LETTERS

Cluster Size Dependence of the Chemical Stereoselectivity in the Nb_x + BrCN Reaction

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The size dependence of the reaction cross section of metal clusters on the relative orientation of the chemical reagent is studied for the reaction of niobium clusters (Nb_x, x = 1–12) with BrCN. An observed rapid decrease in the Nb_xCN^+/Nb_xBr^+ mass peak intensity ratio as x changes from 2 to ≥ 3 suggests that the high selectivity previously observed in beam studies for metal atom reactions with BrCN rapidly disappears as the number of metal atoms in a cluster increases. This observation is qualitatively discussed.

Introduction

The dependence of the physical (e.g., magnetic properties,[1-4] ionization potentials,[5,6] electron affinities,[7,8] etc.) and chemical properties (e.g., reaction with H_2,[9] N_2,[9] NH_3,[10] O_2,[11,12] benzene,[13-15]

unsaturated cyclic compounds,[16] etc.) of metal clusters on their size has been a field of active research during the past decade. In this paper we examine yet another property, the stereochemical selectivity in chemical reactions of small niobium clusters.

Laser vaporization of a solid target within a pulsed supersonic nozzle has been shown to be a powerful method to generate isolated clusters with densities sufficiently high for direct detection[17-20] and further reaction within a fast flow reactor.[9,21,22] Reactions

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of metal clusters with small inorganic molecules and organic compounds have been carried out to study the relative reactivity and kinetics[9,13,14,22,23] as a function of cluster size.

The reaction of niobium clusters with benzene has recently been reported by this group.[13] The conversion probability of $Nb_xC_6H_6$ to Nb_xC_6 was studied as a function of cluster size. Under the conditions used in our report, a threshold for this dehydrogenation reaction was observed at $x = 4$ with a maximum of reactivity at $x = 5, 6$, and 11 and a minimum at $x = 8$ and 10. These observations were explained in terms of the relative stabilities of benzene and the different size niobium clusters.[13] A subsequent photochemical study was carried out in which the ionization laser power dependence of the niobium clusters plus benzene reaction was examined. Again most of the observations could be explained in terms of the thermodynamical stabilities of the products and reactants.[15] The reactions of niobium clusters with benzene and deuteriated benzene under different ionization wavelengths have also been reported more recently by Kaldor's group.[14] Besides the similarities as reported in our work, they found that there is an isotope effect and a wavelength dependence of the conversion probability mentioned above.

Chemists have known for a long time the importance of relative orientation of two reacting species in producing products. The steric factors or the entropy of activation introduced in the Eyring transition-state theory[24] emphasizes the importance of the stereochemical specificity in a chemical reaction. It was not until 1966 when Beuhler, Bernstein, and Kramer,[25] as well as Brooks and Jones,[26] using the electric hexapole technique of Kramer and Bernstein,[27] oriented CH_3I molecules and quantitatively demonstrated the steric effects in the reaction between metal atoms and the oriented CH_3I molecules. From these studies,[25,26] differences in reactivity of the reaction of metal atoms with oriented CH_3I molecular beams were observed for "heads" vs "tails" orientations. In more recent molecular beam experiments, the branching ratio of the products of metal atoms reacting with each end of BrCN molecules was found to be far from unity (at least 10:1).[28,29]

Reactions of metal atoms, M, with a number of other halides, AX (where A can be an alkyl group or CN while X represents a halogen), were studied by different techniques.[30] In the reaction of alkali-metal atoms with saturated monohalides where A is an alkyl group, the reactive scattering cross section decreases significantly as the size of A increases[31] and it also decreases as the electron affinity of X becomes more negative.[32,33] In the reaction of alkali-metal atoms with inorganic halides such as BrCN and ICl, it was found that the branching ratio of MCN/MBr and MCl/MI is greater than unity.[28,29] This could be attributed to the exothermicity of the different products.[34]

The question immediately arises as to whether this trend in chemical selectivity in the reaction with the halides depends on the number of atoms in a metal cluster. It is the purpose of the present work to answer this question. To do so, BrCN is reacted
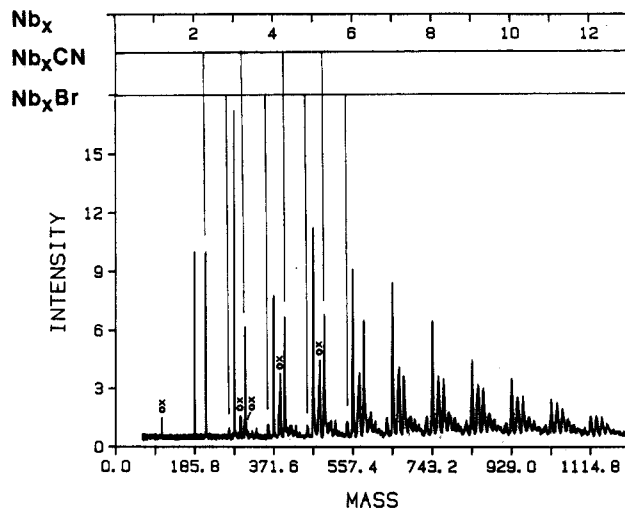

Figure 1. Product distribution with about 30% BrCN seeded in He carrier gas with a total pressure of 5 psig. The amount of products is maximized by changing the timing between the ionization and the vaporization lasers as well as the total amount of reactant injected into the fast flow reactor. Peaks denoted "ox" refer to the bare cluster oxides.
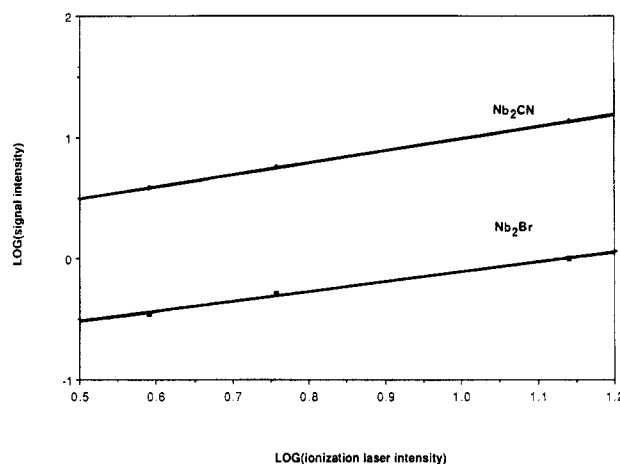

Figure 2. Plot of log (signal intensity) vs log (ionization laser intensity). This demonstrates that, with the laser fluences employed, the formation of Nb_2CN^+ and Nb_2Br^+ is linear with respect to the ionization laser intensity. Other products show similar dependence within this power intensity range.

in a fast flow reactor with small niobium clusters made by the laser vaporization technique.[35-37] From the analysis of the product distribution by time-of-flight mass spectrometry using excimer laser ionization, the mass peak intensity ratio of Nb_xCN^+/Nb_xBr^+ is measured as a function of cluster size x. The results suggest that the selectivity is lost very rapidly as x increases, with small but measurable fluctuation between $x = 3$ and $x = 7$. The results are qualitatively discussed.

Experimental Section

The experimental details have been described elsewhere.[15] Briefly, niobium clusters are generated by laser vaporization (6 mJ of 355-nm laser light) of a solid niobium rod in a pulse of helium. The metal atom plume formed from the niobium rod is entrained and quenched in the helium pulse where condensation/nucleation results in cluster formation. The clusters are then expanded into a fast flow reactor where a pulse of reactant gas mixture overlaps with the metal cluster beam. The reactant is

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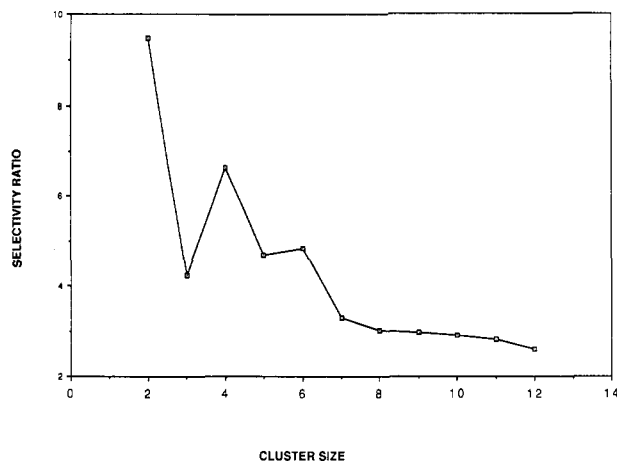
CLUSTER SIZE

Figure 3. Mass peak intensity ratio of Nb_xCN^+/Nb_xBr^+ as a function of cluster size. The signal intensity is integrated, and the contribution from an $Nb_xO_2^+$ mass peak to an Nb_xCN peak is deconvoluted by enlarging the mass spectrum and assuming a symmetric shape of a mass peak.

seeded into a helium carrier gas resulting in a mole fraction of about 0.3. This reactant–He mixture is introduced into the reactor through a General valve. The total amount of the reactant can be controlled by changing the electrical pulse width for the General valve. The timing between the vaporization laser and the reactor pulser is adjusted to maximize the product signal. The retention time of the metal clusters in the reactor is approximately 120 μs with an estimated reaction temperature of 300–400 K. The cluster mixture is then expanded into a high-vacuum region where a sudden decrease in density and temperature stops further reaction from occurring.

The cluster expansion passes through a 2-mm skimmer to form a well-collimated molecular beam. Detection of the niobium clusters and their reaction products is done in a time-of-flight mass spectrometer with an ArF excimer laser (Lambda Physik EMG 101) as the ionization source (193 nm, 6.4 eV).

The photoions formed are accelerated and analyzed by a 1.7-m TOF mass spectrometer and collected on a microchannel plate ion detector. The signal is amplified and digitized by a LeCroy 8828 transient digitizer and stored in an IBM computer. The spectrum then is analyzed and plotted as a function of mass.

Results

Figure 1 shows a typical product distribution of the niobium clusters after 5 psig total backing pressure of a BrCN–He mixture being introduced into the reactor. (The mole fraction of BrCN is approximately 0.3.) The total amount of products can be controlled by changing the width of the electrical pulse which drives the General valve for the fast flow reactor. In this experiment, that pulse width is adjusted to approximately 300 μs in order to get enough products and a relatively good cluster distribution. The major products observed under these conditions are Nb_xCN and Nb_xBr where $x = 2$–12. These product peaks are observed at masses just before those for Nb_xO_2 and Nb_{x+1}, respectively. A power dependence study in the range from 30 to 120 μJ over a 2-mm-diameter aperture shows that log (intensity of Nb_xCN^+ or Nb_xBr^+ signal) vs log (intensity of the ionization laser) plot has a slope of unity (see Figure 2). This observation strongly suggests that the formations of these ions are results of one-photon processes. It further suggests that nonlinear processes are not taking place at these low ionizing laser fluences (below 1500 μJ/cm²). The experiment reported in this work was carried out in this low-intensity regime to minimize multiphoton ionization and fragmentation.

Figure 3 shows the ratio of the integrated mass peak intensity of Nb_xCN^+ to that of Nb_xBr^+ as a function of cluster size. This is done by enlarging the mass spectrum and integrating the area under the Nb_xCN^+ and Nb_xBr^+ signals, subtracting out the $Nb_xO_2^+$ signal which overlaps with the Nb_xCN^+ signal in the large

cluster region as the resolution is reduced. This ratio decreases rapidly as the cluster size increases and levels off beyond Nb_7. The measurement of this ratio for clusters smaller than Nb_9 is very reliable since Nb_xCN^+ and $Nb_xO_2^+$ are fairly well resolved. The measurement of this ratio for clusters with x larger than 9, however, is uncertain due to the difficulties arising from poor resolution in that region.

The ratio R of the integrated mass signal of Nb_xCN^+ to that of Nb_xBr^+ is given by

$$R = \frac{\sigma_{Nb_xCN}}{\sigma_{Nb_xBr}} \frac{\Phi_{(Nb_xCN)^+}}{\Phi_{(Nb_xBr)^+}} \frac{D_{(Nb_xCN)^+}}{D_{(Nb_xBr)^+}}$$

where σ is the average reaction cross section for the formation of each cluster product, Φ is the ion yield for each cluster product at the excimer laser wavelength, and D is the detection constant for each cluster product ion. R can measure the average reaction cross section ratio only if $\Phi_{(Nb_xCN)^+}/\Phi_{(Nb_xBr)^+}$ and $D_{(Nb_xCN)^+}/D_{(Nb_xBr)^+}$ are not far from unity for each cluster product. The latter is expected to be unity since the collection and sensitivity of detecting these ions with not too large a mass separation should be very similar. The former can be satisfied if the ionization cross sections and the photochemical decomposition probabilities at the excimer laser wavelength are not very different for these two products. Under low ionizing laser intensity when single-photon ionization is dominant in producing the observed ion signals, this requirement is likely to be satisfied. In this case, multiphoton chemistry is less likely to take place. Even in the absence of photochemistry, it is expected that binding Nb_x with Br should perturb its ionization continuum in a different manner than binding with the CN group. The variation of this difference with x could indeed give variation in the observed value of R with x. This might very well explain the observed fluctuation of the value R in Figure 3 for $x = 3$–7.

In this experiment, $NbCN^+$ and $NbBr^+$ were not observed. Either they are not formed possibly due to thermodynamic reasons or they are formed but not detected due to the possibility that their ionization potentials are higher than the one-photon energy of the ionizing laser. The latter is the more likely reason.

Discussion

Figure 3 shows that the ratio of the ion signals of Nb_xCN to that of Nb_xBr drops rapidly when x changes from 2 to 3. This result suggests that the stereochemical affinity of the reaction changes as x increases by one. From previous molecular beam studies,[28,29] the single Ba atom reaction with BrCN is highly specific with an MCN/MBr ratio of at least 10:1. From Figure 3, a smooth extrapolation to $x = 1$ gives a branching ratio of approximately 15:1. This number is not accurate because we know very little about the change in the relative ionization yields of these compounds at the one-photon excimer laser wavelength. However, the general conclusion that a rapid drop of the stereochemical specificity as the number of metal atoms increases which levels off at $x = 7$ is probably correct. If one assumes, as was done in the past, that $x = 7$ represents what might be observed on the surface of the bulk metal, then according to stereochemical criteria it only takes few atoms (approximately seven) to make a metal. (This illustrates the danger of using the convergence of the properties of metal clusters in determining the number of atoms that makes a metal. This number will undoubtedly depend on the property being measured.)

The rapid loss of the chemical stereospecificity of the reaction with increasing number of metal atoms might strongly reflect the rapid change in the anisotropy of the potential surfaces along the reaction coordinate as the number of metal atoms in a cluster changes. For a single atom, it is the impulsive collisions that lead to the reaction products. The potential is highly anisotropic leading to a much larger cross section if the metal atom binds the CN group than when it binds the Br atom. As the number of atoms increases, the potential becomes less anisotropic and nonimpulsive type collisions could also lead to product formation. Thus, bridge binding between BrCN and a cluster with more than one metal atom becomes a possible mechanism for product formation. This kind of reaction path is expected to be less stereospecific.

One last remark about metal catalysis should be mentioned. The above results suggest that if one were to look for a metal surface to catalyze the MCN but not MBr formation, the structure of the active site on this surface has to be made of as few metal atoms as possible.

Monte Carlo Study of the Dielectric Saturation in Molecular Solutions. Physical Basis of the C Mode in Electron-Transfer Reactions

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By a Monte Carlo simulation of polar solution using a spherical hard-core model for molecules, we have demonstrated that a thin dielectric saturation shell exists just around a charged solute molecule. The curvature of the free energy curve as a function of solvent polarization corresponding to this dielectric saturation shell is found to be greatly increased with increase of the charge of the solute molecule. The reorientational solvent motion with this property of dielectric saturation is deemed to be the coordinated solvent mode (c mode) which has played a crucial role in the energy gap law of the electron-transfer reaction.

Introduction

Electron transfer (ET) is the most fundamental process in chemistry and biology as well as in physics. Many theoretical and experimental studies have been made so far for the various phases of materials.[1-3] Among them, the ET in polar solution has been a field of current lively investigation.[4-9] The regulation mechanism of the ET rate by means of the free energy difference between the initial and final states, called the energy gap law, was one of the central problems.[4-15] That is, the existence or nonexistence of the "inverted region" at the large energy gap has been extensively investigated.[10-15] In this respect, we have recently proposed a theoretical treatment with a new aspect of the solvent motion that the potential curvature for the reorientation of solvent molecules around a charged solute molecule (reactant or product) will be much larger than that around a neutral solute molecule

(reactant or product).[16] This solvent mode is called the solvent-coordinated mode (c mode, for brevity). Taking into account the c-mode, we have derived three different energy gap laws with respect to the three types of the ET reaction:[15-19] (i) no appreciable inverted region for the charge separation reaction ($A\cdots B \rightarrow A_s^-\cdots B_s^+$), (ii) moderate inverted region for the charge shift reaction ($A_s^-\cdots B \rightarrow A\cdots B_s^-$), and (iii) quite remarkable inverted region for the charge recombination reaction ($A_s^-\cdots B_s^+ \rightarrow A\cdots B$). All those theoretical predictions were consistent with most of the available experimental data.[10-15]

Since the above theoretical treatments were based on the assumption of a large frequency change of the solvent motion around a molecular reactant, it is necessary to prove the validity of its assumption more directly. At this point, it should be noticed that so far as the solvent polarization is linear to an external field, the force constant of the solvent motion around the neutral molecule is the same as that around the charged molecule. This fact indicates that a nonlinear response of the solvent polarization, probably due to the solvent dielectric saturation, must be responsible to a large change of the force constant of the solvent motion.

In the following, we conduct the Monte Carlo simulation of polar solution and investigate to what extent the dielectric saturation is realized and the force constant is changed, depending upon the magnitude of a charge of the solute molecule.

Method of Monte Carlo Simulation

We adopt the following simple model for a polar solution: A solute molecule has a charge ze and its shape is a sphere with a hard-core radius r_0. The solvent molecule has a point dipole moment μ and it has a spherical hard core with a radius a. The molecular ion is always fixed at the center of a large spherical

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