Photochemical Generation of Methane within NO−Ethene Heteroclusters†

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Multiphoton ionization time-of-flight mass spectroscopy has been used to study heterogeneous cluster ions containing NO and ethene. As previously noted in the literature for other NO clusters, NO−ethene heterogeneous cluster ions show a tendency to form even-electron species. In addition to this effect, we also observe a number of ion−molecule reactions that occur within the heterogeneous clusters. These reactions lead to cluster ion series which contain new molecular species. Deuterium isotope experiments explicitly indicate that both CH_4 and NO_2 are formed as cluster ion products. We speculate that the methane formation occurs via this reaction within the photoionized cluster: $\{C_2H_4\}_{m+1}\{NO\}_{n+1}\{NO^+\} \rightarrow \{C_2H_4\}_m\{NO\}_n\{CH_4^+\} + N_2O + CO$.

Introduction

The study of ion−molecule reactions of the NO^+ cation has been the subject of much research due to its importance in atmospheric chemistry.[1,2] Heterogeneous reactions of NO on droplets and particles are of particular interest both because of their importance and the difficulty of modeling their effect on stratospheric and tropospheric chemistry, especially their interaction with ozone formation.[3] A number of studies of NO have been conducted to explore both homogeneous[4] and heterogeneous cluster[4−9] formation. One of the key results of this work is the tendency of NO clusters to show even−odd intensity alternation. That is, complexes with an even number of electrons tend to be much more intense than odd-electron complexes. This is true for both homogeneous[4] and heterogeneous clusters.[8] Another key result is that previous multiphoton ionization and electron impact studies have demonstrated that heterogeneous clusters containing NO tend to exhibit a rich and not always predictable series of ion−molecule reactions.[5−10]

Pure ethene clusters have also been the subjects of much research[11−18] mainly in connection with the tendency of clusters of unsaturated hydrocarbons to polymerize in electron impact studies. Reaction of NO−ethene mixtures on metal catalysts has been the subject of a number of studies mainly with respect to oxidation of the NO.[19−21] Such catalytic reactions using ethene in DeNOx processes are of great interest.

However, to the best of our knowledge, there has been only one previous study of heterogeneous NO−ethene clusters. Mouhandes and Stace[22] used an IR laser to photofragment $[(C_2H_4)(NO)_n]^+$ cluster ions. They noted the loss of C_2H_4, NO, and 2NO and the tendency of decay channels to form even-electron ions. The present work will describe the multiphoton ionization study of NO−ethene cluster ions with emphasis on its ion−molecule chemistry.

Experiment

Cluster ions were studied using laser multiphoton ionization and time-of-flight mass spectroscopic detection of expansions of NO−ethene seeded in argon. The basic experimental apparatus has been previously described.[23,24] Mixtures containing 5.0% NO in Ar and 10.0% C_2H_4 in Ar were obtained from Matheson Gas Company. They were expanded as received to study the pure homogeneous complexes or combined in a mixing chamber to form the heterogeneous complexes. 99 atom % C_2D_4 was obtained from Aldrich Chemical company. Mass spectrometric analysis of this tank in our lab revealed no detectable presence of CD_4 (i.e., <0.1%). The gas in this cylinder was then mixed with argon or the 5% NO/argon mixture in the mixing chamber to study both the homogeneous and heterogeneous clusters of deuterated ethene. The cluster beam was generated using a pulsed valve with an 800 μm diameter (General Valve Series 9) at a backing pressure of +25 psig using a homemade driver box. After skimming by a 1.0 mm conical skimmer, the neutral cluster beam was ionized using the unfocused radiation from a Lambda-Physik EMG 150 excimer laser operating at 248 nm with a nominal pulse width of approximately 20 ns. The resulting cluster ions were accelerated into a reflectron time-of-flight mass spectrometer (R. M. Jordan Co.) which features a 140 cm flight tube followed by the reflectron, a second 61 cm flight tube and finally a microchannel plate detector. The background pressure was maintained below 5×10^{-7} Torr by a turbomolecular pump, a 10-in. diffusion pump, and a liquid nitrogen cryopump. The electronic signals from the microchannel plate were recorded and averaged by a transient digitizer (LeCroy 9310A) and transferred to a computer.

Results and Discussion

To understand the NO−ethene spectrum, a careful analysis of the single component cluster spectra was done under similar experimental conditions. Figure 1 shows the multiphoton ionization time-of-flight mass spectrum of a 5% NO in argon mixture at a backing pressure of +25 psig. Note that in addition to the homogeneous cluster ion series, $[(NO)_x]^+$, we also observe the formation of products containing NO_2. Even-electron products are preferred, especially for the products of the series $[(NO)_x(NO_2)_y]^+$. This mass spectrum is similar to that observed by Desai, Feigerle, and Miller,[9] although for the present

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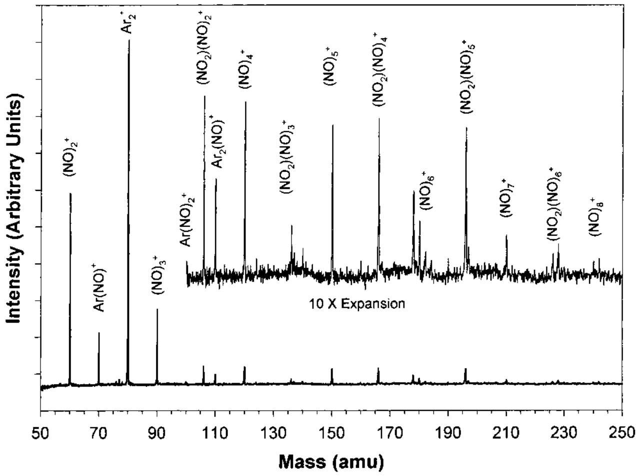

Figure 1. Mass spectrum of a 5% NO in argon mixture at a backing pressure of +25 psig. Under the present expansion conditions and ionization conditions, in addition to the homogeneous cluster ion series, $[(NO)_x]^+$, note the formation of products containing NO_2. Even-electron products are preferred, especially for the products of the series $[(NO)_x(NO_2)_y]^+$.[29]

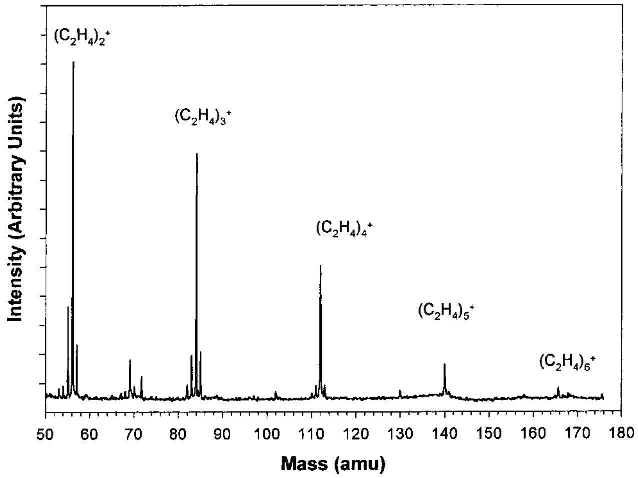

Figure 2. Mass spectrum of a 10% C_2H_4 mixture in argon at a backing pressure of +25 psig. Simple van der Waals clustering dominates under these conditions. Aside from the parent cluster ions and the fragment ions gaining one H or losing one or two H atoms, there are very few products.

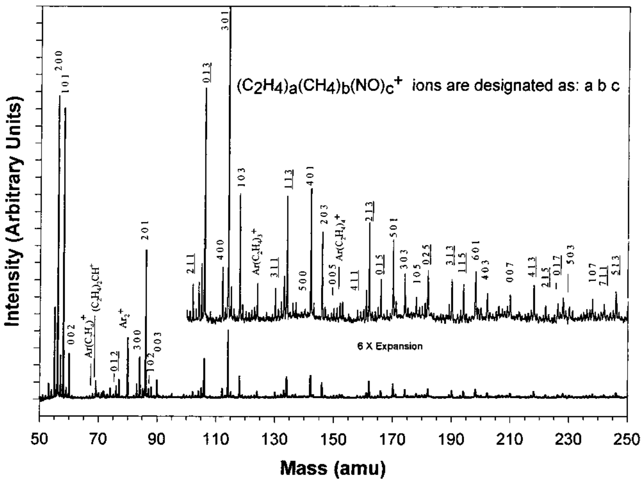

Figure 3. Mass spectrum of a 3% NO, 5% C_2H_4 mixture in argon at a backing pressure of +25 psig. Homogeneous NO and homogeneous C_2H_4 peaks are present. In addition there are heterogeneous C_2H_4-NO clusters and some reaction products that are displaced by 16 amu from any combination of NO and C_2H_4. As explained in the text, the 16 amu addition is due mainly to the formation of methane (CH_4). Overall the products can be designated as falling into the series $[(C_2H_4)_a(CH_4)_b(NO)_c]^+$.

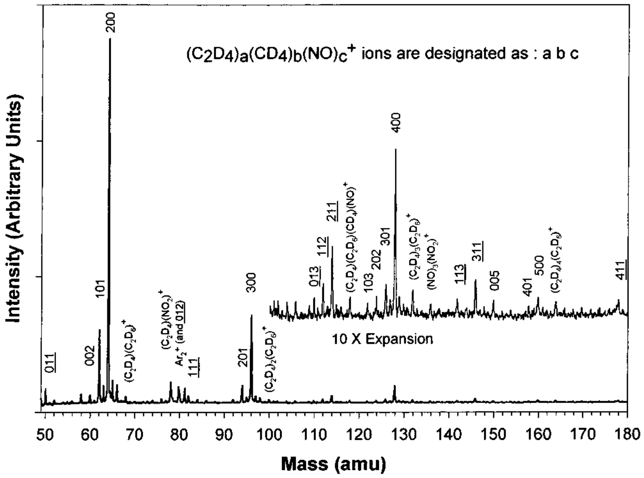

Figure 4. Mass spectrum of a 3% NO, 3% C_2D_4 mixture in argon at a backing pressure of +25 psig. The deuterated product spectrum shows predominately ions of the series $[(C_2D_4)_a(CD_4)_b(NO)_c]^+$, indicating that the 16 amu displacement products observed in the nondeuterated spectrum are mainly due to methane formation. However, some ions containing NO_2 are also observed, indicating that this is also a reaction product. It is interesting to note the formation of products tentatively containing C_2D_6.[30]

conditions the intensity alternation is less pronounced for the homogeneous clusters.

Figure 2 shows the multiphoton ionization time-of-flight mass spectrum of a 10% C_2H_4 mixture in argon at a backing pressure of +25 psig. Simple van der Waals clustering dominates under these conditions. Aside from the parent cluster ion peaks, there are satellite peaks corresponding to the gain of one H or the loss of one or two H atoms from the van der Waals cluster. There is a strong product peak at 69 amu that has been previously noted in the ethene spectrum.[11]

Figure 3 shows the multiphoton ionization time-of-flight mass spectrum of a 3% NO, 5% C_2H_4 mixture in argon at a backing pressure of +25 psig. The spectrum is very complex, showing homogeneous NO peaks, homogeneous C_2H_4 peaks, heterogeneous C_2H_4-NO peaks, and product peaks due to ion−molecule reactions (indicated by a ine under the peak assignment). Note the strong tendency to form cluster ions containing an even number of electrons which corresponds to clusters containing an odd number of NO molecules. The most interesting product series is displaced by 16 amu from any combination of NO and C_2H_4 molecules. There are also small nearby peaks that may be due to loss of one or more H atoms from the main series. There are two obvious possible assignments for the 16 amu displacement product peaks: they are either due to formation of NO_2, as occurs in the homogeneous NO chemistry, or due to the formation of CH_4.

To distinguish between these two possibilities, isotope studies were done employing C_2D_4. Figure 4 shows the multiphoton ionization time-of-flight mass spectrum of a 3% NO, 3% C_2D_4 mixture in argon at a backing pressure of +25 psig. Interestingly, the deuterated spectrum exhibits peaks which are displaced by 20 amu, the mass of CD_4. This indicates that the products displaced by 16 amu in the nondeuterated spectrum and by 20 amu in the deuterated spectrum are mainly due to methane product formation within the NO−ethene cluster. Smaller peaks due to NO_2 formation were also observed. Since NO_2 is produced in pure NO mixtures, this chemistry may not directly involve the ethene. One other interesting series of product peaks is observed at mass differences of 36 amu. These cluster ion peaks may be due to the formation of C_2D_6, deuterated ethane in the heterogeneous mixture. Only trace amounts of C_2D_6 were observed in the pure C_2D_4 spectrum. The formation of ethane cannot be detected in our apparatus in the nondeuterated NO−C_2H_4 spectrum due to the isobaric interference between C_2H_6 (30 amu) and NO (30 amu).

There seems to be little doubt that the positive charge resides on the NO species in the heterogeneous NO−hydrocarbon cluster ions. The ionization potential of NO (9.26 eV) is substantially smaller than that of C_2H_4 (10.51 eV), CH_4 (12.61 eV), and C_2H_6 (11.52 eV).[25] Even allowing for the moderate decrease in the ionization potential that generally accompanies cluster formation, the extremely low ionization potential of the NO should ensure that the charge is primarily localized on the NO.

Although the ion spectra displayed in Figures 3 and 4 indicate a number of product ions, the intensity of the product peaks are somewhat less than has been observed for other NO−reactive-molecule systems[7−10] and therefore the signal-to-noise is rather poor. For example in the case of NO−CH_3OH, conditions can be achieved in which there is an almost complete conversion of the NO−CH_3OH cluster ions to product cluster ions containing methyl nitrite, CH_3ONO. This can be interpreted as a somewhat lower reactivity of the ethene in NO clusters compared to molecules such as alcohols, NH_3, and H_2O.

The origin of the reaction products in the multiphoton cluster chemistry has been previously discussed in detail for the NO−CH_3OH system.[8] There are two possible and fundamentally different product formation mechanisms under the present experimental conditions of a 20 ns laser pulse, photochemical reactions followed by ionization or multiphoton ionization followed by ion−molecule reactions. Smith and Miller[26] have reported that there is no fundamental difference in the mass spectra obtained with nanosecond and picosecond lasers. This is in agreement with our observations of the similarity of homogeneous NO cluster distributions between our nanosecond laser experiments[8] and Castleman's group's femtosecond experiments[27] and Miller's group's picosecond experiments.[26] This similarity would favor the mechanism in which multiphoton ionization is followed by ion−molecule reaction because after the very different ionization time scales the similarity of the products would be due to the commonality of the ion−molecule reactions.

A second argument also tends to favor the ion−molecule reaction mechanism. For the present work, as well as other studies,[8,28] the products predominantly formed are the most stable ions that contain an even number of electrons. If photochemical reactions preceded ionization the most stable neutrals containing an even number of electrons would tend to form, and upon ionization, ions with an odd number of electrons would then be more common. The possibility of photochemical reactions preceding ionization cannot be eliminated, however, the collective experimental results of a number of studies leads us to favor the ion−molecule reaction mechanism.

To rationalize the methane generation, we have examined a variety of ion−molecule candidates. The only reaction which appears to be viable is the following 3-body reaction, where for both the reagent and products, the molecule with the lowest ionization potential has been assigned the positive charge.[25]

$$C_2H_4 + NO + NO^+ \rightarrow CH_4^+ + N_2O + CO \qquad (1)$$

We note that this reaction, as written, is slightly exothermic ($\Delta H_{rxn} = -5$ kcal/mol)[25,31] and could account for the observed methane production via the following analogous cluster reaction:

$$\{C_2H_4\}_{m+1}\{NO\}_{n+1}\{NO^+\} \rightarrow \{C_2H_4\}_m\{NO\}_n\{CH_4^+\} + N_2O + CO \qquad (2)$$

In this current work we are limited to direct observation of the product cluster ions, and must therefore infer the production of N_2O and CO. We hope, in the future, to continue to study this system using tandem mass spectrometry, to more fully elucidate this interesting chemistry and observe directly the elimination of both N_2O and CO from a mass selected cluster ion.[32]

Conclusions

The multiphoton ionization mass spectrum of NO−C_2H_4 cluster ions is very complex consisting of NO clusters, C_2H_4 clusters, heterogeneous NO−C_2H_4 clusters, and a variety of products presumably formed by ion−molecule reactions. Formation of clusters containing methane is confirmed by both C_2H_4 and C_2D_4 mixture studies. Formation of products containing ethane can only be observed in deuterated spectra due to isobaric interference in the nondeuterated spectra. The NO_2 produced in the mixtures may be dependent on the NO and not on the ethene since it is a characteristic of homogeneous NO cluster chemistry. The existence of this rich chemistry in clusters has important implications for the type of chemistry which may occur in aerosols and on small droplets and particles present in the atmosphere.

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(29) The small peaks at 178 and 228 amu are background oil peaks.

(30) The unassigned peak at 81 amu is an impurity which is also present in the spectrum of C_2D_4 in argon without NO added.

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