

Size dependence of gaseous cluster reactivity as a mechanistic probe

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Abstract. The determination of the mechanisms of chemical and physical changes is one of the principal occupations of many chemists today. To accomplish this, the dependence of the change being examined on a number of intensive variables such as temperature, pressure, concentration of reactants as well as the pH is usually studied. In this account, we summarize our recent studies on the reactivity and dynamics of niobium gaseous clusters in which their changes with size are used as a new degree of freedom that assists in deducing the mechanism of the change studied.

Keywords. Gaseous cluster reactivity; mechanistic probe; niobium gaseous cluster.

1. Methodology

The clusters are made by techniques similar to those used by Smalley and his group (Geusic *et al* 1985) which utilizes laser evaporation–supersonic expansion techniques. The 355 nm harmonic of a Quanta-Ray YAG pulsed laser is used for evaporation of Nb atoms from a rotating rod. This is followed by the opening and closing of a pulsed nozzle with 3–5 atm backing pressure of helium gas. The collision with the helium cools off the hot Nb atoms and the unidirectional expansion greatly reduces the spread in the velocity of the expanding gases of helium and the Nb vapor. Collision between the cold Nb atoms leads to clustering. The gas mixture passes through the reactor in which dilute mixtures of different reagents can be introduced with helium gas. The gases can then be expanded to eliminate further collisions and are passed through a skimmer to select the clusters and their products that are moving along the expansion axis that leads to the laser focus of the ionization region of a home built laser time-of-flight mass spectrometer. The laser used for ionization is the 193 nm excimer line from Lambda Physik. Except for the monomer, the one-photon energy of this laser is sufficient to ionize all the niobium clusters and their products. This, in addition to the fact that Nb has only one isotope, makes Nb clusters best suited for studies by which laser mass spectrometric techniques are used for detection.

2. Benzene dehydrogenation: Is there a size-threshold?

In the mass spectrum of the reaction products of Nb_x with benzene (St Pierre and El-Sayed 1987), two dominant types of products are observed, $Nb_x(C_6H_6)$ and $Nb_x(C_6)$. For small clusters, the $Nb_xC_6H_6$ mass peaks are intense and for $x = 1$ and 2, mass peaks for $Nb_x(C_6H_6)_2$ are observed. At $x > 4$, the mass peaks resulting from

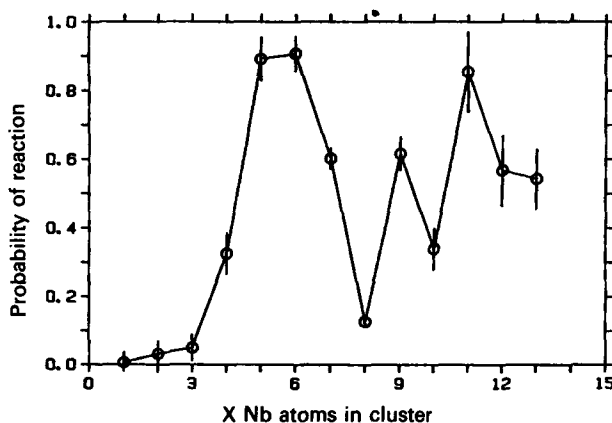


Figure 1. The observation of size threshold in the dehydrogenation of benzene by niobium clusters (at $x = 4$).

the $\text{Nb}_x\text{C}_6\text{H}_6$ are found to decrease while those due to the Nb_xC_6 mass peaks increase. This suggests competing channels resulting from the fact that the dehydrogenation of the $\text{Nb}_x\text{C}_6\text{H}_6$ leads to the formation of Nb_xC_6 . If one assumes that the ratio of the mass peak intensity of Nb_xC_6 to the sum of those for Nb_xC_6 and $\text{Nb}_x\text{C}_6\text{H}_6$ can be taken as a measure of the dehydrogenation probability for cluster Nb_x , the size dependence of the dehydrogenation process can be represented by the results of figure 1. This figure shows a threshold-type behavior at $x = 4$ with maxima at 5, 6 or minima at 8 and 10. The minima at 8 and 10 can be explained by the known high stability of Nb_8 and Nb_{10} clusters. The sudden increase at $x = 4$ or 5 could either be catalytic or thermodynamic. If it is the latter, it suggests that a minimum number of Nb-carbide bonds are needed to be formed to drive the reaction. If the former, it suggests that a minimum number of Nb atoms are required to anchor the benzene ring for effective activation of the carbon-hydrogen bonds. Obviously, theoretical calculation might be able to distinguish between these two possibilities.

Other studies (St Pierre *et al* 1988) in our group have yielded two conclusions regarding the dehydrogenation process. In order to observe it on the time scale of our experiment (microseconds), the reagent is required to have at least one double bond. Furthermore, only the loss of an even number of hydrogen atoms is observed for the dehydrogenation of hydrocarbons. The former conclusion suggests a mechanism involving complex formation (involving the π -electronic system) and the latter suggests the formation and evaporation of molecular hydrogen.

3. Size dependence of stereochemical specificity

From molecular beam studies (Levy 1979), it is known that in reactions of metal atoms like Ba or Sr with CN, MCN is formed with higher cross section than MX. This was attributed to the higher exothermicity of MCN formation. The question thus arises as to what would happen if a metal cluster is sufficiently large (compared to the BrCN molecule) and polarizable enough to form a complex as an intermediate

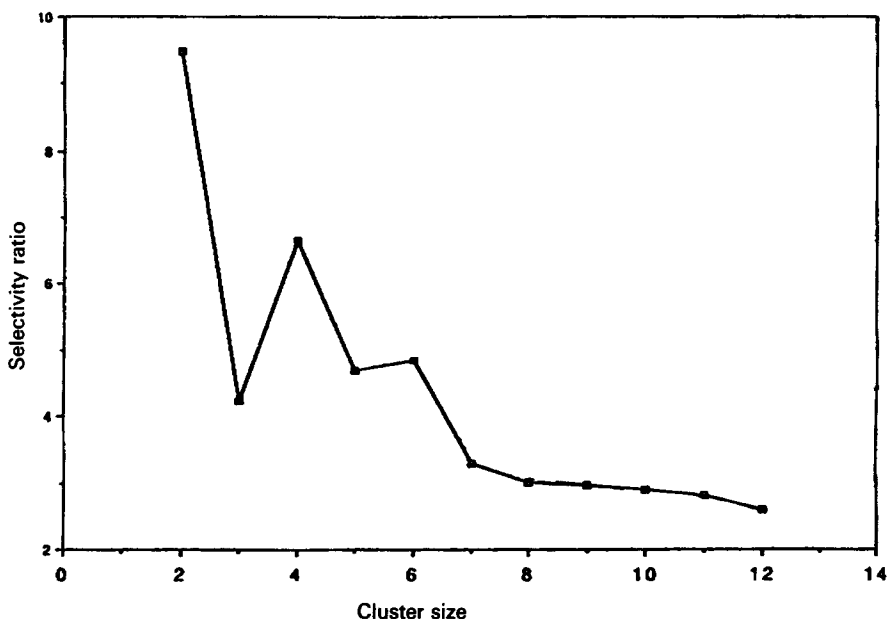


Figure 2. The decrease of the stereochemical specificity with cluster size in the reaction between niobium clusters and BrCN (at $x = 7$ it disappears).

for the reaction. Would this diminish or eliminate the stereochemical specificity observed for the monomer?

The reaction of BrCN was studied (Song *et al* 1988) with Nb_x clusters. The ratio of the mass peak intensity for Nb_xCN to that of Nb_xBr is determined and plotted as a function of x as shown in figure 2. If one would draw a smooth curve (to remove fluctuation in the ratio for small sizes resulting most likely from variation in the ionization cross sections), one reaches the conclusion that, indeed, the stereochemical selectivity is diminished rapidly. For $x \geq 7$, the probability for the reaction leading to either product becomes independent of size with a value of ~ 2 . This is the mass peak ratio of $Nb_xCN^+ : NbBr^+$, which is related to $[NbCN]/[NbBr]$ by the ratio of ion yields from the corresponding neutrals.

The above conclusion is not surprising. For small x , the collision is of the impulsive type. Thus the outcome would depend on which end of the BrCN molecule the metal atom or dimer or small cluster collides with. As the cluster size increases, complex formation would result, irrespective of which end of BrCN the cluster collides with.

4. Steric effects due to cluster size

Let us (Song *et al* 1988) examine the bromine abstraction reaction by niobium clusters from two organic reagents, in one the bromine is not sterically shielded, e.g. CH_3CH_2Br , while in the other it is, e.g. $CH_3CHBr-CH_3$. The mass peaks Nb_xBr were normalized to an NbI peak in each spectrum produced from the reaction of Nb clusters with the same amount of CH_3I in each experiment. The results are shown in figure 3. The reaction with both reagents gave the same yield of Nb_xBr from small

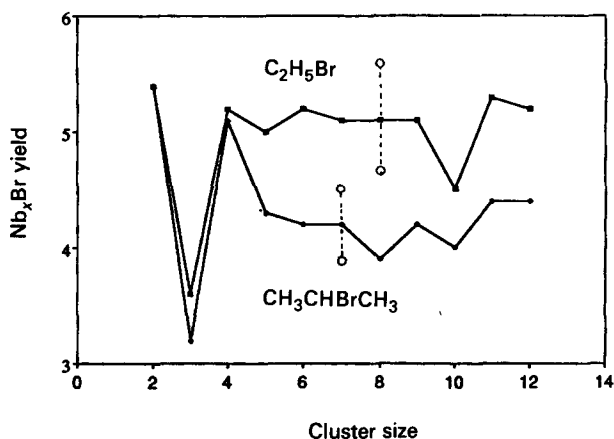


Figure 3. The stereochemical effect of the cluster size in its reaction with sterically hindered group (e.g. bromine). For $x = 4$, a large difference in the reaction cross section with C_2H_5Br and the more sterically hindered $CH_3CHBrCH_3$ molecule.

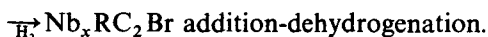
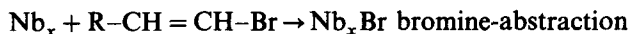
clusters ($x < 5$), including the fluctuation resulting from the ion yield dependence on x for small x . For $x \geq 5$, the yield of $Nb_x Br$ from $H_3C-CHBr-CH_3$ is reduced by $\sim 20\%$ when compared to that produced from the reaction with the less sterically hindered reagent (CH_3CH_2-Br).

5. Size dependence of the reactivity as a monitor of the reaction mechanisms in multiple reactions

When more than one product is observed from the reaction of clusters with a certain reagent, the question is usually raised as to whether the reactions involved are competing with, or they are parallel to, one another. Using the change in the cluster as an additional degree of freedom, one can distinguish between these two possibilities.

If the multiple products result from competing channels, i.e. result from complex formation that decomposes to give either one or the other, one expects that as the size is changed, an increase in the mass peak intensity of one product should result in a decrease of the peak intensity of the other. This is shown in figure 4 (Song *et al* 1989) for the reaction of Nb_x with CO_2 . In this reaction, for small clusters, $Nb_x O$ is observed. As the cluster size increases, $Nb_x O$ mass peak intensity diminishes while that for $Nb_x CO_2$ increases. We believe (St. Pierre *et al* 1987) that the cluster first forms the complex $(ONb_x CO)$ which is very hot since no cooling collisions take place. As a result the complex cools off by evaporating CO. As the cluster size increases, the increase in the internal degrees of freedom is sufficient to absorb the amount of heat produced in the exothermic complex formation process.

If multiple products result from different types of collisions, the cluster size at which a new channel opens up does not affect the probability of the product formation of the other product. An example of this mechanism is the reaction of Nb_x with $R-CH=CHBr$ to give two products:



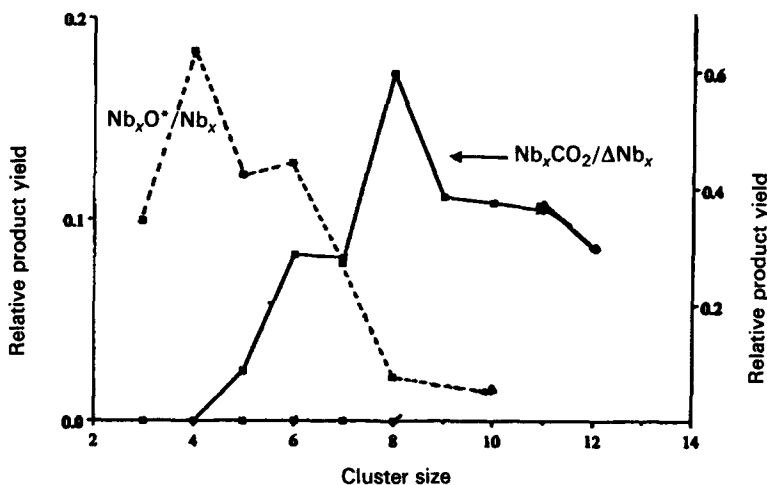


Figure 4. An example of competing reactions: The $CO_2 + Nb_x$ reaction. As the size changes, the appearance of a new product (Nb_xCO_2) at $x = 5$ decreases the yield of the other (Nb_x) (Song *et al* 1989).

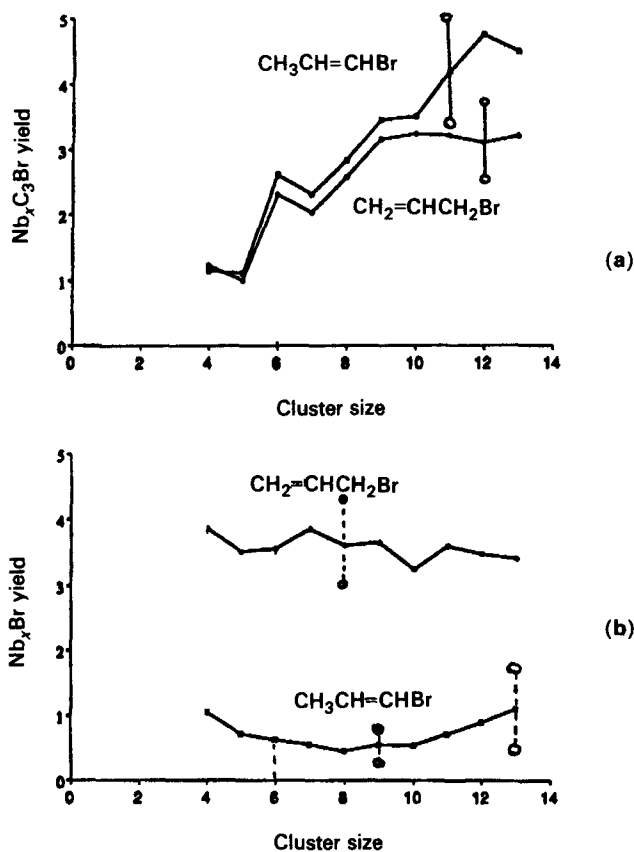


Figure 5. An example of parallel reactions: As the cluster size increases, the appearance of a new product does not affect the yield of the other: The dehydrogenation (a) vs bromine abstraction (b) reaction. As dehydrogenation sets in (at $x = 6$) in (a), no effect is observed in the bromine abstraction product (Nb_xBr) in (b) (Song *et al* 1988).

Figure 5 shows the change in the relative yields of $\text{Nb}_x\text{C}_3\text{Br}$ (a) and Nb_xBr (b) as a function of x for the reaction with both $\text{H}_3\text{C}-\text{CH}=\text{CHBr}$ and $\text{H}_2\text{C}=\text{CHCHBr}$ unsaturated organic bromides. As shown in the figure 5a, at $x = 6$, the threshold of the dehydrogenation reaction (which requires complex formation with the π -electronic system of the organic reagent), no significant change is observed in the mass intensity of the abstraction yield in figure 5b. This suggests that bromine abstraction results from a different type of collision (impulsive type) than the sticky type collision involved in the complex leading to the dehydrogenation process.

Acknowledgement

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