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The chemical reactions of small gas-phase niobium clusters with benzene derivatives and a few unsaturated non-aromatic reagents are studied by the supersonic beam-laser ablation method to form the clusters, and the laser-mass spectrometric technique for detection. The molecular addition and dehydrogenation reactions of these reagents are compared to those for benzene. New reaction channels are observed for the reaction of niobium clusters with pyridine, pyrimidine and 1,5-Hexadiyne. The loss of  $C_2H_2$  and  $H_2$  is observed to be a favorable product channel for the reaction with some of the small niobium clusters. In the reaction of niobium clusters with acetaldehyde, all of the reaction channels leading to the formation of stable molecules such as  $CH_3OH$ ,  $CO$ ,  $H_2$ ,  $HCHO$ ,  $H_2O$  and  $CH_4$  are observed. In all the reactions studied, the observed reaction product distributions are found to be greatly determined not only by the stability of the reactant but also by that of the neutral molecular product formed along with the cluster product detected. ORGANIC CHEMISTRY. 45

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The Reaction of Niobium Clusters with Some Benzene  
Derivatives and Unsaturated Non-aromatic Hydrocarbons

by

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The Journal of Physical Chemistry, accepted for publication

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# **The Reaction of Niobium Clusters with Some Benzene Derivatives and Unsaturated Non-aromatic Hydrocarbons**

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## **Abstract**

The chemical reactions of small gas-phase niobium clusters with benzene derivatives and a few unsaturated non-aromatic reagents are studied by the supersonic beam-laser ablation method to form the clusters, and the laser-mass spectrometric technique for detection. The molecular addition and dehydrogenation reactions of these reagents are compared to those for benzene. New reaction channels are observed for the reaction of niobium clusters with pyridine, pyrimidine and 1,5-hexadiyne. The loss of  $C_2H_2$  and  $H_2$  is observed to be a favorable product channel for the reaction with some of the small niobium clusters. In the reaction of niobium clusters with acetaldehyde, all of the reaction channels leading to the formation of stable molecules such as  $CH_3OH$ ,  $CO$ ,  $H_2$ ,  $HCHO$ ,  $H_2O$  and  $CH_4$  are observed. In all the reactions studied, the observed reaction product distributions are found to be greatly determined not only by the stability of the reactant but also by that of the neutral molecular product formed along with the cluster product detected.

## Introduction

Metal clusters have been a focus of research interest for many years. The technological importance of metal clusters ranges from areas such as catalysis<sup>1</sup> to materials processing.<sup>2-3</sup> Fundamentally metal clusters are interesting because they are between atoms and the bulk materials. By studying the detailed properties of metal clusters as a function of cluster size, transitions from atomic properties to bulk properties might be better understood. Over the past few years, research has been dedicated to investigate many properties of metal clusters as a function of cluster size. The following techniques have been used to study metal clusters: mass intensity distribution as a function of cluster size to identify "magic numbers";<sup>4-8</sup> measurement of electronic properties including ionization potentials<sup>9-13</sup> and electron affinities and photoelectron spectroscopy;<sup>14-17</sup> measurements of magnetic properties;<sup>18-19</sup> photodissociation of clusters;<sup>20-21</sup> investigation of collision induced dissociation.<sup>22-25</sup>

Chemical reactivity of metal clusters as a function of cluster size has also been investigated. Due to its fundamental importance especially, the reaction of H<sub>2</sub> with transition metal clusters of V, Fe, Ni, Pt, Nb, Cu and Co has been extensively studied.<sup>26-33</sup> Correlation of the chemical reactivity with the ionization potentials of the bare clusters has been suggested.<sup>30</sup> However, the importance of the changes in the cluster geometry in determining both the ionization potentials and the reactivity was also suggested.<sup>34</sup> The importance of cluster geometry was also inferred in the reaction of Fe clusters with NH<sub>3</sub>.<sup>35</sup>

The reactions of metal clusters with CO and N<sub>2</sub> were also studied.<sup>29,36</sup> In the reaction with N<sub>2</sub>, the reactivity pattern was found to be similar to that observed for H<sub>2</sub>. In contrast, CO showed only a monotonic increase with

cluster size. One explanation for the dramatic differences between these two isoelectronic species could be that the dissociative chemisorption of nitrogen is activated but CO chemisorption takes place without any significant barrier.

Due to the importance of C-H bond activation, there have been quite a few studies on the chemical reactions of metal clusters with aliphatic<sup>34,38</sup> and aromatic<sup>34,39-40</sup> hydrocarbons. It was found that the reaction probability is much higher for unsaturated hydrocarbons.<sup>41</sup>

In the reaction of niobium clusters with benzene<sup>34,39</sup> and deuterated benzene<sup>40</sup>, molecular addition as well as total dehydrogenation products were observed. The observed dehydrogenation probability was found to require a minimum of 4 or 5 atoms in the cluster and to vary with cluster size, the ionization laser intensity<sup>39</sup> and the ionization laser wavelength.<sup>40</sup>

From the reaction of niobium clusters with several cyclic hydrocarbons, it was shown that at least one double bond in the reactant is needed for the addition and dehydrogenation reaction to be observed to occur.<sup>41</sup> From the extent of dehydrogenation, it was concluded that the stability of both the reactant and the product is also very important in cluster chemistry.

In our previous studies on the reaction of Nb clusters with BrCN, it was found that the stereoselectivity drops very rapidly as the size of the cluster increases.<sup>42,43</sup> The selectivity levels off for  $x \geq 7$  ( $x$  is the number of niobium atoms in a cluster). In the reaction of Nb clusters with CO<sub>2</sub>, the molecular addition reaction was found to have a size threshold near  $x=5$  while the oxygen abstraction showed no size threshold.<sup>44</sup> The anti-correlation between the oxygen abstraction and the molecular addition leads to the conclusion that these two reaction channels are competitive. However, the bromine abstraction and the dehydrogenated molecular addition ( a reaction in which

the addition is followed by dehydrogenation ) in the reaction of Nb clusters with unsaturated bromopropenes were found to be non-competitive, suggesting these two channels result from different collisions.<sup>45</sup> In the reaction of vanadium clusters with halopropenes both halogen atom abstraction and displacement were observed. The latter lead to the observation of products with an odd number of hydrogen atoms.<sup>46</sup>

In the present work, we report studies on the chemical reactions of niobium clusters with substituted benzene (chlorobenzene, benzonitrile, pyrimidine and pyridine) and non-aromatic unsaturated hydrocarbons (hexadiene, hexatriene and acetaldehyde). From the results of all these reactions, one concludes that in addition to the stability of the reactants, the stability of the neutral molecular products formed along with the cluster product greatly determines the observed reaction channels.

## Experimental

The experimental details have been described elsewhere.<sup>39</sup> 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 by the laser beam 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 seeded in helium carrier gas of 10 to 20 psi. This reactant-He mixture is introduced into the reactor through a pulsed 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  $\mu$ s. The cluster mixture is expanded into a high vacuum region after leaving the flow reactor 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 unfocused ArF excimer laser ( Lambda Physik EMG 101) as the ionization source ( 193 nm, 6.4 eV). The fluence of the ionization laser was kept low (below 2 mJ/cm<sup>2</sup>) in order to minimize the effect of two-photon absorption and dissociation which complicate the interpretation of the observed mass spectrum. The signal intensity of the products and the unreacted metal clusters was maximized by adjusting the timing of the ionization laser and that of the pulsed reactor valve.

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 by a video amplifier (Pacific Instruments) and digitized by a LeCroy 8828 transient digitizer, and stored in an IBM compatible computer (Acer 1100). The spectrum is then analyzed and plotted as a function of flight time.

## **Results and discussion**

### **A. The reaction of Nb<sub>x</sub> with chlorobenzene**

A mass spectrum of Nb<sub>x</sub> after reacting with chlorobenzene in the flow reactor is shown in Figure 1a. The mole fraction of chlorobenzene is 0.01 and the total backing pressure of He is 5 psig. From the mass distribution, no

product was observed for  $x=1$  ( the monomer), whereas for the dimer, relatively strong  $\text{Nb}_2\text{C}_6\text{H}_3\text{Cl}$  and  $\text{Nb}_2\text{C}_6\text{HCl}$  peaks were observed, suggesting the loss of one and two  $\text{H}_2$  molecules. The molecular addition product  $\text{Nb}_2\text{C}_6\text{H}_5\text{Cl}$  was not observed under the same conditions.

For larger clusters ( $x \geq 3$ ), the mass resolution is gradually lost due to the overlap of the product and the cluster monoxides. Dehydrogenation product of the form  $\text{Nb}_x\text{C}_6\text{HCl}$  was partially resolved up to  $x=7$ . In reality, the resolution is not good enough to distinguish between  $\text{Nb}_2\text{C}_6\text{HCl}$  and  $\text{Nb}_2\text{C}_6\text{Cl}$ . However, according to our chemical intuition and results observed for smaller clusters, it is believed that only the loss of even number of hydrogen atoms is possible during the dehydrogenation process.

In this experiment, abstraction products such as  $\text{Nb}_x\text{Cl}$  and  $\text{Nb}_2\text{C}_6\text{H}_5$  were not observed. This indicates that the abstraction reaction of either Cl or  $\text{C}_6\text{H}_5$  is a relatively higher energy channel than the addition-dehydrogenation reaction. Unfortunately, the limitation in our experiment is the low vapor pressure of the organic sample. A heated pulsed nozzle is required in order to get higher vapor pressures and observe other reaction products.

Benzene was found to add molecularly<sup>34,38-39</sup> to  $\text{Nb}_x$  for  $x \leq 3$ . Dehydrogenation was observed to occur for  $x \geq 4$ . In the case of chlorobenzene, dehydrogenation was observed for all molecular addition products for  $x \geq 2$ . Chlorine substitution seems to catalyze the dehydrogenation process from the aromatic ring. This could be explained by the changes either in the thermodynamic factor such as the enthalpy of dehydrogenation, or kinetic factor such as the activation energy barrier, or both. Since the structure of the product is unknown, none of the quantities mentioned above can be evaluated.



According to the results of benzene adsorbed on metal surfaces at high temperatures,<sup>47</sup> benzene dissociates first and then dehydrogenation occurs. Therefore,  $Nb_xC_6HCl$  might very well represent  $Nb_yC_6$  and  $Nb_zHCl$ , where  $y+z=x$ . The  $Nb_xC_6H_3Cl$  cluster product could be composed of  $Nb_yC_6$ ,  $Nb_zHCl$  and  $Nb_k2H$ , where  $y+z+k=x$ . If this is the case, then the first transition upon the addition of the organic molecule to  $Nb_x$  is the formation of the carbide type species plus the formation of  $Nb_xH_2$  or  $Nb_xHCl$ . It is quite possible that such a composite cluster is hot. If the cluster cools off by evaporating molecular hydrogen, the so-called molecular addition products will not be observed.  $HCl$  is probably bonded more strongly to  $Nb_x$  than  $H_2$ . This might account for the lack of the observation of  $Nb_xC_6$  at the temperatures of the clusters formed in our experiment.

#### B. The reaction of $Nb_x$ with benzonitrile ( $C_6H_5CN$ )

Although the over all product intensity is relatively weak, the molecular addition product, the multiple molecular addition product, and the dehydrogenation product were observed for the reaction of benzonitrile with niobium clusters.

Figure 1b shows a product distribution spectrum after  $C_6H_5CN$  was introduced into the flow reactor. The vapor pressure of  $C_6H_5CN$  at room temperature was seeded in 5 psi He and the mixture was allowed through the reactor pulsed valve (the mole fraction of  $C_6H_5CN$  is about 0.002). No molecular addition product was observed for the niobium monomer whereas a relatively strong  $Nb(C_6H_5CN)_2$  mass signal was observed. The absence of  $NbC_6H_5CN$  could be due to its photochemical instability upon the absorption of the ionization laser photon. The bi-molecular addition product might be

photochemically more stable than the mono-molecular addition product. This could be due to differences in the two photon crosssections or else to the fact that more vibrational modes are available for the former to dissipate the excess photon energy than the latter.

Relatively strong mass signals that correspond to  $\text{Nb}_2\text{C}_6\text{H}_5\text{CN}$  and  $\text{Nb}_3\text{C}_6\text{H}_3\text{CN}$  were observed. Weak "total" dehydrogenation products  $\text{Nb}_x\text{C}_7\text{HN}$  were observed for  $x \geq 4$ .

The product distribution pattern for the reaction of niobium clusters with benzonitrile was very similar to that for chlorobenzene. No abstraction products of CN ( $\text{Nb}_x\text{CN}$ ) or the phenyl group ( $\text{Nb}_x\text{C}_6\text{H}_5$ ) were observed. The dehydrogenation of benzonitrile did not start until  $x=3$  compared to chlorobenzene which started to dehydrogenate at  $x=2$ .

In the reaction of niobium clusters with BrCN, both Br and CN abstraction products were observed.<sup>42</sup> Cl abstraction product was also observed in the reaction of  $\text{Nb}_x$  with chloropropene. The absence of  $\text{Nb}_x\text{Cl}$  in the reaction of  $\text{Nb}_x$  with chlorobenzene as well as the absence of  $\text{Nb}_x\text{CN}$  in the reaction of  $\text{Nb}_x$  with benzonitrile could be due to the difference in the types of collisions involved. In the abstraction of Cl or CN, an impulsive collision with these functional groups give rise to the reaction product. In the reaction with the benzene derivatives, however, a complex formation with the  $\pi$ -system of the phenyl group could give rise to the observed addition-type reaction products.

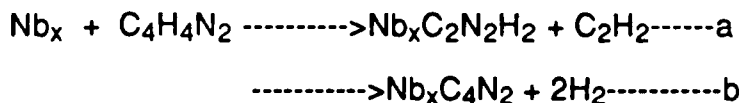
#### C. The reaction of $\text{Nb}_x$ with pyrimidine ( $\text{C}_4\text{H}_4\text{N}_2$ )

A mass spectrum of niobium clusters and their reaction products with pyrimidine in the flow reactor is shown in Figure 2. The vapor pressure of

pyrimidine at room temperature was seeded in 5 psig He and pulsed into the reactor. For  $x=1$ , only a very weak molecular addition product  $\text{NbC}_4\text{H}_4\text{N}_2$  was observed in contrast to a stronger  $\text{NbC}_2\text{H}_2\text{N}_2$  mass peak. The latter is a result of the loss of a stable  $\text{C}_2\text{H}_2$  molecule from the molecular addition product. The loss of  $\text{C}_2\text{H}_2$  was also observed for the reaction of  $\text{Nb}_x$  with some other aromatic compounds to be discussed later. This strongly suggests that the aromatic ring opens up followed by the elimination of  $\text{C}_2\text{H}_2$ .

For the niobium dimer and the trimer clusters, the product intensity was very weak. No assignment was made due to the weakness of the signal. However, for clusters with  $x \geq 4$ , a relatively strong total dehydrogenation corresponding to product peak  $\text{Nb}_x\text{C}_4\text{N}_2$  was observed. For  $x=4$  and 8, the total dehydrogenation product was the only product observed. This observation is quite different from the dehydrogenation of benzene on niobium clusters where relatively strong molecular addition products were observed for  $x=4, 8$  and 10.<sup>34,38-39</sup> This means that the extent of dehydrogenation not only depends on the structure of the metal cluster, but also on the structure of both the reactant and the product.

One might explain the above results as follows:



for  $x=1$ , the product is cooled off by evaporating  $\text{C}_2\text{H}_2$ . For larger clusters, evaporation of  $2\text{H}_2$  is sufficient to cool off the cluster product. Apparently, reaction b is more favorable for the reactions involving larger clusters. This could be due to the kinetic and geometric requirement for the total dehydrogenation process. The structure of  $\text{Nb}_x\text{C}_4\text{N}_2$  is not known. There remain many open questions. Could the structure be  $\text{Nb}_y\text{C}_4\text{Nb}_z\text{N}_2$  ( $y+z=x$ )?

Is  $N_2$  present as  $N=N$  bonded or adsorbed to  $Nb_z$  or do we have a  $C_4N_2$  chain or cyclic ring bonded to  $Nb_x$ . Until theoretical and spectroscopic investigations of these clusters are undertaken, we cannot tell for sure.

#### D. The reaction of niobium clusters with pyridine and deuterated pyridine

The reaction product spectra of  $Nb_x$  with pyridine and deuterated pyridine showed some similarities with that of benzene. However, more reaction channels were observed for pyridine on account of the more stable products that can be formed.

A spectrum of  $Nb_x$  after reacting with pyridine (with a mole fraction of 0.08) and deuterated pyridine is shown in Figure 3a and 3b, respectively. The use of deuterated pyridine enables us to distinguish between species such as  $C_2H_2$  and  $CN$  which otherwise have identical mass units. For the mono-molecular addition product, only the "total" dehydrogenation product  $Nb_xC_5HN$  ( $Nb_xC_5DN$ ) was observed for  $x \geq 3$ . For small clusters, the multiple molecular addition product and its partial dehydrogenation products as well as products due to the loss of some other molecules were observed. The results can be summarized as follows:

(1) Mono-molecular addition product of the form  $Nb_xC_5H_yN$  ( $y=1, 3, 5$ ) was observed for  $x \geq 1$ . For the niobium monomer, no dehydrogenation was observed for the molecular addition product whereas for the niobium dimer, both  $Nb_2C_5H_5N$  and  $Nb_2C_5H_3N$  were found. The latter was a result of losing one  $H_2$  molecule from the molecular addition product. For  $x \geq 3$ , only  $Nb_xC_5HN$ , the product with maximum extent of loss of molecular hydrogen (or referred to as the "total" dehydrogenation product) was observed. So partial dehydrogenation starts at  $x=2$ , and maximum dehydrogenation at  $x=3$ .

The number threshold for the total dehydrogenation to occur on niobium clusters is therefore shifted from 4 for the reaction with benzene to 3 for the reaction with pyridine.

(2) Bi-molecular addition product ( in which two reactant molecules are added to one niobium cluster molecule ) of the form  $\text{Nb}_x(\text{C}_5\text{H}_5\text{N})(\text{C}_5\text{H}_y\text{N})$  ( $y=1,3,5$ ) was also observed. For  $x=1$ , both  $\text{Nb}(\text{C}_5\text{H}_5\text{N})_2$  and  $\text{NbC}_5\text{H}_5\text{NC}_5\text{H}_3\text{N}$  were observed. Therefore, partial dehydrogenation was observed to start at  $x=1$  for the bi-molecular addition products. For  $x=2$ ,  $\text{Nb}_2\text{C}_5\text{H}_5\text{NC}_5\text{H}_3\text{N}$  was the dominant product. For  $x \geq 3$ , the addition product gave dominantly  $\text{Nb}_x\text{C}_5\text{H}_5\text{NC}_5\text{HN}$ . Again, the maximum dehydrogenation of one of the pyridine molecules was complete by  $x=3$  if one assumes that the loss of  $\text{H}_2$  molecules results from only one of the pyridine molecules.

For each of the bi-molecular addition products, products due to the loss of  $\text{C}_2\text{H}_2$  followed by further dehydrogenation ( loss of  $n\text{H}_2$ ,  $n=1,2$ ) were also observed. For  $x=1$ , strong  $\text{NbC}_5\text{H}_5\text{NC}_3\text{H}_3\text{N}$  (loss of  $\text{C}_2\text{H}_2$ ) and weak  $\text{NbC}_5\text{H}_5\text{NC}_3\text{HN}$  (loss of  $\text{C}_2\text{H}_2+\text{H}_2$  or loss of  $\text{C}_2\text{H}_4$ ) were observed. For  $x=2$ , only  $\text{NbC}_5\text{H}_5\text{NC}_3\text{HN}$ (loss of  $\text{C}_2\text{H}_2+\text{H}_2$  or loss of  $\text{C}_2\text{H}_4$ ) was observed. From  $x=3$  to 5,  $\text{Nb}_x\text{C}_5\text{H}_3\text{NC}_3\text{HN}$  was observed. The product of this form was either due to the loss of  $\text{C}_2\text{H}_2 + 2\text{H}_2$ , the loss of  $\text{C}_2\text{H}_4 + \text{H}_2$  and/or the loss of a  $\text{C}_2\text{H}_6$ . The former is more likely because we observe that more dehydrogenation occurs on larger clusters. Furthermore, in the latter process hydrogen atoms from different pyridine molecules have to come together in order to form a  $\text{C}_2\text{H}_6$  molecule.

(3) For the tri-molecular addition product, relatively strong  $\text{Nb}(\text{C}_5\text{H}_5\text{N})_3$  and  $\text{Nb}(\text{C}_5\text{H}_5\text{N})_2\text{C}_5\text{H}_3\text{N}$  were observed. For  $x=2$ ,  $\text{Nb}_2(\text{C}_5\text{H}_5\text{N})_2\text{C}_5\text{H}_3\text{N}$  was observed. For  $x=3$ ,  $\text{Nb}_3(\text{C}_5\text{H}_5\text{N})_2\text{C}_5\text{HN}$  was observed.

As observed for the bi-molecular addition product, products due to the loss of  $C_2H_2$  followed by further dehydrogenation were also observed for the tri-molecular addition products. For  $x=1$ , relatively strong  $Nb(C_5H_5N)_2C_3H_3N$  was observed. From  $x=2$  to  $x=4$ , weak  $Nb_x(C_5H_5N)_2C_3H_3N$  and  $Nb_x(C_5H_5N)_2C_3HN$  were observed.

In a product of the form  $Nb_x(C_5H_5N)_yC_5HN$  ( $y=1,2$ ), the loss of two  $H_2$  molecules could result from the same pyridine molecule or from two different pyridine molecules. In the former, a "total" dehydrogenated pyridine molecule is formed. In the latter, two partially dehydrogenated pyridine molecules are formed. Further spectral methods are necessary in order to identify these species.

It is interesting to note that in the mono-molecular addition product, the loss of  $C_2H_2$  and other molecules was not observed. However, in the bi- and tri- molecular addition product of the form  $Nb_x(C_5H_5N)_2$  and  $Nb_x(C_5H_5N)_3$ , the loss of  $C_2H_2 + nH_2$  ( $n=0,1,2$ ) were observed for  $x$  ranging from 1 to 4. This is very difficult to explain at the moment. It is possible that the loss of  $C_2H_2$  is photochemically induced which might be more probable for polypyridine cluster products as a result of the higher multiphoton absorption cross section at the ionization laser wavelength. Another explanation might be that fact that the formation of  $C_2H_2$  is such an exothermic channel that unless the cluster is sufficiently large, the cluster products cannot be stabilized in the absence of binary collisions. The presence of an extra one or two pyridine molecules in the cluster could act as a collision partner to stabilize the products of such an exothermic channel.

Although  $NbC_5H_5N$  showed no dehydrogenation as discussed earlier,  $Nb(C_5H_5N)_2$  showed significant dehydrogenation. From Figure 3a, it can be

seen that  $\text{NbC}_5\text{H}_5\text{NC}_5\text{H}_3\text{N}$  is about 40%, and  $\text{Nb}(\text{C}_5\text{H}_5\text{N})_2$  is about 60% of the total bi-molecular addition product intensity. Therefore, the extent of dehydrogenation is not only affected by the size of the metal cluster, but also by the number of the organic molecules in the cluster product.

(4) For the small clusters and their products mentioned above, much less dehydrogenation was found when pyridine was replaced by deuterated pyridine. This can be seen from Figure 3b. This kind of isotope effect was also observed for deuterated benzene before.<sup>40</sup>

From the observation above, it can be seen that the loss of  $\text{C}_2\text{H}_2$  ( $\text{C}_2\text{D}_2$ ) is a very favorable channel in the multiple molecular addition products of Nb clusters with pyridine. In the reaction of  $\text{Nb}_x$  with benzene, this channel was never observed. This is not surprising as pyridine is known to be chemically different from benzene.<sup>48</sup> The presence of nitrogen in the aromatic ring affects the type of bonding of the products with niobium as well as the case by which the ring ruptures.

The above results strongly suggest that the "total" dehydrogenation probability has a niobium number threshold, as was concluded for benzene. If dehydrogenation occurs as a result of boiling off  $\text{H}_2$  to cool the cluster products, then one would expect to observe the loss of  $\text{H}_2$  molecules with a higher probability on smaller than on larger clusters. However, the exothermicity of the reaction depends on the number of C-Nb bonds formed in the reaction product. This increases with  $x$  (the number of atoms in the metal cluster). These opposing effects could lead to a threshold number of  $x \geq 4$ . This number thus arose<sup>34</sup> from the formation of a minimum number of C-Nb bonds needed to energetically drive the reaction. A geometric factor that is

required to activate the proper number of the C-H (C-D) bonds can also be important in determining this number.<sup>34</sup>

#### E. The reaction of $Nb_x$ with 1,5-hexadiyne and 1,3,5-hexatriene

Figure 4a shows a product distribution of  $Nb_x$  when the vapor of 1,5-hexadiyne was seeded in 5 psig He and pulsed into the flow reactor (the mole fraction of 1,5-hexadiyne is 0.2). All of the molecular addition products are apparently dehydrogenated to some extent.

For the mono-molecular addition product, dehydrogenation was observed to start at  $x=1$  and the total dehydrogenation was observed to start at  $x=3$ . The bi-molecular addition product was observed for  $x=1$  and 2. Partial dehydrogenation of the 1,5-hexadiyne molecule was observed with the loss of  $H_2$ ,  $2H_2$ ,  $3H_2$  for the di-molecular addition product. The loss of  $C_2H_2$  and other small molecules were also observed.

For  $x=1$ , up to three hexadiyne molecules were observed in the addition products.  $NbC_6H_4$  was observed which is due to the loss of one  $H_2$  molecule from the original molecular addition product.  $Nb(C_6H_6)_2C_6H_4$ ,  $Nb(C_6H_6)_2C_4H_2$ ,  $Nb(C_6H_6)_2C_4$ ,  $Nb(C_6H_6)_2C_3$ ,  $Nb(C_6H_6)_2C_2$ ,  $Nb(C_6H_6)_2$ ,  $NbC_6H_6C_6H_4$ ,  $NbC_6H_6C_4H_2$ ,  $NbC_6H_6C_4$  were observed for the niobium monomer. Losses of  $H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_4H_6$  were possible to account for the products mentioned above. It is not clear whether the loss of  $C_4H_6$  is a sequential process of losing one  $H_2$  and two  $C_2H_2$  molecules or just a single step of losing one  $C_4H_6$ . It is quite possible that all or most of these products result from the photodecomposition of larger ionic cluster products.



For  $x=2$ ,  $Nb_2C_6H_2$  and  $Nb_2C_4H_2$  were observed. The former is a result of losing two  $H_2$  molecules from the molecular addition product  $Nb_2C_6H_6$ , the latter a result of losing a  $C_2H_4$  or a  $C_2H_2$  and one  $H_2$  from  $Nb_2C_6H_6$ .

For  $x=3$ , about 60% of  $Nb_3C_6H_2$  and 40% of  $Nb_3C_6$  were observed. The product for  $x=4$  was weaker but apparently it had contribution from both  $Nb_4C_6H_2$  and  $Nb_4C_6$ . Starting at  $x=5$ , only the total dehydrogenation product  $Nb_xC_6$  was observed.

Although 1,5-hexadiyne is a structural isomer of benzene, it undergoes partial dehydrogenation much more easily than benzene due to its non-aromaticity. As a result, all of the products were partially or totally dehydrogenated. Also, the loss of small molecules such as  $H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_4H_6$  might be responsible for the observed product distribution. It should be mentioned, however, that if these and the partial dehydrogenation products result from thermal or photodissociation of larger clusters, these results then might suggest that larger cluster product of  $Nb_x$  with 1,5-hexadiyne is less stable to decomposition than the product of  $Nb_x$  with benzene.

Figure 4b shows a spectrum of  $Nb_x$  when the vapor of 1,3,5-hexatriene at room temperature was seeded in 5 psig He and pulsed into the flow reactor. For  $x=1$ ,  $NbC_6H_6$  (strong),  $NbC_6H_4$  (very weak),  $NbC_6H_6C_6H_8$  (weak),  $Nb(C_6H_6)_2$  (strong) and  $NbC_6H_6C_6H_4$  (weak) were observed. The loss of one  $H_2$  molecule is a very favorable channel. For  $x=2$ ,  $Nb_2C_6H_6$ ,  $Nb_2C_6H_4$  and  $Nb_2C_4H_4$  were observed. All of the three mass signals were relatively strong. Weak  $Nb_3C_6H_4$  mass signal was observed for the trimer. Weak  $Nb_4C_6H_4$ ,  $Nb_4C_6H_2$  and  $Nb_4C_6$  were observed for the tetramer. Complete dehydrogenation was observed for all cluster sizes for  $x \geq 4$ .

#### F. Comparison of dehydrogenation probability in the diyne and the triene with benzene

In order to compare the extent of dehydrogenation of 1,5-hexadiyne and 1,3,5-hexatriene with benzene, table 5-1 lists the  $m$  values of the strongest  $Nb_xC_6H_m$  product mass signal intensity for each compound for different cluster size  $x$ .

From this table, one can see that in 1,5-hexadiyne resonance between the  $\pi$ -electrons in the triple bonds is absent, resulting in the lowest hydrogen content in the addition product. On the other hand, benzene has an aromatic structure with strong resonance (i.e. high stability), and its hydrogen content in the addition product is the highest. Furthermore, benzene shows very little dehydrogenation on cluster  $Nb_8$ , whereas all the other compounds do not show this behavior. This suggests that due to the benzene stability, the driving force for the reaction is not sufficiently strong that fluctuations in the cluster stability with size can be detected. 1,3,5-Hexatriene has a  $\pi$ - $\pi$  resonance but is not aromatic, so its hydrogen content in the addition product is in between (the resonance energy of benzene is 36 kcal/mol while the resonance energy of 1,3,5-hexatriene can be estimated to be 10 kcal/mol<sup>48</sup>).

In the reaction of  $Nb_x$  with cyclohexene and cyclohexadiene,<sup>41</sup> only  $Nb_xC_6H_6$  was observed for  $x \leq 3$ . The  $C_6H_6$  species was believed to be benzene. On larger clusters,  $Nb_xC_6H_m$  ( $m=4,2,0$ ) was observed. No product resulting from the loss of  $C_2H_2$  was observed. In this study, 1,5-hexadiyne and 1,3,5-hexatriene were found to undergo differing degrees of dehydrogenation on small clusters ( $x \leq 4$ ) and total dehydrogenation on larger clusters. Further, products resulting from the loss of  $C_2H_2 + H_2$  were observed

as a new reaction channel which was not found in the reaction of niobium clusters with the cyclic hydrocarbons. If not due to the differences in the cluster temperature, this observation could be due to the fact that both cyclohexene and cyclohexadiene can dehydrogenate to form a very stable benzene molecule, while 1,5-hexadiyne and 1,3,5-hexatriene cannot fold over to form a stable benzene molecule on small niobium clusters. The fact that on larger clusters  $Nb_xC_6$  was observed in the reactions with cyclohexene and cyclohexadiene as well as with 1,5-hexadiyne and 1,3,5-hexatriene might suggest that on large niobium clusters, the stability and the structure of the final product is more important in determining the outcome of the reaction channel than that of the reactant. On the other hand, different reaction channels were observed on small niobium clusters ( $x \leq 4$ ) for the cyclic and chain hydrocarbons. This suggests that the stability and the structure of the reactant and product are important in determining the final product distribution. Therefore, the relative importance of the factors governing the reaction process might change as the size of the metal cluster changes.

The reactivity of metal clusters and the dehydrogenation of an organic molecule are obviously affected by the structure of the metal cluster and the structure of the organic compound as well as that of the product. After understanding all of the details of these reactions, it might be possible to establish a systematic way to probe the change in the structure of the metal clusters. The probing molecules should not be too reactive or too inert, otherwise the structure change in metal clusters as a function of cluster size might not be observed. This technique is not expected to be as powerful as the structural measuring techniques such as the X-ray diffraction or electron diffraction,<sup>49</sup> but in the absence of such studies at the moment, probing

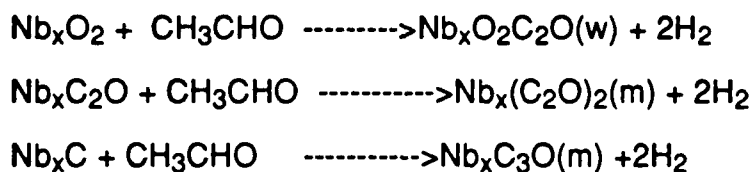
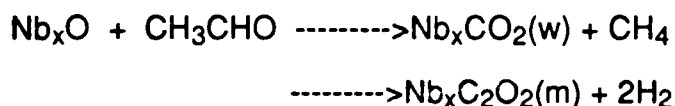
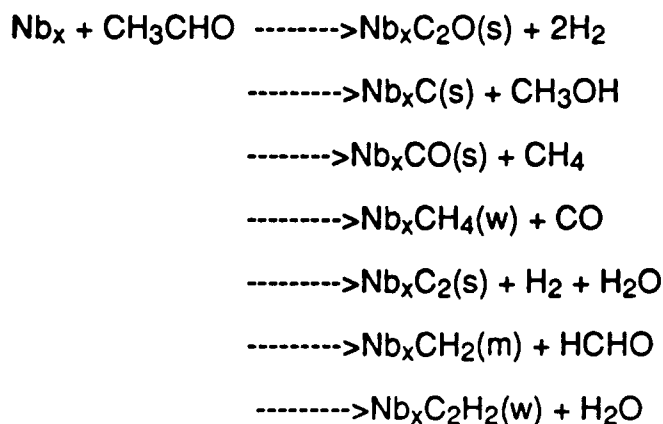
structural changes by changes in chemical reactivity is shown to be useful.<sup>35,50</sup>

#### G. The reaction of $Nb_x$ with acetaldehyde ( $CH_3CHO$ )

Figure 5 shows a mass spectrum of niobium clusters and their reaction products with acetaldehyde (with a mole fraction of 0.3). In this spectrum, many products are observed.

For  $x=1$ , no product was found. For  $x=2$ ,  $Nb_2C$  (loss of  $CO+2H_2$ ),  $Nb_2CH_2$  (loss of  $CO+H_2$ ),  $Nb_2CH_4$  (loss of  $CO$ ),  $Nb_2C_2$  (loss of  $H_2+H_2O$ ),  $Nb_2C_2H_2$  (loss of  $H_2O$ ) and  $Nb_2CO$  (loss of  $CH_4$ ) were all observed. All of these products result from many different reaction channels. For larger clusters, other new product channels were observed beside the ones mentioned above. For example, for  $x=3$ ,  $Nb_3C_2O$ , as well as  $Nb_3C_3O$ ,  $Nb_3OC_2O$ ,  $Nb_3O_2C_2O$  and  $Nb_3(C_2O)_2$  were observed. The observation of  $Nb_3(C_2O)_2$  and  $Nb_3C_3O$  suggests reactions of  $Nb_x$  with at least two  $CH_3CHO$  molecules. It is not certain whether or not the molecular addition product of the form  $Nb_xCH_3CHO$  was produced as the mass peak of this product overlaps with that of  $Nb_xCO_2$ . Isotopic substituted  $CD_3CDO$  would help to clarify this problem.

The product formation channels can be summarized in the following equations: (s, m, and w indicate the relative product intensity being strong, medium or weak, respectively)



The above equations present only some of the possible processes that can account for the observed mass peaks. Indeed, all the stable molecules (  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{HCHO}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  ) are observed to be released from the reaction adduct, suggesting that the channels forming these products are energetically similar. Since no structural information is available, the product written as  $\text{CH}_3\text{OH}$ , could be  $\text{CO} + 2\text{H}_2$  or  $\text{HCHO} + \text{H}_2$ .

## Conclusions

The reactions of benzene derivatives and unsaturated non-aromatic hydrocarbons provide some insight into the dependence of the reaction product distributions and the possible reaction mechanisms on the reactant structure. The dehydrogenation probability is found to depend on the size of niobium cluster as well as on the structure and stability of the organic molecule. Substituted benzenes such as chlorobenzene and benzonitrile form molecular addition type reaction products followed by dehydrogenation to different extents which depends on the size of the niobium cluster. In the reaction of  $Nb_x$  with pyridine, products due to the loss of  $C_2H_2$  ( $C_2D_2$ ) and  $H_2$  are important channels for the multiple molecular addition products, suggesting the opening of the aromatic ring. Due to the non-aromaticity and lack of resonance in 1,5-hexadiyne, cluster products due to the loss of  $C_2H_2$ ,  $C_3H_6$  and  $H_2$  are also observed to be important reaction channels. In the reaction of  $Nb_x$  with acetaldehyde, all of the reaction channels leading to the formation of stable molecules e.g.  $H_2$ ,  $CO$ ,  $CH_3OH$ ,  $HCHO$ ,  $H_2O$  and  $CH_4$  are observed. This suggests that in this case, stable product formation drives the reaction. All of the above results suggest that the reactivity of the metal clusters is determined not only by the structure and stability of the metal clusters but also by those of the reagent molecules and the final product molecules.

## Acknowledgment

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Table5-1 A list of the m values of the strongest Nb<sub>x</sub>C<sub>6</sub>H<sub>m</sub> product mass signal intensity as a function of cluster size.

| compounds        | m value as a function of cluster size |     |     |     |   |   |   |   |
|------------------|---------------------------------------|-----|-----|-----|---|---|---|---|
|                  | x= 1                                  | 2   | 3   | 4   | 5 | 6 | 7 | 8 |
| 1,3,5-hexatriene | m= 6                                  | 4,6 | 4   | 4   | 0 | 0 | 0 | 0 |
| 1,5-hexadiyne    | m= 4                                  | 2   | 0,2 | 0   | 0 | 0 | 0 | 0 |
| benzene          | m= 6                                  | 6   | 6   | 0,6 | 0 | 0 | 0 | 6 |

## Figure Captions

**Figure 1a.** A mass spectrum of  $Nb_x$  after reacting with chlorobenzene in the flow reactor (with a mole fraction of 0.01). Numerical numbers indicate the value of  $x$  in  $Nb_x$ . The products labelled P1 are  $Nb_2C_6HCl$ ,  $Nb_3O$ , and  $Nb_2C_6H_3Cl$ , respectively. Products labelled P are  $Nb_xC_6HCl$  and  $Nb_{x+1}O$  with  $x=3, 4, 5, 6$  from left to right, respectively. Satellite peaks on the right of each peak labelled "P" are  $Nb_xO_2$  and  $Nb_xO_3$ , respectively. This also applies to all of the other figures where these satellite peaks are not labelled due to spatial congestion.

**1b.** A mass spectrum of  $Nb_x$  after reacting with benzonitrile ( $C_6H_5CN$ ) in the flow reactor (with a mole fraction of 0.002). Each number set in this figure indicates the  $x, y, z$  values in  $Nb_xC_yH_z$ . Product labelled C is the partial dehydrogenation product  $Nb_3C_7H_3N$ . D is the "total" dehydrogenation product  $Nb_5C_7HN$ .  $Nb_2M$  and  $NbM_2$  stand for  $Nb_2C_6H_6CN$  and  $Nb(C_6H_6CN)_2$ , respectively. Peaks labelled "I" are due to contamination of pyrimidine in the flow reactor.

**Figure 2.** A mass spectrum of  $Nb_x$  after reacting with pyrimidine. Relatively strong product  $NbC_2H_2N_2$  (due to the loss of  $C_2H_2$  from  $NbC_4H_4N_2$ ) was observed on the far left of the mass spectrum. The number sets ( $x,y,z$ ) indicate the  $x, y, z$  values in  $Nb_xC_yH_zN_2$ .

**Figure 3a.** A mass spectrum of niobium clusters after reacting with pyridine in the flow reactor (with a mole fraction of 0.08). Each number x indicates the value of x in  $Nb_x$ . Each number set (x, y, z, w) indicates the values of x, y, z, w in  $Nb_xC_yH_zN_w$ . For example, the number 1,15,15,3 represents  $Nb(C_5H_5N)_3$ . After losing one  $H_2$  molecule, it is presented by 1,15,13,3.

**3b.** Similar to 3a, but with deuterated pyridine at low concentration (with a mole fraction of 0.02). All numbers have the same meaning as explained for 3a.

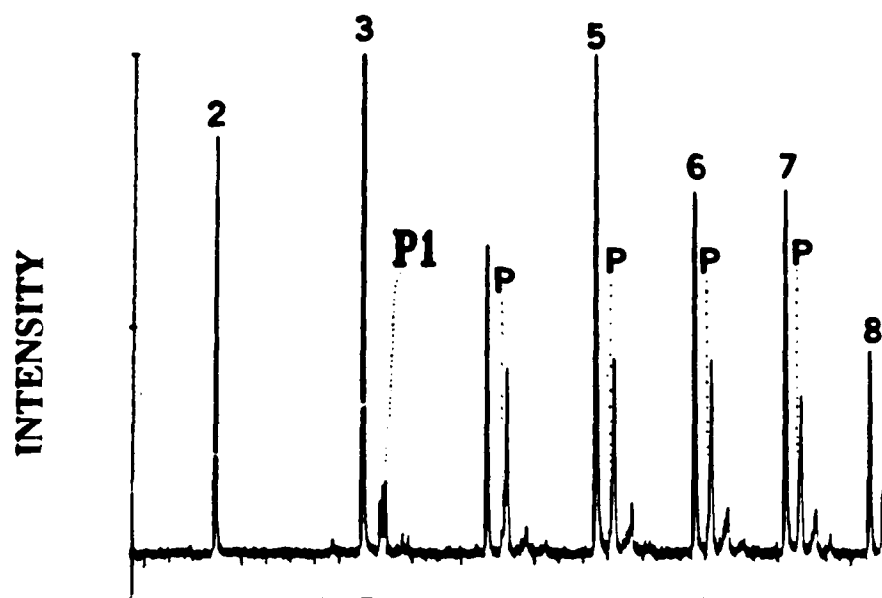
**Figure 4a.** A mass spectrum of  $Nb_x$  after reacting with 1,5-hexadiyne. The number set (x,y,z) indicates the values of x, y, z in  $Nb_xC_yH_z$ . Each number x indicate the x value in  $Nb_x$ . Products labelled a, b, c, d, e are  $Nb_2C_6H_2$ ,  $Nb(C_6H_6)_2C_2$ ,  $Nb(C_6H_6)_2C_3$ ,  $Nb(C_6H_6)_2C_4H_2$ ,  $Nb_3C_6H_2$ , respectively.

**4b.** A mass spectrum of  $Nb_x$  after reacting with 1,3,5-hexatriene Each number x indicates the x value in  $Nb_x$ . Each set of numbers of (x,y,z) indicates the values of x, y, z in  $Nb_xC_yH_z$ .

**Figure 5.** A mass spectrum of  $Nb_x$  after reacting with  $CH_3CHO$ . Not all the products are labelled due to the spatial limitation. The letters in the figure represent:

a:  $Nb_2C$ ; b:  $Nb_2C_2H_2$ ; c:  $Nb_2CH_4$ ; d:  $Nb_2C_2$ ; e:  $Nb_2C_2H_2$ ; f:  $Nb_2CO$ ; g:  $Nb_3C_3O$ ; h:  $Nb_3OC_2O$ ; i:  $Nb_3O_2C_2O$ ; j:  $Nb_3(C_2O)_2$ .

(a)  $\text{Nb}_x + \text{Chlorobenzene}$



(b)  $\text{Nb}_x + \text{C}_6\text{H}_6\text{CN}$

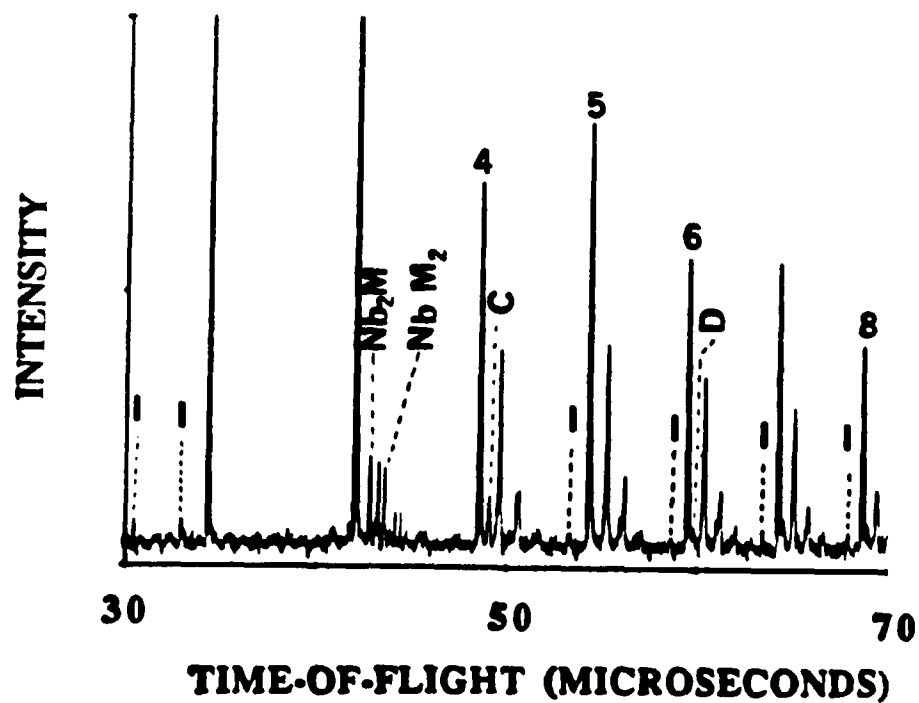


Figure 1

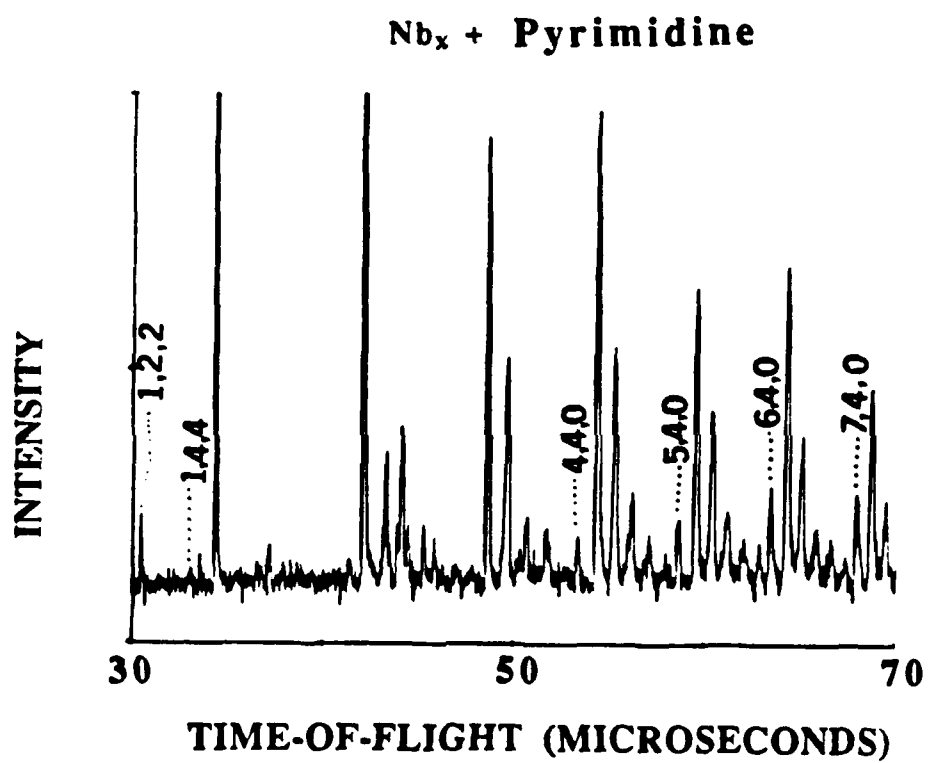
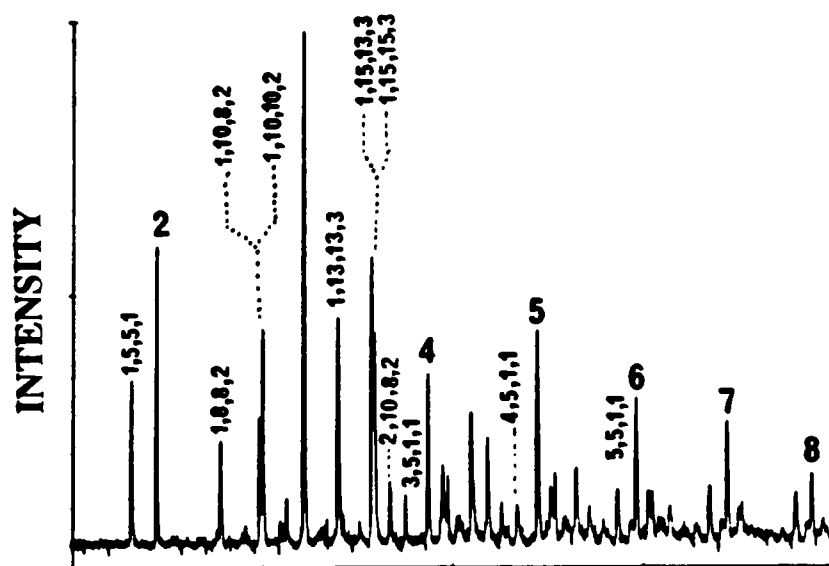


Figure 2

**(a) Nb<sub>x</sub> + Pyridine**



**(b) Nb<sub>x</sub> + Deuterated Pyridine**

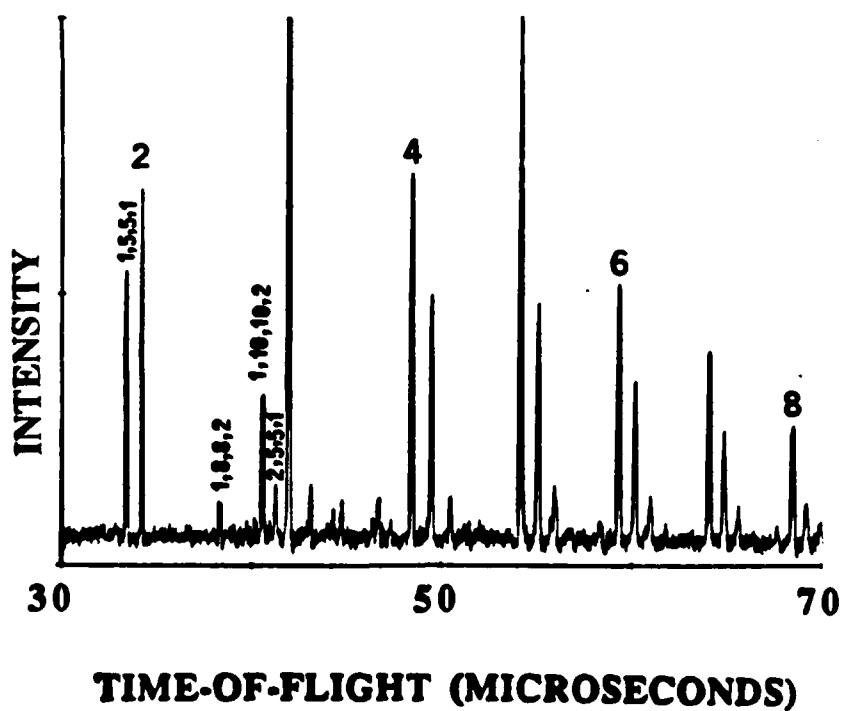


Figure 3



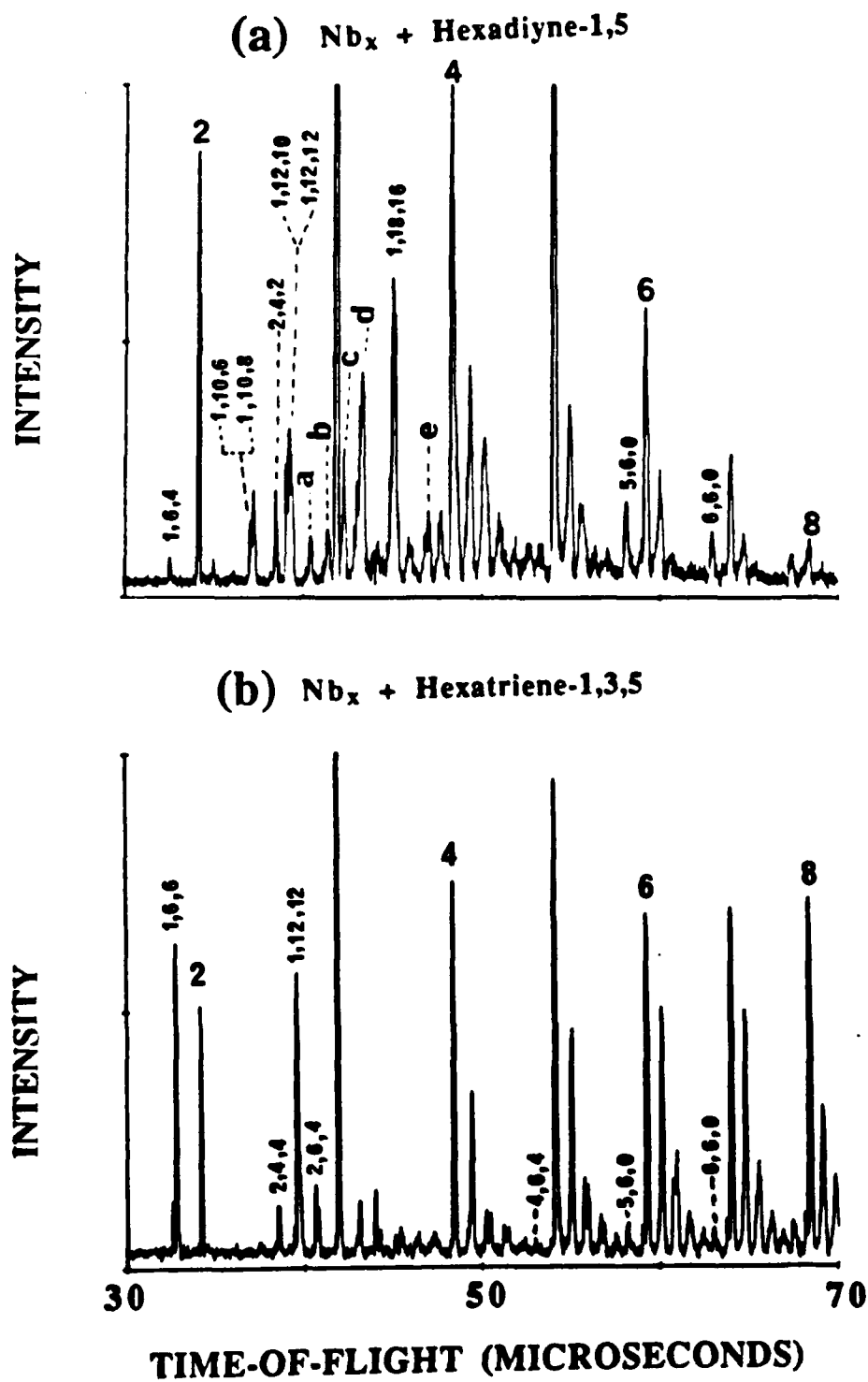


Figure 4



Figure 5

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