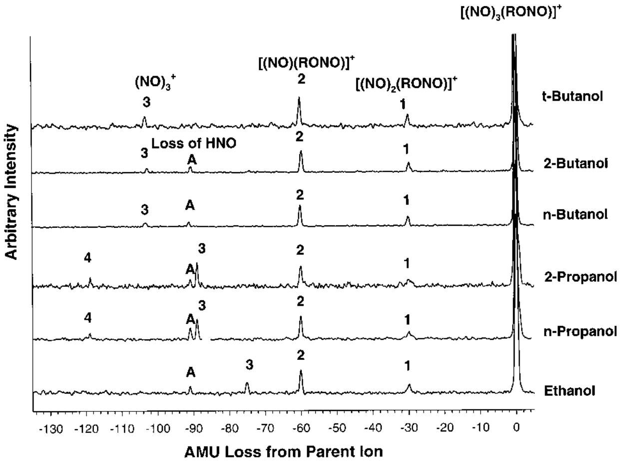

Figure 4. A composite plot showing CID of the mass selected $[(NO)_3(RONO)]^+$ cluster ion for all six NO/alcohol expansions studied. The cations labeled are identified as follows: **A**, $[(NO)(R{=}O)]^+$; **H**, $[(NO)_2(RONO)]^+$; **I**, $[(NO)(RONO)]^+$; **J**, $(NO)_3^+$; **L**, $(NO)_2^+$; **M**, loss off 32 mass units from the parent.

The ion labeled A, observed for five of the alcohols, is formed via direct loss of HNO from the $[(NO)(RONO)]^+$ ion. This product ion appeared in the survey spectra for all five alcohols. The relevent ion molecule reaction can be represented as

$$[(NO)(RONO)]^+ \rightarrow HNO + [(NO)(R{=}O)]^+ \qquad (2)$$

We note that in the *tert*-butyl alcohol CID spectrum, this reaction is not detected, since the *tert*-butyl alcohol is a tertiary alcohol and would not be expected to form a ketone or aldehyde product. The CID spectrum of the NO/*tert*-butyl alcohol has been included to establish that the identity of the ion at *m*/*z* 133 is the $[((CH_3)_2CO)(ROH)H]^+$ cluster ion, not the $[(NO)_2(RO)]^+$ ion, as is the case for the *n*-butanol and 2-butanol.

The ion labeled B is the NO^+ ion formed by loss of ethyl nitrite, as a result of CID from the $[(NO)(ETONO)]^+$ ion.

As has been discussed, the ion at *m*/*z* 133 in the NO/*tert*-butyl alcohol expansion is identified as the $[((CH_3)_2CO)(ROH)H]^+$ ion. The origin and ion molecule reactions of this ion have been previously investigated,[18,19,20] and the product ions in the CID spectra are identified as follows:

label	identification	AMU from parent
C	$[((CH_3)_2CO)((CH_3)_3C)]^+$	18
D	$[((CH_3)_2COH)(H_2O)]^+$	56
E	$[(CH_3)_3COH_2]^+$	58
F	$[(CH_3)_2COH)]^+$	74
G	$[(CH_3)_3C)]^+$	76

Complicating interpretation of the NO/*tert*-butyl alcohol CID data is the presence of isobaric interference in the mass spectrum. The isobaric effects are illustrated in Figures 3 and 4, where the $[(NO)((CH_3)_3ONO)]$ and the $[((CH_3)_2CO)(ROH)H]^+$ cluster ions and the $[(NO)_3((CH_3)_3ONO)]$ and the $[(NO)_2((CH_3)_2CO)(ROH)H]^+$ cluster ions both have the same nominal mass ($m/z = 133$ and $m/z = 193$, respectively). The ambiguities due to isobaric interference between the $[(NO)_n((CH_3)_3ONO)]^+$ cluster series and the $[(NO)((CH_3)_2CO)(ROH)H]^+$ cluster ion series in the NO/*tert*-butyl alcohol expansions can only be eliminated by CID experiments. The correct identity of the cluster ions at *m*/*z* 133 and 193 being investigated can only be established by the CID spectrum of the cluster ion in question. In the case of the *m*/*z* 133 ion, we conclude that there does not appear to be any major contribution in the spectrum from the $[(NO)((CH_3)_3ONO)]^+$ ion and that the large intensity of the $[((CH_3)_2CO)(ROH)H]^+$ ion effectively obscures any contribution from the nitric oxide containing cluster ion. The degree of obfuscation is such that no trace of the $[(NO)((CH_3)_3ONO)]^+$ ion can be found, including even simple loss of NO monomers from a nonreactive parent ion. In the CID of the cluster ion at *m*/*z* 193 in the NO/*tert*-butyl alcohol expansion the $[(NO)_3(RONO)]^+$ appears to be the dominant cluster ion as shown in Figure 4.

Figure 4 is a composite of the CID spectra of the $[(NO)_3(RONO)]^+$ cluster ion for the six different NO/alcohol expansions studied. Where appropriate, the fragment ions have been given the same labels as in Figure 3. Common product channels of all expansions are the losses of nitric oxide monomers at −30 amu and −60 amu, labeled 1 and 2, respectively.

The cluster ion labeled A is again the neutral loss of HNO from the $[(NO)(RONO)]^+$ cluster ion. This loss of neutral HNO is presumably the result of reaction 1 and is specific to the cluster ion $[(NO)(RONO)]^+$ as shown in Figure 3. This reaction only occurs with the $[(NO)(RONO)]^+$ cluster ion and is not observed as a loss channel in CAD of higher order heterogeneous clusters.

The cluster ions labeled 2 are the $[(NO)(RONO)]^+$ ions and correspond to the parent ions in the CID experiment shown in Figure 3. The assignment of the rest of the ions follows.

The ions labeled 3 are the $[NO]_3^+$ ion and are the result of loss of neutral RONO from the parent cluster ion. Unlike the nitric oxide/propanol expansions shown in Figure 3, there is no difficulty in separating out the parent $[(NO)_3(RONO)]^+$ ion from the $[NO]_4^+$ ion in these spectra. This may be due to the lower overall intensity of the corresponding $[NO]_4^+$ cluster ions at this higher mass. As previously discussed, the pure NO cluster ions containing an even number of NO molecules are less stable than those containing an odd number of nitric oxide molecules, with the opposite being true for the heterogeneous clusters. At some point the greater relative stability of the $[(NO)_n(RONO)]^+$ ion compared to the stability of $[NO]_y^+$ cluster ion, in which *n* and *y* are both even, may greatly suppress the intensity of, or even eliminate, the pure nitric oxide clusters that may leak through the mass filter and appear in the CID spectrum of the desired heterogeneous parent ion.

The cluster ion labeled 4 is the $[NO]_2^+$ ion formed from loss of the neutral fragment [(NO)(RONO)] in the NO/propanol expansions.

Discussion

In examining the CID spectra of the $[(NO)_n(RONO)]^+$ cluster ion series it is interesting to note that the clusters rapidly lose NO monomers until they reach the $[(NO)(RONO)]^+$ ion. The next step is not to lose another NO monomer, but rather to undergo an intracluster reaction in which the alkyl nitrite expels HNO forming an aldehyde or ketone depending upon the structure of the original alcohol. The driving force behind this reaction may be the electronic instability of the $[RONO]^+$ which would result in an uneven electron species.

In the particular case of ethanol the reaction scheme takes the form

$$[(NO)(CH_3CH_2ONO)]^+ \rightarrow HNO + [(NO)(C_2H_4O)]^+ \qquad (7)$$

The corresponding product ion appears in all of the NO/alcohol expansions in which the alcohol used is a primary or secondary alcohol but not for the tertiary alcohol *tert*-butyl alcohol.

Both collision cell pressure and collision energy studies were performed upon the NO/ethanol and NO/*n*-butanol expansions and for both systems all product ion intensities maximized at 25 eV collision energy. The collision cell pressure studies revealed a preference for the parent ions to decompose to form even electron product ions, mimicking the intensity distributions observed in the survey spectra.

Estimation of the enthalpy of reaction 1 can be arrived at by using the $\Delta H_{f,gas}$ of the reactants and the products and applying Hess's law. The estimated enthalpies[22] of reaction range as follows: NO/ethanol, −43 kcal/mol; NO/*n*-propanol, −50 kcal/mol; NO/2-propanol, +104 kcal/mol; NO/*n*-butanol, +119 kcal/mol; NO/2-butanol, +120 kcal/mol. This estimation, however, is based upon reactions of the neutral molecules and does not take into account any differences in the cluster binding energy between the reactant and product ions. We note, however, that the observation of the formation of HNO from an intracluster reaction for the primary or secondary alcohol heterogeneous clusters with NO is in agreement with the work of Spanel and others who have previously reported similar results in the reaction of alcohols with NO^+.[23,24]

Winkel and Stace have also previously reported cluster size dependent formation of methyl nitrite in experiments using nitric oxide and methanol, where it was observed that the reaction required a certain minimum cluster size to occur.[25] In the present work, for the primary and secondary alcohols we observe a reaction which is very size specific for cluster ions of the type $[(NO)(RONO)]^+$. Higher order clusters of the form $[(NO)_{n>1}(RONO)]^+$ exhibit only loss of nitric oxide monomers until the $[(NO)(RONO)]^+$ cluster ion is formed, whereupon the elimination of a neutral HNO can then can take place.

References and Notes

(1) Fergusson, E. E.; Arnold, F. *Acc. Chem. Res.* **1981**, *14*, 327.

(2) Arijs, E.; Barassin, A.; Kopp, E.; Amelynck, C.; Catoire, V.; Fink, H. P.; Guimbaud, C.; Jenzer, U.; Labonnette, D.; Luithardt, W.; Neefs, E.; Nevejans, D.; Schoon, N.; Van Bavel, A.-M. *Int. J. Mass Spectrom.* **1998** *181*, 99.

(3) Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Chem. Phys.* **1992**, *97*, 3, 1793.

(4) Martin, M. Z.; Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Phys. Chem.* **1996**, *100*, 8170.

(5) Bergman, K.; Huber, J. R. *J. Phys. Chem.* **1997**, *101*, 259.

(6) Stace, A. J.; Winkel, J. F.; Lopez Martens, R. B.; Upham, J. E. *J. Phys. Chem.* **1994**, *98*, 2012.

(7) Poth, L.; Shi, Z.; Zhong, Q.; Castleman, A. W. *J. Phys. Chem.* **1997**, *101*, 1099.

(8) Shin, D. N.; DeLeon, R. L.; Garvey, J. F. *J. Phys. Chem. A* **1998**, *102*, 7772.

(9) Shin, D. N.; DeLeon, R. L.; Garvey, J. F. *J. Chem. Phys.* **1999**, *110*, 5564.

(10) Lykley, M. Y. M.; Roycroft, T.; Garvey, J. F. *J. Phys. Chem.* **1996**, *100*, 6427.

(11) Rexer, E. F.; DeLeon, R. L.; Garvey, J. F. *J. Chem. Phys.* **1997**, *107*, 4760.

(12) Camparge, R. *J. Phys. Chem.* **1984**, *88*, 4466.

(13) The spectra are averages of between 380 and 2500 sweeps depending upon the intensity of the original parent peak. Not surprisingly it was found that the different NO/alcohol expansions behaved differently, and some minor adjustments to the expansion conditions were required for the individual systems. In addition, the overall intensity of the parent peak being investigated varied from system to system and parent ion to parent ion, which is why some CAD spectra were averaged for a few hundred sweeps while others required up to 2500 sweeps.

(14) In some spectra isobaric interference causes some ambiguities. For example, in the mass spectrum of the NO/ethanol the *m*/*z* of the cluster series $[(NO)_n(RO)_2]^+$ in which *n* is 3 or greater coincides with that of pure nitric oxide clusters beginning with $[NO]_6^+$, both having an *m*/*z* of 180. Thus, although there are cluster ions at the appropriate *m*/*z* in the NO/ethanol spectrum, assignment of the actual identity of the ion or ions at this *m*/*z* is ambiguous.

(15) Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Chem. Phys.* **1994**, *101*, 4526.

(16) Poth, L.; Shi, Z.; Zhong, Q.; Castleman, A. W. *J. Phys. Chem.* **1997**, *101*, 1099.

(17) Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Phys. Chem.* **1994**, *101*, 4526.

(18) Beauchamp, J. L.; Caserio, M. C.; McMahon, T. B. *J. Am. Chem Soc.* **1969**, *91* 6243.

(19) Shukla, A. K.; Stace, A. J. *J. Phys. Chem.* **1988**, *92*, 2579.

(20) Karpas, Z.; Eiceman, G. A.; Ewing, R. G.; Harden, C. S. *Int. J. Mass Spectrom.* **1994** *133*, 47.

(21) Lias, S. G.; Bartmess, K. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. W. *J. Chem. Phys Ref. Data* **1988,** *17* (Suppl. 1).

(22) Afeefy, H. Y.; Liebman, J. F., Stein, S. E. Neutral Thermochemical Data in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Mallard, W. G., Linstrom, P. J., Eds.; November 1998, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

(23) Spanel, P.; Smith, D. *Int. J. Mass Spectrom.* **1997**, *167/168*, 375.

(24) Harrison, A. G. In *Chemical Ionization Mass Spectrometry*, 2nd ed.; CRC Press: Boca Raton, 1992.

(25) Winkel, J. F.; Stace, A. J. *Chem. Phys Lett.* **1994**, *221*, 431.

(26) The $[NO]_4^+$ has an *m*/*z* of 120, one amu away from the *m*/*z* of the parent ion $[(NO)(RONO)]^+$ for propanol which has an *m*/*z* of 119. Due to the requirement to maintain the intensity of the desired $[(NO)(RONO)]^+$ parent ion, we are unable to completely filter out the $[NO]_4^+$ ion and we see some contribution from this ion in our CAD spectra, especially the presence of the very stable $[NO]_3^+$ ion.