The elucidation of the chemical nature of the neutral products by the present technique is particularly important since SIMS only provided information on the charged products. For instance, it was quite possible that the previously unobserved nitrogen-rich neutral byproduct from the bombardment of NO, whose formation needs to be postulated in order to account for the observed cluster ion stoichiometry, is N_2O rather than N_2 (thermal decomposition of solid NO yields N_2O and N_2O_4[11]). Yet, in IR spectra, we observe no N_2O formation upon bombardment of solid NO. The reactions triggered in solid NO by fast ion or atom impact are quite different from those triggered by macroscopic heating or explosion.

In summary, the present results lend credence to the mechanistic proposal for SIMS of solid nitrogen oxides[3,4] and, by extrapolation, of low-temperature solids in general.[2] They also establish fast atom bombardment as a viable tool for the production of reactive matrix-isolated species. Its effects are similar to those of ion bombardment, but it is not subject to the same sample charging difficulty.

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Registry No. Ar, 7440-37-1; Ar^+, 14791-69-6; N_2O, 10024-97-2; NO, 10102-43-9; N_2O_2, 16824-89-8; NO_2, 10102-44-0; N_2O_4, 10544-72-6.

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(11) Melia, T. P. *J. Inorg. Nucl. Chem.* **1965**, *27*, 95.

(12) **Note Added in Proof**: Prof. Knight's results with FAB matrix isolation have now appeared in print: Knight, L. B., Jr.; Steadman, J.; Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 3700.

Triple-Quadrupole Secondary Ion Mass Spectrometry of Low-Temperature Solids: Collision-Activated Dissociation of Large Cluster Ions

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In secondary ion mass spectrometry (SIMS), primary ions with energies in the kilovolt region impact a solid and cause the ejection of neutral and charged secondary particles; the latter are detected in a mass spectrometer.[1] The method and its variant in which the primary particles are uncharged (FAB) are acquiring rapidly growing importance in analytical chemistry of nonvolatile insulating solids and solutions, but the mechanism of secondary ion formation is still poorly understood. In several of the mechanistic studies the samples were kept at low temperatures.[2] We have investigated simple molecular solids held at 15-30 K and found that the impact of heavy primary ions such as Ar^+ produces secondary cluster ions of large size and often unexpected compositions.[3-9] Now we wish to report the results of a triple-quadrupole collision-activated dissociation (CAD) study of the internal structure of these clusters, which offers some of the first direct evidence in favor of the mechanistic hypothesis proposed[5-9] to account for their formation and composition.

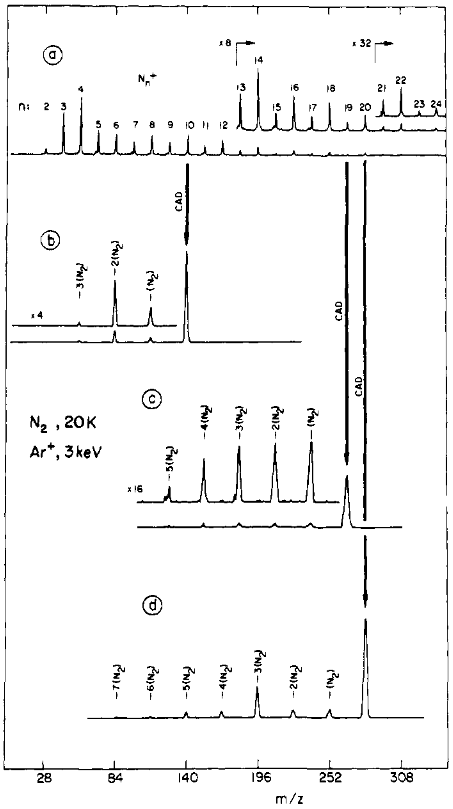

Figure 1. (a) Positive SIMS spectrum of solid N_2 obtained with a 3-keV Ar^+ beam. (b-d) Daughter ion spectra obtained by dissociating N_{10}^+, N_{19}^+, and N_{20}^+ ion with Ar under single-collision conditions.

The measurements were performed on an instrument described earlier,[3] modified by replacing the quadrupole mass filter by a triple quadrupole assembled from components purchased from Extranuclear Laboratories, Inc. The collision gas was argon in the low 10^{-5}-torr range so that only a small fraction of the clusters undergo more than a single reactive collision. The energy transferred to the cluster per collision was estimated to be on the order of at most a few electron volts from the known binding energies of protonated water clusters.[10]

The positive SIMS of solid nitrogen obtained with Ar^+ bombardment[3] contains the cluster series N_n^+, which extends through the range of our mass spectrometer (1000 amu). The most intense peaks are N_3^+ and N_4^+, and the intensities decay approximately exponentially as n increases. In the range $n = 7-46$ the peak intensities of the even and odd n series alternate, with those of even n being more intense. Only losses of nitrogen molecules are observed in the CAD spectra of N_n^+ clusters with $n = 1-30$ (Figure 1), indicating that the fundamental solvating unit is N_2. The CAD spectra of the even and odd cluster series differ in their intensity distributions.

The odd series preferentially loses a single N_2 molecule and the chance of losing several N_2 molecules decreases monotonically with their number, albeit only slowly at first. The same pattern is shown by the even series, but in addition a single very intense loss peak is present for each parent cluster. In small even clusters up to N_8^+, this is the loss of N_2, in the range $N_{10}^+-N_{18}^+$, this is the loss of $2N_2$, and for $N_{20}^+-N_{30}^+$, it is the loss of $3N_2$. Unlike

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(1) Benninghoven, A., Evans, C. A., Jr., Powell, R. A., Shimizu, R., Storms, H. A., Eds. *Springer Ser. Chem. Phys.* **1979**, *9*. Day, S. E.; Unger; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 557A.

(2) Jonkman, H. T.; Michl, J.; King, R. N.; Andrade, J. D. *Anal. Chem.* **1978**, *50*, 2078. Jonkman, H. T.; Michl, J. *J. Chem. Soc. Chem. Commun.* **1978**, 751. Lancaster, G. M.; Honda, F.; Fukuda, Y.; Rabalais, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 1951. Barber, M.; Vickerman, J. C.; Wolstenholme, J. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 549. Murray, P. T.; Rabalais, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 1007.

(3) Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1981**, *103*, 733.

(4) Orth, R. G.; Jonkman, H. T.; Powell, D. H.; Michl, J. *J. Am. Chem. Soc.* **1981**, *103*, 6026.

(5) Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1981**, *103*, 1564.

(6) Orth, R. G.; Jonkman, H. T.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 1834.

(7) Orth, R. G.; Jonkman, H. T.; Michl, J. *Int. J. Mass. Spectrom. Ion Phys.* **1982**, *43*, 41.

(8) Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *53*, 341.

(9) Michl, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *53*, 255.

(10) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

0002-7863/84/1506-5040$01.50/0

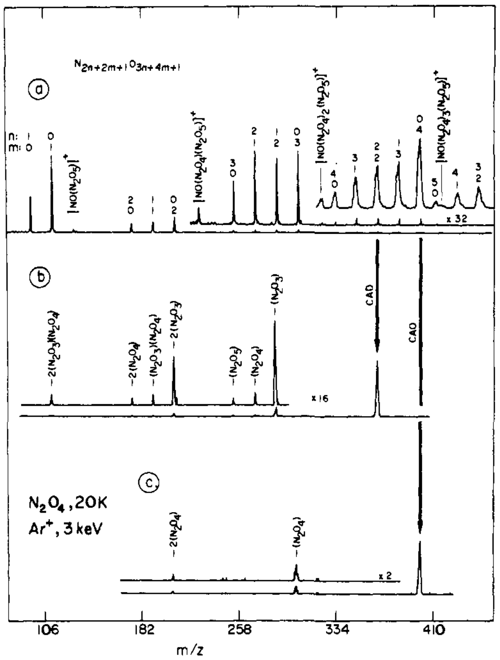

Figure 2. (a) Positive SIMS spectrum of solid N_2O_4 obtained with a 3-keV Ar^+ beam. (b,c) Daughter ion spectra obtained by dissociating $N_9O_{15}^+$ and $N_9O_{17}^+$ ions with Ar under single-collision conditions.

the rest, these specific losses are collision gas pressure independent and originate in long-lived metastable clusters.

The positive SIMS of NO obtained with Ar^+ is dominated by the cluster series $N_{2n+1}O_{3n+1}^+$ whose intensity decays approximately exponentially as n increases. The positive SIMS of N_2O and N_2O_4 is similarly dominated by the cluster series $N_{2n+2m+1}O_{3n+4m+1}^+$, which decreases in intensity as both n and m increase, more rapidly with n. The CAD study of the $N_{2n+1}O_{3n+1}^+$ series shows that these clusters only fragment by losing units of 76 amu. This suggests that the internal structure is $NO^+(N_2O_3)_n$. The CAD spectra of the $N_{2n+2m+1}O_{3n+4m+1}^+$ series obtained from solid N_2O_4 contain daughter ions corresponding to losses of N_2O_3, N_2O_4, and minor losses of N_2O_5 (Figure 2). No other losses were observed. This implies a structure $NO^+(N_2O_3)_n(N_2O_4)_m$ with the loss of N_2O_5 accounted for by small amounts of $NO^+(N_2O_3)_{n+1}(N_2O_4)_{m-2}(N_2O_5)$. The loss of N_2O_3 is between 4 and 10 times more likely than the loss of N_2O_4 when both are present in the cluster. CAD measurements on the same cluster series generated from Ar^+ bombardment of solid N_2O produced similar results, indicating that the composition and structure of the clusters are independent of whether the target was solid N_2O or N_2O_4.

The proposed mechanism for cluster formation from insulating low-temperature solids is outlined in detail elsewhere.[9] It consists of the following steps: (i) primary damage center formation in the solid, (ii) conversion of primary to secondary damage centers by chemical reactions, (iii) ejection of a large molecular aggregate containing a central charge, (iv) conversion of the aggregate into the final stable cluster by evaporative loss of the least firmly held constituent molecules accompanied by cooling. Although the mechanism is compatible with the available observations, until recently it was only supported indirectly. The observation of the secondary damage centers in solid nitrogen oxides by matrix-isolation spectroscopy[11] has now provided the first direct support for steps i and ii.

The present CAD results lend credence to the proposed steps i–iv in that they show the clusters to have the internal structure demanded by these steps: they consist of a central ion and one or more loosely attached solvating molecules. The central ion appears to be derived from that species within the impacted region of the solid which has the lowest ionization potential. The preferred solvating molecules appear to be selected from among all those present in the impact region as being the most polarizable and polar, i.e., most likely to become attached to the central ion before or during the ejection process and least likely to be shaken off during the ejection or thereafter.

The observed cluster metastability also supports the proposed step iv.[12] It is reasonable that vibrational excitation should be the longest lived and metastability the easiest to observe on the even N_n^+ clusters: V–R and V–T energy transfer from a vibrationally excited species will be particularly slow when no low-frequency vibrations are available in the central ion (N_2^+, as opposed to N_3^+) and the solvating molecules (N_2).[13] Once the transfer occurs, the energy provided is adequate for the ejection of a small number of relatively firmly held solvating molecules from a small cluster or a larger number of more loosely held ones from a large cluster. Additional complications would arise if some of the clusters were solid and some liquid.[14]

Acknowledgment. This work was supported by the National Science Foundation (CHE 81-21122).

Registry No. N_2, 7727-37-9; NO, 10102-43-9; N_2O, 10024-97-2; N_2O_4, 10544-72-6; Ar^+, 14791-69-6; N_2O_3, 10544-73-7; N_2O_5, 10102-03-1.

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[11] Liang, J.; Michl, J. *J. Am. Chem. Soc.*, preceding paper in this issue.

[12] Metastable clusters from particle-induced desorption on room-temperature solids have been reported before: Blakley, C. R.; Carmody, J. J.; Vestal, M. *Anal. Chem.* **1980**, *52*, 1636. Campana, J. E.; Green, B. N. *J. Am. Chem. Soc.* **1984**, *106*, 531 and references therein.

[13] Oxtoby, D. W. *Annu. Rev. Phys. Chem.* **1981**, *32*, 77; *Adv. Chem. Phys.* **1981**, *47*, 487. Legay, F. In "Chemical and Biomedical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1978; Vol. 2.

[14] For a leading reference to the "melting" and "freezing" of clusters, see: Berry, R. S.; Jellinek, J.; Natanson, G. *Chem. Phys. Lett.* **1984**, *107*, 227.

Stereocontrolled 1,1,2-Trialkylation of Ketones

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Intermolecular addition of carbon electrophiles to olefins not bearing heteroatom substituents (e.g., enol ethers, enamines, etc.) has achieved little synthetic use due to the requirements of fairly potent electrophiles and the instability of the initial cations which lead to products derived from rearrangements or further condensations.[1] The ability of silicon to stabilize positive charge has led to its introduction as a regio- and chemoselectivity control element.[2] The potential importance of addition of carbon electrophiles to olefins has been shown by the rapid adoption of allyl- and vinylsilanes as important synthetic building blocks. The ability of a cyclopropyl ring to stabilize an adjacent positive charge and the utility of strained rings for further structural elaboration[3] led

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[1] For some recent examples, see: Shono, T.; Nishiguchi, I.; Sasaki, M.; Ikeda, H.; Kurita, M. *J. Org. Chem.* **1983**, *48*, 2503 and references therein. Klein, H.; Erbe, A.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 82. Wada, Y. Yamazaki, T.; Nishiura, K.; Tanimoto, S.; Okano, M. *Bull, Chem. Jpn.* **1978**, *51*, 1821. Snider, B. B.; Cordova, R.; Price, R. T. *J. Org. Chem.* **1982**, *47*, 3643. Wookulich, P. M.; Uskokovic, M. R. *Ibid.* **1982**, *47*, 1600. Snider, B. B.; Rodini, D. J.; van Straten, J. *J. Am. Chem. Soc.* **1980**, *102*, 5872. Beak, P.; Berger, K. R. *Ibid.* **1980**, *102*, 3848. Hoffmann, H. M. R.; Tsushima, T. *Ibid.* **1977**, *99*, 6008. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.

[2] For excellent reviews, see: Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983. Magnus, P. D.; Sarkar, T.; Djuric, S. *Comp. Organomet. Chem.* **1982**, *7*, 515. Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. Fleming, I. *Comp. Org. Chem.* **1979**, *3*, 539. Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.