Theoretical Studies of Structures and Energetics of Benzene Complexes with Nb$^+$ and Nb$_2^+$ Cations

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Ab initio calculations of the ground and excited states have been carried out for the Nb$_n^+$−benzene ($n = 1$, 2) complexes and for the reaction products Nb$_n$C$_6$H$_4^+$ and NbC$_6^+$ using state-of-the-art computational techniques. It is found that the chemical bonds in Nb$_n$C$_6$H$_6^+$ complexes are formed as a consequence of electronic density transfer from the π electrons of benzene to the Nb metal. This process has significant impact on the benzene ring and leads to the destruction of aromaticity for the Nb$_2$C$_6$H$_6^+$ complex. The reaction products that contain dehydrogenated benzene exhibit σ bonds that are formed at the sites where the metal replaces hydrogens. The formation of the "physisorbed" Nb$_n$C$_6$H$_6^+$ complex has been found as a preferable channel for the Nb$_n^+$ reactions with benzene for small values of n considered here. Our computed energetics for the physisorbed and chemisorbed species are extensively compared with the Fourier transform ion cyclotron resonance mass spectrometric study of Bondybey and co-workers. Our theoretical results support the experimental observations on the "cooling" of the reaction products through the evaporation of H$_2$ from the surface of the cluster and also the relative stabilities of chemisorbed and physisorbed species.

I. Introduction

A primary reason for the increased interest in the reactivity of transition metal clusters with hydrocarbons is that such reactivity studies could provide valuable insight into heterogeneous catalysis. Many industrially important reactions rely on catalysis, although the catalytic processes are still far from being understood at the microscopic level. Transition metals are the most widely employed catalysts. The initial process in heterogeneous catalysis is the adsorption of the reactant molecules on the catalyst surface, and consequently, the study of the interaction between the reactant and the transition metal surface could provide vital insight into heterogeneous catalysis. Generally, the adsorbing reactants on surfaces exhibit two kinds of characteristics called "physisorption" and "chemisorption". The two features have been often juxtaposed in experiments. The former involves no change to the structure of the reactants and generally less binding compared to the latter, while the latter involves actual removal of some atoms from the reactants during adsorption. Consequently, in the former case the adsorbed molecule may be desorbed through thermal energy if the bonding is not very strong.

Metal clusters represent simplified model systems that facilitate the study of elementary reaction steps in heterogeneous catalysis at the microscopic level, since the surface−reactant interaction is often local in nature, involving an atom to a few atoms on the surface. Transition metal clusters, their properties, and reactivities have been studied as a function of their composition, size, and charge.[1−32] The experimental results, however, often lack information on geometric and electronic structures of the clusters and how these features influence the nature of interactions.[3] Theoretical studies can thus provide very valuable information for modeling such reaction mechanisms.

The reactions of neutral and positively charged niobium clusters with benzene have received considerable attention and

have been studied with a number of techniques such as fast flow reactor[4−8] and drift cell experiments.[9] The Fourier transform ion cyclotron resonance (FT-ICR) mass spectroscopic technique was developed by Marshall and Komisarov[33,34] and subsequently used by Smalley and co-workers[32] who have employed this method in conjunction with an external laser vaporization source. This technique was used by the authors to study the reactions of Nb clusters with H$_2$ as a function of cluster size.

Bondybey and co-workers[3] have recently employed the FT-ICR technique to study the gas-phase reactivity of Nb$_n^+$ cluster cations with a variety of hydrocarbons[3] under single-collision conditions. In particular for the reaction with benzene, these authors find that the smaller clusters of Nb$_n^+$ yield long−lived "physisorption" products, while the larger Nb cluster ions yield fully dehydrogenated Nb$_n^+$C$_6$ carbides. Two channels were observed with size-dependent branching ratios. The rate of the reaction was found to fall steeply and the degree of dehydrogenation to increase with the cluster size. These experimental findings differ from those of El-Sayed and co-workers[6−8] for neutral niobium clusters and the fast flow reactor experiments of Kaldor, Cox, and co-workers[4,5] as well as drift cell experiments. The studies employing high-pressure fast flow reactors[5] detect physisorbed Nb$_n$C$_6$H$_6^+$ and chemisorbed Nb$_n$C$_6$H$_4^+$ complexes. But the FT-ICR experiment[3] exclusively produces chemisorbed complexes for larger values of n. It should be noted that while there are essentially no secondary collisions in the FT-ICR, in the flow reactor and drift tube experiments such collisions do occur and that collisional stabilization may affect the observed product distribution. Since there are no high-resolution gas-phase experimental spectroscopic or structural studies on such systems, theoretical calculations provide useful information for unequivocal interpretation of the experimental data. A recent ab initio study of the interaction of benzene with

5802 *J. Phys. Chem. A, Vol. 103, No. 29, 1999*

Roszak et al.

Rh$_n^+$ cations[10] has shown the usefulness of theoretical approaches in facilitating valuable interpretations of experimental findings.[11]

The ab initio studies of Nb$^+$ and Nb$_2^+$ interactions with benzene are the focus of the present paper. The study deals with investigations of structural, energetic, and bonding aspects of both chemisorbed and physisorbed complexes of Nb$^+$ and Nb$_2^+$ with benzene. A variety of structures and their energies are considered and optimized at different levels of theory. The reaction products were studied in detail with an attempt to interpret reaction pathways different from the minimum energy geometries and the enthalpies of different channels.

II. Methods of Computation

The computations presented here have been performed by applying the complete active space multiconfiguration self-consistent field (CAS-MCSCF), multireference singles and doubles configuration interaction (MRSDCI), and density functional theory (DFT)[12] techniques. The DFT work used Becke's three-parameter functional[13] with the local correlation part provided by Vosko, Wilk, and Nusair[14] and the nonlocal part by Lee, Yang, and Parr[15] (in short, B3LYP). The geometry searches were made using the Berny algorithm.[16] All the calculations were carried out using relativistic effective core potentials (RECPs), which retained the outer $4s^2 4p^6 4d^4 5s^1$ shells of Nb in the valence space.[17] For carbon, RECPs that retained the outer 2s and 2p shells in the valence space[18] were employed. The most diffuse exponents in the original basis sets were left uncontracted, leading to 5s3p2d and 3s3p valence basis sets for Nb and C, respectively. The carbon basis set was supplemented with a set of six-component 3d Gaussian functions proposed by Dunning and Hay.[19] Van Duijneveldt's[20] (4s) basis set contracted to 2s was employed for the hydrogen atom. This choice of basis sets leads to 146 and 172 atomic basis functions for the Nb$^+$−benzene and Nb$_2^+$−benzene complexes, respectively.

The dissociation energy for the benzene−Rh$^+$ complex was studied within the CASMCSCF approach. The active space consists of molecular orbitals corresponding to the 4d and 5s atomic orbitals of Nb and the highest occupied molecular orbitals of benzene. This constitutes four a$_1$, two b$_2$, two b$_1$, and one a$_2$ orbitals. Ten electrons were distributed in all possible ways among these nine molecular orbitals. In all, six a$_1$, four b$_1$, four b$_2$, and two a$_2$ orbitals containing 32 electrons were kept inactive. No excitations were allowed from these orbitals, but they were allowed to relax. Configuration interaction calculations were carried out following the CASMCSCF calculations using the multireference singles and doubles method to include higher-order electron correlation effects. The MRSDCI calculations included up to 1.5 million CSFs.

The DFT calculations were carried out using the GAUSSIAN-94 package of codes.[21] All CASMCSCF and MRSDCI computations were made using a modified version of Alchemy II[22] to include RECPs.[23]

III. Results and Discussion

A. Geometrical and Electronic Structure of the Nb−Benzene and Nb$^+$−Benzene Complexes. The geometry of the benzene molecule was optimized for comparison with experimental results. The carbon−carbon bond lengths of 1.398 Å and the carbon−hydrogen bonds of 1.091 Å are in an excellent agreement with the experimental values of $r(C−C) = 1.397 \pm 0.005$ and $r(C−H) = 1.084 \pm 0.005$ Å.[24] The calculated ionization potential of 6.9 eV for Nb agrees with the experi-

TABLE 1: Geometries and Energy Separations (ΔE) for the Various Low-Lying Energy States of the Nb−Benzene and Nb$^+$−Benzene Complexes[a]

| state | symmetry | geometrical parameters (Å) | | | | ΔE (eV) |
		a	b	c	d	
		NbC$_6$H$_6$				
^{2}A$_1$	C_{6v}	1.444		2.240		0.0
^{4}A$_1$	C_{2v}	1.461	1.415	2.321	2.427	0.36
^{6}B$_1$	C_{2v}	1.421	1.412	2.607	2.681	1.12
		NbC$_6$H$_6^+$				
^{3}A$_1$	C_{2v}	1.458	1.417	2.284	2.379	0.0
^{5}B$_1$	C_{2v}	1.423	1.413	2.522	2.575	0.68
^{1}A$_1$	C_{6v}	1.437		2.237		0.73
^{7}B$_2$	C_{2v}	1.372	1.464	2.906	3.039	4.85

[a] Refer to Figure 1 for the definition of $a−d$ parameters.
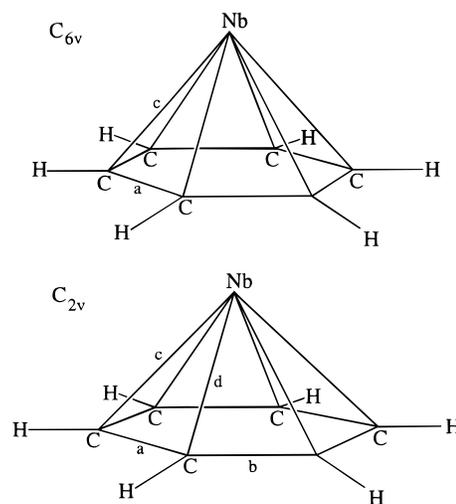
Figure 1. Schematic representations of C_{6v} and C_{2v} structures of the Nb−benzene and Nb$^+$−benzene complexes. The optimized values of $a−d$ can be found in Table 1.

mental value of 6.76 eV.[25] This comparison provides a calibration for the accuracy of the basis sets and the DFT technique used.

The atomic states of Nb were computed to gauge the accuracy of the DFT technique. The DFT method yields the ground state of Nb to be a ^{6}D state arising from the $4d^4 5s^1$ electronic configuration, consistent with the experimental atomic data.[35] The ^{4}F electronic state arising from the $4d^3 5s^2$ configuration is 1490 cm^{-1} above the ^{6}D state at the DFT level, compared to the experimental value of 2450 cm^{-1} obtained using the spin-averaged atomic spectra data.[35] The excited state of Nb is thus computed reasonably well compared to the experimental atomic data.

The results of geometry optimization of the benzene complexes with both neutral Nb and Nb$^+$ positive ion are given in Table 1 and Figure 1. The optimized geometry for the Nb−benzene complex has C_{6v} symmetry (Figure 1) with a ^{2}A$_1$ electronic state. The dissociation energy of the complex for the removal of Nb in the ground electronic state is 143.3 kJ/mol. Although the electronic distribution, as inferred by the Mulliken population analysis, is almost unchanged, the C−C bonds of the benzene ring are elongated by 0.05 Å and the hydrogens are pushed out of plane toward Nb by 2°. The lowest ^{4}A$_1$ excited electronic state is formed by the Jahn−Teller distortion of the ^{4}E state of the molecule, resulting in a distorted C_{2v} structure.

The geometrical structures of the Nb$^+$ complexes with benzene are similar to the Nb−benzene molecular structures, although the enthalpy of formation of the charged complex is

Benzene Complexes

J. Phys. Chem. A, Vol. 103, No. 29, 1999 **5803**

about twice the value of the neutral complex. The ground state of the charged complex is the $^3A_1$ electronic state, which arises from the Jahn−Teller distortion of an ^3E state with a C_{6v} geometry resulting in a distorted C_{2v} geometry. On the other hand, the $^1A_1$ electronic state exhibits a higher C_{6v} symmetry because of a closed-shell configuration and is thus undistorted. These two electronic states are lower in energy compared to other states such as $^3A_1$ with an electronic configuration of $b_1{}^2b_2{}^2a_2{}^2a_1{}^1a_1{}^1$ and the $^5B_1$ state $(b_1{}^2b_2{}^2a_2{}^1a_1{}^1a_1{}^1b_2{}^1)$. The energy separation between these two states is small, and the $^5B_1$ state could be a viable candidate for the ground state. The quintet state (^5E) has been found as the ground state in the C_{6v} symmetry by a modified coupled-pair functional (MCPF) study.[26] Clearly, this state should undergo Jahn−Teller distortion. We also computed the geometry and the energy of the undistorted C_{6v} structure to gain insight into the extent of Jahn−Teller distortion. The Jahn−Teller distortion energy was computed as 0.15 eV for the triplet electronic state and 0.46 eV for the quintet electronic state at the DFT level of theory. Our undistorted C_{6v} geometry is quite close to the one reported in ref 26. Our Nb− ring distance is 2.120 Å, compared to 2.129 Å,[26] our C−C distances are 1.415 Å, compared to 1.421 Å[26] while our C−H distances are 1.089 Å, compared to 1.074 Å.[26] Thus, the geometry of the undistorted structure agrees quite well, although the distortion energy is significant for this state (0.46 eV), which was not addressed in ref 26. The corresponding Nb−C, C−C, and C−H distances for the triple electronic state of the undistorted geometry are 2.322, 1.429, and 1.089 Å, respectively.

The dissociation energy of the Nb$^+$−benzene complex has been computed as 276.6 kJ/mol by the DFT calculations in excellent agreement with an experimental value of 276 ± 29 kJ/mol[27] determined from collision-induced dissociation (CID) experiments. The dissociation energies calculated at the CASMC-SCF and MRSDCI levels of theory are 186.0 and 250.4 kJ/mol, respectively. The inclusion of the Davidson correction after the MRSDCI calculations (MRSDCI + Q) yields a value of 271.6 kJ/mol, close to the experimental CID value. The previous MCPF calculations yielded a D_e of 217.9 kJ/mol.[26]

The chemical bond is formed because of electronic charge transfer from the π electrons of benzene to vacant orbitals of Nb$^+$. The atomic charge of Nb$^+$ was reduced to only 0.4 electron. The niobium cation interacts slightly with the hydrogens, which are moved out of the plane toward Nb$^+$ by 4°. The above results indicate the importance of the inclusion of correlation effects for the proper reproduction of energetics. Although excellent agreement between the DFT(B3LYP) technique and the experimental CID measurement is somewhat accidental, it is apparent that the DFT approach is a reliable tool to study the processes considered in this work. The structures of the Nb complexes with benzene are reminiscent of the Pt[28] and Rh[10] benzene complexes studied earlier.

B. Interaction of Nb$_2{}^+$ with Benzene. Three possible structures were found as optimal structures for the Nb$_2{}^+$−benzene complex, all with C_{2v} symmetries (Figure 2). Two of the candidates for the ground state are separated by only 0.32 eV (Table 2). Both of these states are doublets with equilibrium structures in which Nb$_2{}^+$ is parallel to the benzene plane. The corresponding quartet states are higher in energy. As seen from Figure 2c, a C_{6v} structure in which Nb$_2{}^+$ is perpendicular to the benzene plane is the equilibrium structure for the ^4E electronic state, although this state is considerably higher in energy. The corresponding doublet state is distorted to a C_{2v} geometry because of the Jahn−Teller effect.
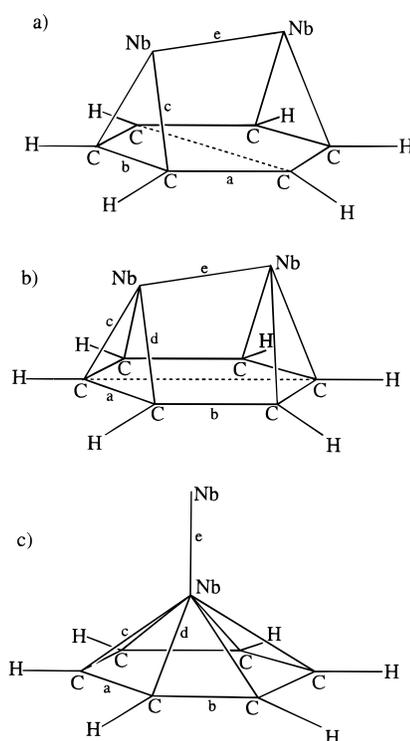
Figure 2. Schematic representations of different C_{2v} structures for Nb$_2{}^+$−benzene complexes. The optimized parameters a−e can be found in Table 2.

TABLE 2: Geometries and Energy Separations (ΔE) for the Various Low-Lying Energy States of the Nb$_2{}^+$−Benzene Complex^a

| structure | state | geometrical parameters | | | | | ΔE (eV) |
		a	b	c	d	e	
in Figure 2a	$^2B_1$	1.432	1.467	2.082		2.373	0.0
	$^4A_1$	1.453	1.414	2.341		2.287	0.86
in Figure 2b	$^2B_1$	1.425	1.439	2.286	2.449	2.269	0.32
	$^4A_1$	1.425	1.439	2.282	2.509	2.390	0.88
in Figure 2c	^4E	1.415	1.415	2.683		2.201	1.53
	$^2A_1$	1.429	1.435	2.347	2.338	2.093	2.62

^{a} Refer to Figure 2 for the definition of a−e parameters.

The dissociation energy to separate Nb$_2{}^+$ from the complex (252.9 kJ/mol) is similar to the value obtained for the Nb$^+$−benzene complex. The bonds are formed because of charge transfer from the π electrons of benzene to the vacant d orbitals in the Nb$_2{}^+$ ion. Although the charge transfer is not large (0.13 electron for the structure in Figure 2a and 0.34 electron for the structure in Figure 2b), it has a localized character and consequently destroys the aromaticity of the benzene ring. The ring is 2-fold bent with angles of 170 and 152° for the doublet and quartet states, respectively, for the structure in Figure 2a. The C_6 ring in the Figure 2b is also puckered with a dihedral angle of 169 and 168° for the doublet and quartet states, respectively. The Nb$_2{}^+$−benzene complex in which the benzene ring is perpendicular to Nb$_2{}^+$ is very similar to that of the Nb$^+$−benzene complex.

C. Interaction of Nb$_n{}^+$ with Dehydrogenated Benzene. The FT-ICR experimental work of Bondybey and co-workers[3] on the reactions of Nb$_n{}^+$ with benzene has revealed some interesting trends. In particular, the reactions of Nb$^+$ and Nb$_2{}^+$ lead often to dehydrogenation of benzene to form the Nb$_n$C$_6$H$_4{}^+$ cations, while larger Nb$_n{}^+$ clusters dehydrogenate benzene completely. To make comparisons with experimental studies on the reactions
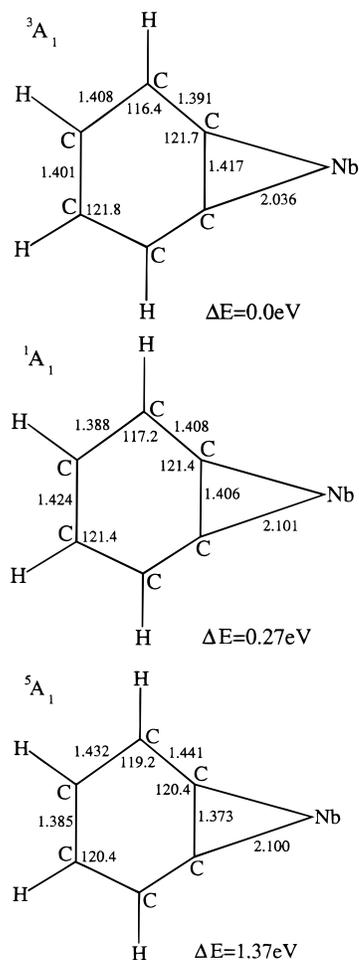
Figure 3. Structures of $NbC_6H_4^+$ for ground and low-lying electronic excited states. The cations exhibit C_{2v} symmetry. The excitation energy (ΔE) is given in electronvolts. Distances are in angstroms and angles in degrees.

Figure 4. C_{2v} structures of $Nb_2C_6H_4^+$. The excitation energy (ΔE) is given in electronvolts relative to the lowest structure. Distances are in angstroms and angles in degrees.

Figure 5. Linear structures of NbC_6^+ complexes. The excitation energy (ΔE) is given in electronvolts. Distances are in angstroms and angles in degrees.

of Nb_n^+ with benzene, we have studied dehydrogenated products or the chemisorbed products.

The ground state of $NbC_6H_4^+$ exhibits a flat structure with C_{2v} symmetry as shown in Figure 3, where Nb^+ completely replaces two hydrogen atoms of benzene. Two viable candidates for the ground state, namely, $^3A_1$ and $^1A_1$ states, are found. The states with higher spin multiplicities are considerably higher in energy. On the other hand, two nearly degenerate electronic states are found for $Nb_2^+-C_6H_4$ shown in Figure 4. The reaction of Nb_2^+ with benzene leads to the dissociation of Nb_2^+; one Nb atom replaces two hydrogens, as in $NbC_6H_4^+$, while the second atom forms a bond through the π electrons of benzene and is attached above the benzene ring, as shown in Figure 4.

Bondybey and co-workers found totally dehydrogenated $Nb_nC_6^+$ species in the FT-ICR experiment for $n > 4$. On the other hand, other types of experiments such as ion drift tube experiments[29] have yielded single Nb^+-carbon cluster complexes. There is also considerable interest in metal$-$carbide clusters. Detailed theoretical studies are available for the carbide clusters of Y and La atoms,[30,31] namely, YC_n and LaC_n.

Several possible electronic states and geometries were considered for the NbC_6^+ ion. The linear and ring structures were expected to be attractive candidates for the ground states on the basis of our previous studies on YC_6 and LaC_6.[30,31] The optimization of the ring structures could result in planar isomers that contain several Nb$-$C bonds. The energetically lowest isomers for the nonlinear structures were the ones that contained

Nb inserted into the carbon rings. The geometries of different arrangements were optimized. Among all such electronic states and structures, a linear structure shown in Figure 5 with a $^3\Sigma^-$ state is the lowest in energy, as seen from Figure 5. A $^3B_1$ electronic state with a ring structure in which Nb is inserted into a ring and is a part of a six-membered ring shown in Figure 6 is the first excited electronic state of NbC_6^+. The $^1\Sigma^+$ linear state is 0.87 eV above the triplet ground state (Figure 5), while other electronic states with ring geometries (Figure 6) are higher in energy.

The chemical bonds between Nb and C in these species are formed as a consequence of charge transfer from the metal to the carbon cluster. The Mulliken population analyses indicate that the charge transfer to the carbon chain is 0.15 electron in linear structures and 0.4 electron in the case of ring complexes. The absorbed electronic density is mostly localized on the carbon atoms directly connected to Nb.

D. Comparison with FT-ICR Experiment of Nb_n^+ ($n = $ 1, 2) Cluster Reactions with Benzene. As indicated before, a primary motivation for this study is the experimental FT-ICR work of Bondybey and co-workers[3] for the reactions of Nb_n^+ with benzene. A striking feature as a function of the cluster size is that the smaller clusters react with partial dehydrogenation while larger clusters form physisorbed complexes with benzene, which undergo rearrangement to yield totally dehydrogenated $Nb_nC_6^+$ carbide ions. Among the smaller clusters, Nb^+ and Nb_2^+ yielded mainly $NbC_6H_4^+$ and $Nb_2C_6H_4^+$ while Nb_3^+ and Nb_4^+

Benzene Complexes

J. Phys. Chem. A, Vol. 103, No. 29, 1999 **5805**
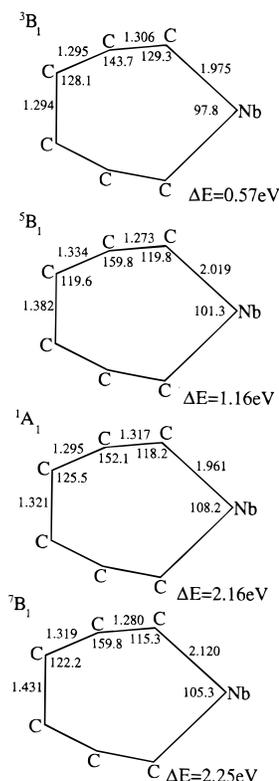
Figure 6. Ring structures for NbC_6^+ complexes. The excitation energies (ΔE) are measured from the $^3\Sigma^-$ ground state. Distances are in angstroms and angles in degrees.

yield $Nb_nC_6H_2^+$ ($n = 3, 4$). Clusters larger than four atoms of Nb yielded totally dehydrogenated carbide clusters. Some of these findings of Bondybey and co-workers differed from other experimental studies such as the drift reactor studies and the fast flow reactor[5] studies. For example, Bowers et al.[9] found a reaction channel yielding $Nb_4C_6H_4^+$ for the interaction of Nb_4^+ with benzene. Bondybey and co-workers[6-8] did not observe this channel. Bondybey and co-workers observed an additional reaction channel with 18% of the total rate corresponding to

$$Nb_4^+ + C_6H_6 \rightarrow Nb_4C_5H^+ + H_2 + CH_3$$

The observations of Bondybey and co-workers also differed from the observations of El-Sayed and co-workers on the neutral clusters.

It would be desirable to shed light on the various experimentally observed channels through our theoretical computations. In particular, our computed results on the structures and energetics of the various species discussed up to now can be utilized to obtain the enthalpies of the reactions associated with the various experimental channels. Although the explanation of the experimentally observed effects through elementary processes seems to be possible, it is complicated because of secondary processes, the presence of low-lying electronic states, and the possibility of extensive vibrational motions. The main difference between the results of the fast flow reactor and FT-ICR experiments is that the physisorbed $Nb_nC_6H_6^+$ complexes are not detected in the FT-ICR experiment. The only exceptions among larger clusters are for cluster sizes $12-19$ and 22, which seem to exhibit a parallel physisorption channel in addition to the chemisorption channel observed in these and other cases.

Bondybey and co-workers have qualitatively rationalized their observed results with a model of potential energy surfaces where a physisorbed minimum is first formed by $Nb_n^+ + C_6H_6$. This

potential energy curve crosses the curve arising from the $Nb_n^+ + C_6 + 3H_2$ dissociation. The crossing results in a barrier, and after the barrier a deep well that corresponds to a chemisorption minimum of $Nb_nC_6^+$ is formed. Thus, a collision of Nb_n^+ with benzene under high vacuum conditions could lead either to the dissociation of the collision complex without any reaction or to the formation of the inner well, especially since Nb forms very stable carbides. The other possibility is that the kinetic energy may be redistributed into internal vibrational modes of the cluster or the low-frequency vibrations of benzene. The strong size dependence of the reaction for larger clusters was attributed by Bondybey and co-workers to kinetic factors rather than thermodynamic factors. The appearance of the physisorbed complexes near $n = 19$ in the FT-ICR experiment was considered surprising by Bondybey et al., since in the absence of ternary collisions the complex may dissociate as they contain enough energy, and thus, fully dehydrogenated carbide clusters would be preferred. However, the product distribution of the smaller clusters would be controlled primarily by thermodynamic factors in very good agreement with the overall energetics and stabilities of the species computed here.

The fast flow reactor experiments of Zakin et al.[4,5] exhibit considerable amounts of $Nb_nC_6H_6^+$ clusters for n less than 10, and for $n = 8$ and 9 the clusters were found to exhibit physisorbed features. However, Bondybey and co-workers do not observe such complexes for these n values, and the smallest n for which physisorbed clusters were found is 11. Bondybey and co-workers rationalize this by assuming that the "warm" physisorbed clusters formed in the primary steps are "cooled" through additional collisions. In the absence of such stabilization, the statistical probability of dissociation of the complex should follow RRKM theory, suggesting strong size dependence, which was not observed by Bondybey and co-workers for larger clusters.

The most obvious difference between the experimental environments is pressures in the cells. The FT-ICR experiment is performed under vacuum conditions,[3] while the fast flow experiment is performed under high pressure.[5] We believe that the overall quality of our computations should be sufficient for at least a qualitative representation of these reactions. The possible reactions and their computed energies are shown below. For the Nb^+−benzene reactions we compute the enthalpies for the reactions as follows:

$$Nb^+ + C_6H_6 = NbC_6H_6^+ \qquad \Delta E = -267.7 \text{ kJ/mol} \qquad (1a)$$

$$= NbC_6H_4^+ + H_2 \qquad \Delta E = 46.5 \text{ kJ/mol} \quad (1b)$$

$$= NbC_6^+ + 3H_2 \qquad \Delta E = 766.4 \text{ kJ/mol} \quad (1c)$$

The enthalpies for reactions involving Nb_2^+ cluster are computed as

$$Nb_2^+ + C_6H_6 = Nb_2C_6H_6^+ \qquad \Delta E = -252.9 \text{ kJ/mol} \quad (2a)$$

$$= Nb_2C_6H_4^+ + H_2 \quad \Delta E = -22.3 \text{ kJ/mol} \quad (2b)$$

$$= NbC_6H_6 + Nb^+ \qquad \Delta E = 55.8 \text{ kJ/mol} \quad (2c)$$
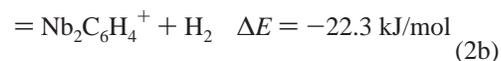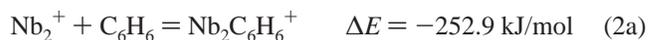
The computed enthalpies for the above reactions indicate that thermodynamically the most favorable reaction channel for $Nb_n^+(n = 1, 2)$ leads to the physisorbed complex. The reaction in which one H_2 molecule is evaporated from the system is much less favorable. However, as mentioned above, warm physisorbed

Roszak et al.

clusters formed in the primary steps must be cooled and stabilized. The probability of the collision in the case of the FT-ICR experiment is very small, and the complex may only dissociate or be stabilized by the release of an H_2 molecule. Cooling due to collisions is possible in the fast flow experiment, and the physisorbed species are observed under those conditions.[5] It was also observed that at higher temperatures, the "chemisorbed" ($Nb_nC_6H_4^+$) species were observed in higher concentration, indicating that cooling through the evaporation of hydrogen from the metal cluster surface is more probable. The chemisorbed species, when formed, are quite stable, and the dissociation energies of the $Nb_nC_6H_4^+$ cations are 372.7 and 437.7 kJ/mol for $n = 1$ and 2, respectively.

These computed results are fully consistent with the FT-ICR spectroscopic study of Bondybey and co-workers. That is, the $Nb(C_6H_2)^+$ and $Nb_2(C_6H_2)^+$ products are highly endothermic and are thus not observed experimentally. That is, the products do not contain adequate energy to evaporate a second H_2 molecule. The lack of significant formation of $NbC_6H_6^+$ computed to be the lowest channel is probably a consequence of the fact that in the absence of collisions, the transiently formed complex cannot be stabilized and thus dissociates.

IV. Conclusions

In this investigation, we have computed the structural properties and energetics of $Nb_nC_6H_6^+$, $Nb_nC_6H_4^+$ ($n = 1, 2$) and NbC_6^+ complexes using state-of-the-art quantum chemical methods. Detailed comparisons have been made with several experimental findings on the reactions of niobium clusters with benzene. The computed results are in excellent agreement with the experimental data. The ground and the lowest excited states were optimized. The low-lying electronic states are very close to the ground state, and we suggest that they could be involved in the experimentally studied processes. The possible geometrical structures lead to a complicated vibrational picture.

Niobium cations form complexes with benzene because of the chemical bond involving π electrons of benzene and the vacant d orbitals of the metal atoms. The electron density transfer has significant impact on the carbon ring and may lead (in the case of the Nb_2^+) to the destruction of the aromaticity of benzene. When a metal replaces hydrogens in a chemisorbed complex, it bonds to the benzene ring through σ type bonds.

We interpret the experimental results on the basis of the computed energetics of the equilibrium structures and the enthalpies of reactions for the various viable channels. We find that the most favorable reaction channel leads to the "physisorbed" species for Nb^+ and Nb_2^+ clusters. However, the cooling of the "warm" physisorbed species would depend on the experimental conditions and whether secondary and tertiary collisions are feasible. It was shown that Nb^+ forms only a physisorbed complex and formation of the dehydrogenated chemisorbed complex is unfavorable for Nb^+. On the other hand, Nb_2^+ forms a physisorbed complex that undergoes transformation into a thermodynamically more stable chemisorbed species through removal of H_2. The computed results are thus fully consistent with experimental results in that larger clusters form chemisorbed species through evaporation of H_2. Although only physisorbed $Nb_nC_6H_6^+$ ions are observed for smaller n, fully dehydrogenated $Nb_nC_6^+$ ions would be stable for larger values of n for which stable carbides with many Nb−C bonds are formed and are energetically preferred over physisorbed species for larger values of n.

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