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Reactions of niobium cluster ions $Nb_x^{\pm}$ ($x = 2$–16) with NO and NO_2

Qifei Wu, Shihe Yang*

Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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Abstract

Gas phase niobium cluster ions, $Nb_x^{\pm}$ ($x = 2$–16), are subjected to reactions with NO and NO_2 in a fast-flow reactor. For cationic niobium clusters, the difference mass spectra for the reactions demonstrate that dissociative chemisorption and molecular adsorption take place in different cluster size regimes. Detailed analysis of the reaction products suggests that the cluster cations are fragmented into two parts in the small cluster range: the nitrogen retained clusters and the niobium oxide species. The relative reactivity of the cluster cations shows a decreasing trend with increasing cluster size. The reactions of the anionic niobium clusters with NO and NO_2 are also studied. The results are discussed in terms of electron transfer reactions. Cluster fragmentation is also extensively observed. (Int J Mass Spectrom 184 (1999) 57–65) © 1999 Elsevier Science B.V.

Keywords: Niobium cluster ions; Reactions; Dissociative chemisorption; Molecular adsorption

1. Introduction

Transition metal clusters are considered capable of providing a good model for understanding the nature of the reactive sites in heterogeneous catalysis. The advent of laser vaporization technique coupled with supersonic expansion [1] resulted in an extensive study on the reactivity of transition metal clusters [2–31]. Niobium clusters have been a prototypical system for studying the reactions of transition metal clusters during the past 15 years. Their reactions with a series of molecules have been studied regarding the reaction patterns and the trend in reactivity. A general observation is that all these attributes show a strong dependence on the cluster size with an overall-increasing trend with increasing cluster size [27]. Attempts were made to correlate the relative reactivity patterns to the ionization potentials and geometries of niobium clusters [6,8,15]. Evidence of isomers for niobium clusters was obtained for some sizes from the reaction kinetics studies [3,4,14,32].

A particularly interesting finding from the reactions of niobium clusters with some molecules is that niobium clusters can be divided into two size regimes according to their reaction behavior toward these molecules (small clusters: $x < \sim 7$; large clusters: $x > \sim 7$). For example, the study on the reaction of Nb_x with BrCN showed that the stereochemical affinity of the clusters oscillates wildly for small clusters ($x < 8$), but almost does not change for large clusters [11]. For the reactions of Nb_x^+ with CO_2, chemisorption products were observed only for small clusters ($x < 7$); the chemisorption proceeds by ejecting CO and forming oxidized niobium cluster cations. On the

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* Corresponding author. E-mail: chsyang@ust.hk

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other hand, only physisorption products were observed for large clusters [30]. This reaction pattern was also found to hold for the neutral niobium clusters [10]. For reactions of Nb_x^+ with saturated hydrocarbons, Bondybey et al. demonstrated that chemisorption occurs only to small clusters ($x < 7$), whereas no reaction was observed for large clusters [21]. We showed further that physisorption can occur to large clusters without leading to any chemisorption [31]. Although it is not clear at present as to why the reaction behavior divides the clusters into the two size regions, it is likely that both thermodynamic and kinetic factors have to be considered.

In this work, we present further examples demonstrating the competition between chemisorption and molecular adsorption in different cluster size regions. We explored the reactions of niobium cluster ions toward NO and NO_2 by using a fast-flow reactor, coupled with a laser vaporization cluster source and a reflectron time-of-flight (TOF) mass spectrometer. Through a comparison between a blank experiment with reactant gas off and a reaction experiment with reactant gas on, the product distribution, the relative reactivity, and the reaction mechanism of the cluster reactions were studied. Our results revealed again that two different reaction patterns (chemisorption and molecular adsorption) of niobium cluster cations toward NO and NO_2 fall into two cluster size regions ($x < 7$ and $x > 7$), respectively.

2. Experimental

The fast-flow tube used in this work was described previously [31]. The overall setup is shown in Fig. 1. The niobium clusters were produced by focusing a pulsed excimer laser beam (308 nm, Lambda Physik, Goettingen) on a 0.1 mm diameter spot of a 3 mm diameter niobium rod (Pure Tech., Inc., Carmel, NY, 99.95%) with a lens ($f = 50$ mm). The niobium rod was translating and rotating driven by a stepper motor (200 steps per revolution). The plasma plume was carried downstream by ultrahigh purity helium (99.999%, 132 psi) from a pulsed valve (R. M. Jordan Co., Grass Valley, CA), and confined in a 2 mm diameter channel for cluster growth. After exiting from the clustering channel, the clusters arrived at the fast-flow tube where they were collided by the reactant gas molecules. The reactant gas NO or NO_2 mixed in argon (99.995%, 5 psi) was introduced into the flow reactor by another pulsed valve (General Valve, Fairfield, NJ, Series 9). After reaction, the parent and the product clusters expanded into a high vacuum chamber with an operating pressure of 3×10^{-6} Torr and were collimated by a 2 mm diameter skimmer (Beam Dynamics, Minneapolis, MN) positioned 10 mm downstream from the exit of the fast-flow reactor.

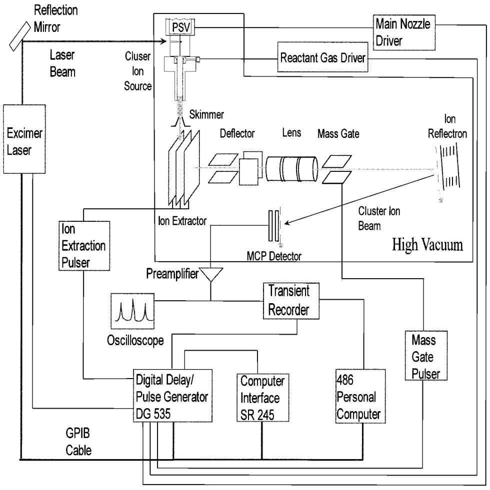

Fig. 1. Schematic of the experimental setup for studying the reactions of niobium cluster ions with NO and NO_2.

The cluster ion beam was extracted vertically and accelerated by a two-mode high voltage pulser (~1000 V): positive mode for cation detection and negative mode for anion detection. The extracted cluster ions were steered by a set of vertical and horizontal deflectors, reflected by a reflectron block, and finally detected by a dual microchannel plate detector (MCP) [33]. The vacuum in the detector region was kept on the scale of 10^{-7} Torr. The signals from the MCP were further amplified by a Model SR445 preamplifier (Stanford Research, Sunnyvale, CA) and digitized by an F903 fast transient recorder (USTC, China). The data were transferred to and stored in a PC-486. A typical TOF mass spectrum was obtained based on an average of over 100–300 experimental cycles. The mass resolution of the reflectron TOF mass spectrometer is estimated to be ~1000. All sequential timing pulses were generated by a Model DG535 delay generator (Stanford Research, Sunnyvale, CA) that was also controlled by the PC-486.

3. Results and discussion

3.1. Reactions of niobium clusters with NO

3.1.1. Positive cluster ions, Nb_x^+ ($x = 2$–15)

Comparative experiments were carried out with and without NO in the reaction tube to examine the depletion of the parent cluster peaks and the appearance of the reaction product peaks. A control mass spectrum was obtained when pure argon was driven into the reaction tube, and a product mass spectrum was recorded when the NO/Ar mixture was allowed to react with Nb_x^+. The total pressure in the reaction tube was kept the same for both the control and reaction experiments. The concentration of NO was varied from 1% to 10% to obtain a suitable product distribution for kinetic studies. When the control mass spectrum was subtracted from the product mass spectrum, a difference mass spectrum ($I_{\text{reagent on}}$–$I_{\text{reagent off}}$), shown in Fig. 2, was obtained. Apparently, the dominant products for small cluster cations ($x < 8$) are dissociative chemisorption products, e.g. Nb_xN^+ that grow with increasing cluster size until $x = 6$. However, the products for larger cluster cations ($x > 8$) are dominated by molecular adsorption products, e.g. $Nb_x^+(NO)$, whose intensity exceeds that of Nb_xN^+ at $x = 9$. Closer examination of the spectra (see inset of Fig. 2) revealed other minor product peaks including $Nb_xN_2^+$ ($4 \leq x \leq 8$), $Nb_xN_2O^+$ ($x \geq 6$), $Nb_xNO_2^+$ ($x \geq 6$), and $Nb_x(NO)_2^+$ ($x \geq 8$).

The collision of a niobium cluster cation with a nitric oxide molecule is likely to form an intermediate complex, e.g.

$$Nb_x^+ + NO \rightarrow (Nb_xNO)^{+*} \tag{1}$$

There are many possible pathways for the decay of the intermediate complex. For example, the reaction of Nb_2^+ with NO may follow the following paths:

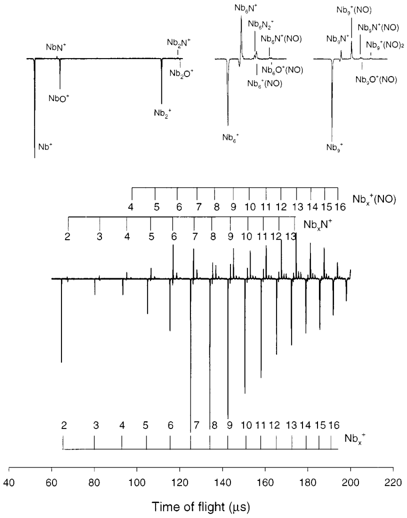

Fig. 2. A typical difference mass spectrum for the reaction of Nb_x^+ ($x = 2$–16) with NO. It is obtained by subtracting the spectrum with the reagent gas on (10% NO mixed in argon) from the spectrum with the reagent gas off (pure argon). The difference spectrum in the regions of Nb^+, Nb_2^+, Nb_6^+, and Nb_9^+ are enlarged in the insets to show the dependence of the products on the cluster size.

$$\text{Nb–Nb}^+ + \text{N–O} \rightarrow [Nb_2^+NO]^* \rightarrow$$

$$Nb_2^+ + NO \text{ (no reaction)} \tag{2a}$$

$$NO^+ + Nb_2 \text{ (electron transfer)} \tag{2b}$$

$$Nb_2^+(NO) \text{ (molecular adsorption)} \tag{2c}$$

$$Nb_2^+O + N \text{ (dissociative chemisorption 1)} \tag{2d}$$

$$Nb_2^+N + O \text{ (dissociative chemisorption 2)} \tag{2e}$$

$$Nb^+(NO) + Nb \text{ (fragmentation-molecular adsorption 1)} \tag{2f}$$

$$Nb^+ + Nb(NO) \text{ (fragment-molecular adsorption 2)} \tag{2g}$$

$$NbN^+ + NbO \text{ (fragment-dissociative chemisorption 1)} \tag{2h}$$

$$NbO^+ + NbN \text{ (fragment-dissociative chemisorption 2)} \tag{2i}$$

The energetics is likely to be the main factor in dictating the final products (Tables 1 and 2). Our data

Table 1
BDEs of some chemical bonds, and IPs and EAs of some relevant species (All values are in eV; All the data are taken from Ref. [37] except those specified otherwise)

Chemical bonds or species	BDE	IP	EA
Nb	. . .	6.76	0.893
Nb–Nb	5.19 [16]	6.2 [32]	. . .
Nb–Nb^+	5.87 [16]	. . .	. . .
Nb–O	7.7	7.91 [34]	. . .
Nb–O^+	6.55[a]	. . .	. . .
Nb–N	4.50[b] $\leq$ 5.53 [34]	7.91 [34]	. . .
Nb–N^+	5.65[b] $\leq$ 6.56 [34]	. . .	. . .
Nb–C	5.7	. . .	. . .
N═O (NO)	6.3	9.3	0.026
O–NO (NO_2)	3.0	. . .	2.273
C═O (CO)	10.8	14.0	. . .
O═CO (CO_2)	5.3	. . .	. . .
N≡N (N_2)	9.4	. . .	. . .
O═O (O_2)	5.0	12.1	0.451
$(NO)_2$	. . .	. . .	≥2.1

[a] D_0(Nb–O^+) are calculated as D_0(Nb–O^+) = D_0(Nb–O) –IP(NbO) + IP(Nb).

[b] The calculations for the lower limits of Nb–N and Nb–N^+ BDEs are given in the text.

indicate that the intermediate complex cannot be stabilized until the cluster size of Nb_x^+ reaches $x > 8$, where extensive molecular adsorption reactions occur on the cluster surface. Channel (2e) is not probable because it involves the breakage of the strong N–O bond [bond dissociation energy (BDE) = 6.3 eV, Table 2] and the formation of a somewhat weaker Nb–N bond (see Table 1). Furthermore, because the Nb–O bond is stronger than the Nb–N bond by as much as 2 eV, dissociative chemisorption would favor the ejection of the N atom, which is contrary to our observation. We therefore believe that the fragment-dissociative chemisorption 1 (2h) should be the main reaction channel. In this connection, it is useful to mention a related work accomplished by Bowers et al. [34]. They studied the reactions of Nb_2^+ with NO by using a drift cell reactor and identified the following channels:

$$Nb_2^+ + NO \rightarrow NbN^+ + NbO\ (50\%) \tag{3a}$$

$$\rightarrow NbO^+ + NbN\ (50\%) \tag{3b}$$

Our data are consistent with this result, but we did not observe the fragment-dissociative chemisorption channel [(2i) or 3(b)], perhaps because of further reactions of NbO^+ in the present experiment. The observation of $Nb_xN_2^+$ indicates that this reaction can continue, e.g.

$$Nb_{x-1}N^+ + NO \rightarrow Nb_{x-2}N_2^+ + NbO \qquad (4 \leq x \leq 8) \tag{4}$$

Similar fragment-dissociative chemisorption was also found for the reaction of Nb_x^+ with O_2 by Bowers et al. [20] and Armentrout et al. [35]. The result was explained by the fact that the Nb–O bond (7.7 eV) is much stronger than the O═O bond (5.0 eV), which

Table 2
BDEs, IPs, and EAs of niobium clusters [All values are in eV; $D_0(Nb_{n-1}^+–Nb)$ are taken from Ref. [16]; $D_0(Nb_{n-1}–Nb)$ are calculated as $D_0(Nb_{n-1}–Nb) = D_0(Nb_{n-1}–Nb) + IP(Nb_n)–IP(Nb_{n-1})$; $D_0(Nb_{n-1}^-–Nb)$ are calcualted as $D_0(Nb_{n-1}^-–Nb) = D_0(Nb_{n-1}–Nb) + EA(Nb_n)–EA(Nb_{n-1})$; $IP(Nb_n)$ are taken from [32]. The lower IP of the isomers is adopted; $EA(Nb_n)$ are taken from [38]. The data are estimated from PES]

n	$D_0(Nb_{n-1}^+–Nb)$	$D_0(Nb_{n-1}–Nb)$	$D_0(Nb_{n-1}–Nb)$	$IP(Nb_n)$	$EA(Nb_n)$
2	5.87	5.19	. . .	6.20	. . .
3	5.01	4.62	. . .	5.81	1.10
4	6.00	5.83	5.83	5.64	1.10
5	5.61	5.42	6.07	5.45	1.75
6	5.68	5.61	5.61	5.38	1.75
7	6.53	6.50	6.47	5.35	1.72
8	5.93	6.11	5.94	5.53	1.55
9	5.78	5.17	. . .	4.92	. . .
10	6.05	6.61	. . .	5.48	. . .
11	6.01	5.27	. . .	4.74	. . .

favors the fragment-dissociative chemisorption. But for other molecules such as CO and N_2, this type of reactions is not favorable because of the extremely strong bonds of the reagent gas molecules relative to the BDEs of Nb–N, Nb–C, and Nb–N.

Because reaction (2h) occurs spontaneously, by using the data in Tables 1 and 2, we obtain: $\Delta H = -D_0(\text{Nb–N}^+) - D_0(\text{Nb–O}) + D_0(\text{Nb–Nb}^+) + D_0(\text{N–O}) \leq 0$. Furthermore, $D_0(\text{Nb–N}^+) \geq 4.50$ eV, and $D_0(\text{Nb–N}) = D_0(\text{Nb–N}^+) + \text{IP(Nb–N)} - \text{IP(Nb)} \geq 5.65$ eV (IP stands for ionization potential).

As for the larger clusters ($x \geq 8$), their larger surface areas and more internal degrees of freedom would help to stabilize the intermediate complex, resulting in molecular adsorption without breaking the bonds of N–O or $[\text{Nb}_{x-1}\text{–Nb}]^+$. Indeed, the molecular adsorption was found to start at $x = 4$, but it is not until $x = 9$ that the intensity of $\text{Nb}_x^+(\text{NO})$ takes over that of Nb_xN^+ and molecular adsorption becomes the dominant channel. From our experimental observations, $\text{Nb}_x^+(\text{NO})$ peaks also showed the typical molecular adsorption characteristic—going up at high reactant gas concentration (10%) and dropping at low reactant gas concentration (1%). For the larger clusters ($x \geq 8$), even dimolecular adsorption products are visible, which are produced presumably by the collision of the primary intermediate complex with another nitric oxide molecule, and followed by stabilization.

The products Nb_xNO_2^+ and $\text{Nb}_x\text{N}_2\text{O}^+$ could be considered as being from the following reactions:

$$\text{Nb}_x\text{O}^+ + \text{NO} \rightarrow \text{Nb}_x\text{O}^+(\text{NO}) \qquad (x \geq 6) \qquad (5)$$

$$\text{Nb}_x\text{N}^+ + \text{NO} \rightarrow \text{Nb}_x\text{N}^+(\text{NO}) \qquad (x \geq 6) \qquad (6)$$

$$\text{Nb}_x(\text{NO})_2^{+*} \rightarrow \text{Nb}_x\text{N}^+(\text{NO}) + \text{NbO} \qquad (x \geq 6) \qquad (7)$$

Fig. 3 plots the relative reactivity of Nb_x^+ toward NO as a function of cluster size. The calculation of the relative reactivity is based on the extent of depletion of the parent Nb_x^+ because of the reaction ln ($I_{\text{reagent on}}/I_{\text{reagent off}}$), assuming a pseudo-first-order reaction kinetics. Interestingly, the reactivity of Nb_x^+ decreases with increasing cluster size for small clusters ($x = 2–10$), but increases slowly with cluster size for larger clusters ($x = 10–16$). The decreasing reactivity with increasing cluster size we observed is in contrast to the reaction behavior of many other reagents, e.g. CO, N_2, etc. This unusual result could be traced to the dependence of the reaction products on the cluster size. Clearly, fragment-dissociative chemisorption dominates for the small clusters ($x = 2–7$), whereas molecular adsorption takes over for the large clusters ($x = 9–16$). Because larger clusters have larger surface areas and more internal degrees of freedom, the lifetime of the intermediate complexes may be sufficiently long to dissipate the excess energies of the intermediate complexes without breaking the N–O bond.

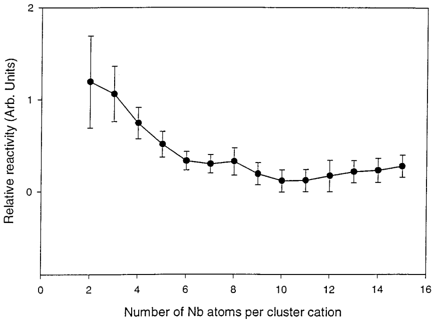

Fig. 3. The relative reactivity of Nb_x^+ ($x = 2–16$) toward NO as a function of cluster size. The error bars are based on an average of ten independent experiments under the same reaction conditions. The data of each experiment are the average of 100 laser shots with the reagent gas on and another 100 laser shots with the reagent gas off.

3.1.2. *Negative cluster ions, Nb_x^- ($x = 5–16$)*

The difference mass spectra for the reactions between Nb_x^- and NO at two different concentrations of the nitric oxide mixed in argon are shown in Fig. 4. At the lower concentration ($< 1\%$), the dominant product is NO_2^-. At the higher NO concentration (10%), however, the major products are the oxidized cluster anions, e.g. NbO_2^-, NbO_3^-, Nb_2O_5^-, and Nb_2O_7^-. A plausible explanation is based on surface reactions of NO molecules on the anionic metal clusters Nb_x^- [reactions (8) and (9)], leading to the production of abundant NO_2^- species.

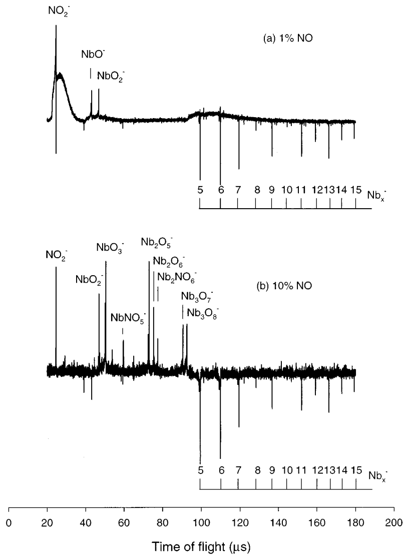

Fig. 4. Difference spectra for the reaction of Nb_x^- ($x = 2$–15) with NO mixed in Ar (NO/Ar = 1% and 10%, respectively).

$$Nb_x^- + NO \rightarrow [Nb_xNO]^{-*} \quad (8)$$

$$[Nb_xNO]^{-*} + NO \rightarrow NO_2^- + Nb_xO \quad (9)$$

This reaction is understandable considering the fact electron affinity (EA) [$(NO)_2$] $\gg$ EA [Nb_x] (Table 1). When the NO concentration is sufficiently high, even the reaction between NO_2^- and Nb_x is possible, e.g.

$$Nb_x + NO_2^- \rightarrow Nb_{x-1}O_2^- - NbN \quad (10)$$

$$Nb_{x-1}O_2^- + NO \rightarrow Nb_{x-2}O_3^- + NbN \quad (11)$$

Further similar reactions may lead to an extensive niobium oxide anions $Nb_xO_y^-$.

The relative reactivity of Nb_x^- toward NO as a function of cluster is plotted in Fig. 5 for $x = 5$–16. Unlike the cluster cations, the reactivity of Nb_x^- displays an increasing trend in a zigzag manner with increasing cluster size (see Fig. 5). This demonstrates that the reaction patterns are quite different for clusters of different charge states. Another message from Fig. 5 is that the even-numbered clusters are more inert, and an extreme case is provided by Nb_{10}^-. This appears to correlate with the observation that the even-numbered clusters have a lower intensity in the mass spectra of Fig. 4.

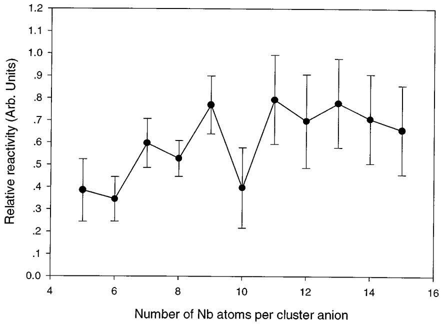

Fig. 5. The relative reactivity of Nb_x^- ($x = 5$–15) toward NO as a function of cluster size. The error bars are based on an average of ten independent experiments under the same reaction conditions. The data of each experiment are the average of 100 laser shots with the reagent gas on and another 100 laser shots with the reagent gas off.

3.2. Reactions of niobium clusters with NO_2

Understandably, the reactivity of NO_2 toward Nb_x^+ was found to be higher than that of nitric oxide. With the concentration of roughly 10% NO_2, both the parents and the products could not be observed because of the thorough depletion of the niobium cluster cations through extensive reactions. Normally, the concentration was controlled to be below 1% and the reagent nozzle pulse width was carefully adjusted to avoid excessive reactions.

A typical difference mass spectrum is presented in Fig. 6. For the reaction of small cluster cations ($x < 11$) with NO_2, the major products Nb_xO^+ and Nb_xNO^+ may be from the following dissociative chemisorption processes:

$$Nb_x^+ + NO_2 \rightarrow (Nb_xNO_2)^{+*} \rightarrow Nb_xO^+ + NO \quad (12)$$

$$\rightarrow Nb_{x-1}NO^+ + NbO \quad (13)$$

It is interesting that the reaction (12) is very similar to what occurs in the reaction of Nb_x^+ with CO_2 [30]. On the other hand, the reaction (13) is analogous to that between Nb_x^+ and NO.

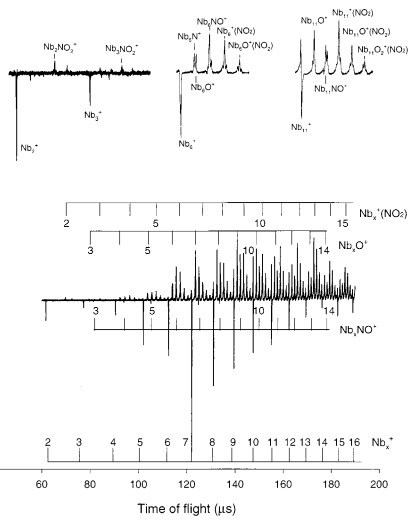

Fig. 6. A typical difference mass spectrum for the reaction of Nb_x^+ ($x = 2$–16) with NO_2 mixed in argon (1%). The details in the regions of Nb_2^+, Nb_3^+, Nb_6^+, and Nb_{11}^+ are enlarged in the insets to show the dependence of the products on cluster size.

As shown in Fig. 6, Nb_xN^+ were also observed with a decreasing intensity as x increases, and their intensities are comparable to those of Nb_xO^+ only for small clusters ($n < 8$). One would speculate that this product may be from the reaction between Nb_x^+ and NO with NO being from reaction (12). Further analysis indicates that some mass peaks appear to be associated with the molecular adsorption products, with $Nb_2NO_2^+$ being the most prominent one. We believe, however, that this species may have a structure such as $Nb_2^{2+}(NO_2)^-$ that is not a simple molecular adsorption complex. As the cluster size increases up to $x = 11$, the intensity of the molecular adsorption products exceeds that of the dissociative chemisorption products. In much the same way as for the reaction of Nb_x^+ with NO, the more degrees of freedom of the larger cluster cations are believed to allow the complex to be stabilized, forming the molecular adsorption products without fragmentation.

For the reactions between Nb_x^- and NO_2, the difference mass spectra are shown in Fig. 7 for different concentrations of NO_2. At lower concentration of NO_2 (0.1%), the dominant channel is via electron transfer, forming NO_2^-. This electron transfer reaction could be observed even with a very small amount of NO_2 in the fast-flow reactor. We attribute this to the fact that the EA of NO_2 (2.273 eV, see Table 1) is quite high compared to niobium clusters as well as other simple gas molecules (including NO), thus NO_2 acts as a strong electron acceptor. At higher concentration (1%), niobium–oxygen composite cluster anions $Nb_xO_y^-$ are formed, possibly consisting of blocks of NbO_2, NbO_3, etc. Similar structures of niobium cluster oxides were observed by Castleman et al. for niobium oxide cluster cations [36]. These multiple oxide products may be ascribed to successive reactions of (12).

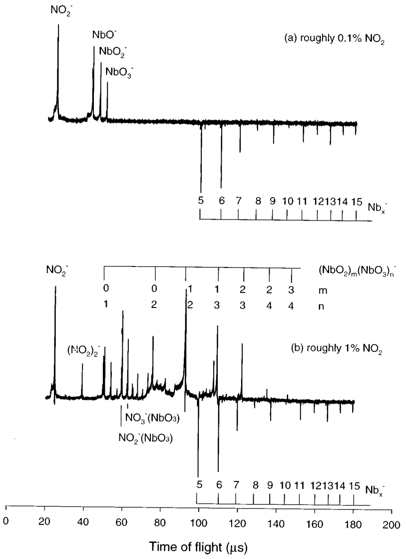

Fig. 7. Difference mass spectra for the reaction of Nb_x^- ($x = 2$–15) with NO_2 mixed in argon ($NO_2/Ar = 0.1\%$ and 1%, respectively).

4. Conclusion

We have identified two pathways for the reactions of cationic niobium clusters with NO. They are fragment-dissociative chemisorption reactions for the small clusters ($x < 8$) and molecular adsorption reactions for the larger clusters ($x \geq 8$). As the cluster size increases, the abundance of the dissociative chemisorption products decreases, accompanied by an increase of the abundance of the molecular adsorption products. This is explained by the fact that larger clusters have larger surface areas and more internal degrees of freedom for the stabilization of the intermediate complex, leading to the molecular adsorption type products. The relative reactivity of the cationic niobium clusters is found to decrease with increasing cluster size for small clusters, but increase slowly with increasing cluster size for large clusters. This is accounted for by the dominance of the relatively fast fragment-dissociative chemisorption reactions in the small cluster size range and the molecular adsorption reactions in the large cluster size range. The reaction of anionic niobium clusters with NO is dominated by electron transfer reactions from the cluster anions to the nitric oxide molecules to form an abundant NO_2^- moiety. Cluster fragmentation to NbO_2^-, $Nb_2O_5^-$, etc. was also observed. The relative reactivity of the anionic clusters is found to increase with increasing cluster size.

The reactivity of niobium cluster ions toward NO_2 appears to be higher than that toward NO. Even with the relatively low concentrations, the reactions could still be observed. For the cationic clusters Nb_x^+, the fragment-dissociative chemisorption channel with NbO elimination and the simple dissociative chemisorption channel with NO ejection compete with each other in the small cluster size range. When the cluster size reaches $x > 11$, the molecular adsorption reactions take over. For the anionic clusters, the reaction leads to the formation of the stable niobium oxide cluster anions with building blocks of NbO_2, NbO_3, etc. The electron transfer reactions are always observed, even with rather low reagent concentrations.

Acknowledgements

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