Dehydrogenation of Xylene Isomers on Niobium Cluster Cations Nb_n^+ ($n = 2-26$)

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The dehydrogenation of the mono-, di-, and trimethyl-substituted benzenes (toluene, *o*-, *m*-, *p*-xylene, and mesitylene) on niobium cluster cations Nb_n^+, $n = 2, ..., 26$, in the gas phase was investigated in an FT-ICR mass spectrometer. While most Nb_n^+ clusters dehydrogenate the compounds completely, a partial dehydrogenation is observed for very small clusters with $n \leq 6$ and clusters in the range $15 \leq n \leq 19$. Selectively deuterated xylenes are used to clarify the mechanisms of the isomer specific dehydrogenation reactions, and the observed results and trends are discussed.

1. Introduction

Adsorption of atoms and molecules on surfaces of transition metals is of great interest in surface chemistry as an initial step in heterogeneous catalysis.[1,2] The dehydrogenation of hydrocarbons on transition metal surfaces has been studied extensively.[2-4] The reactions of hydrocarbon molecules with atomic transition metal cations have also been reviewed.[5] Metal clusters, with their large ratio of the number of surface atoms to the total number of atoms, are chemically interesting systems, representing the transition between the chemistry of metal atoms and surface chemistry.[6-8] The laser vaporization technique permits easy generation of such neutral and ionized metal clusters,[9,10] and their reactions have also been the subject of some intensive studies.[11] In particular, the reactions of niobium clusters with some hydrocarbons were studied to a certain extent.[12] By recording optical emission spectra, it was shown only recently that multiple reactions with oxygen may heat niobium clusters up to temperatures of 3200 K.[13a] Mixed transition metal–carbon clusters which seem to favor particular stoichiometries such as Nb_8C_{12} were coined metallohedrenes (Met-cars) in recognition of a likely spheroidal structure.[13b-l]

In a recent study we have investigated the reactions of positively charged niobium clusters Nb_n^+ in the range $2 < n < 28$ with a variety of simple organic compounds in a FT-ICR mass spectrometer under single-collision conditions.[14] Particularly interesting were the reactions with benzene. For larger clusters, two reaction channels were found: "chemisorption", leading to total dehydrogenation of the benzene molecule and formation of a "carbide cluster" $Nb_nC_6^+$, and "physisorption", consisting simply in addition of benzene, that is, formation of $Nb_nC_6H_6^+$ product ion. The branching ratio between the two processes was strongly size dependent, with for some values of n only the total dehydrogenation being observed. The second channel, C_6H_6 addition or "physisorption", was detectable for $n = 22$ and in the range $n = 12-19$, and for $n = 19$ it actually was the dominant process. Otherwise in the range studied, up to $n = 28$, the dominant reaction was total dehydrogenation. Partial dehydrogenation was in no case observed for clusters with $n > 4$. Interestingly, some exploratory experiments involving the reactions of toluene exhibited considerable differences when compared with those of the unsubstituted benzene. The physisorption process was considerably suppressed, being detected only for $n = 17$ and 18. More importantly, while most larger clusters dehydrogenated toluene completely, those in the $n = 15-19$ range exhibited also partial dehydrogenation with loss of one H_2 molecule. In the present paper we examine this problem in somewhat more detail. In particular, we examine separately the three isomers of xylene, as well as mesitylene. We also perform experiments with deuterated and partially deuterated compounds in order to determine whether the hydrogens are lost from the methyl substituent or from the aromatic ring and to gain deeper insight into the mechanisms and dynamics of the dehydrogenation reactions.

2. Experimental Section

The experimental setup was described previously.[14] Briefly, the experiments were performed in a modified FT-ICR mass spectrometer (Spectrospin CMS47X) equipped with an external ion source chamber for molecular beam sources, a 4.7 superconducting magnet, and a 60 × 60 mm cylindrical "infinity" cell.[15] Niobium cluster cations were produced by pulsed laser vaporization of compressed niobium powder (<65 μm, 99%, HERAEUS). Focused 532 nm radiation of a Spectra Physics GCR3 Nd:YAG laser (spot size on target ~500 μm) operating at 25 Hz with about 12 mJ per 5 ns pulse was used to produce the initial metal plasma, and no post-ionization was needed. The vaporization was synchronized with a helium pulse (11 bar, 50 μs) from a home-built piezoelectric valve. The helium-entrained plasma was subsequently cooled and clustered by flowing it through a confining channel (45 mm, 2 mm i.d.) and subsequent supersonic expansion into vacuum. The cluster ions produced were accelerated downstream from a 400 μm skimmer, transferred into the high-field region of the superconducting magnet, decelerated, and stored inside the ICR cell.

To study the bimolecular cluster ion–molecule reactions, the pressure inside the ICR cell was raised from the base value of 1×10^{-10} mbar to about 1.2×10^{-8} mbar by controlled admission of the reactant species. Commercially available *o*-, *m*-, and *p*-xylene (anhydrous, 99+%, Aldrich), mesitylene (98%, Aldrich), and *p*-xylene-d_6, -d_{10} (99 + atom %, Aldrich) were used without further purification. Mass spectra were taken after varying reaction times, typically 0, 0.5, and 1 s. Relative rate constants for the first reaction step were extracted from the parent and product cluster ion intensities assuming pseudo-first-order kinetics.

3. Results

To summarize first our previous results, in our recent study[14] we concluded that the reactions of the Nb_n^+ clusters in the size range $2 < n < 28$ with a variety of simple organic compounds proceed with almost collision rates. In no case was a loss of Nb atom observed, even though it would be easily detectable. With a single exception, there was also no observable fragmentation and loss of carbon atoms from the hydrocarbon. Complete dehydrogenation was in most cases the dominant process for all clusters larger than about $n = 6$. Only toluene behaved anomalously in this respect, as noted above, in that it also exhibited partial dehydrogenation. Clusters in the size range $n = 15-18$ reacted with the loss of a single H_2 molecule. In addition, the $n = 17$ and 18 exhibited also "physisorption", that is, reaction without any hydrogen loss. In fact, for $n = 18$ all three channels, that is, complete dehydrogenation (loss of $4H_2$), partial dehydrogenation (loss of $1H_2$), and no dehydrogenation (toluene addition), occured with approximately equal probabilities. In reactions with a mixture of xylene isomers no addition without dehydrogenation was detected, but otherwise they exhibited a similar overall reactivity pattern as toluene. Again there was a complete dehydrogenation for most clusters with $n > 6$, but as for toluene there was a "reactivity gap" and only partial dehydrogenation in a similar range $n = 15-19$. In the hope of gaining a better understanding of this reactivity pattern and of the mechanisms of the dehydrogenation reactions, we have examined the reactions of individual xylene isomers one at a time. We have also performed studies with partially deuterated samples and examined briefly reactions of mesitylene.

3.1. Reactions of o-, m-, and p-Xylenes. The reaction rates of o-, m-, and p-xylene with the niobium clusters are summarized and compared in Figure 1. Small niobium clusters Nb_n^+, $n = 2-6$, dehydrogenate xylenes only partially. The reactivity pattern in this size range is very similar for all three isomers, with the degree of dehydrogenation increasing with the number of niobium atoms. Reactions with Nb_2^+ clusters result mainly in the loss of two H_2 molecules, while those with $n = 3$ clusters yield mainly $3H_2$ loss. For the $n = 4$ clusters there is a branching between $3H_2$ and $4H_2$ loss. For $n = 5$ the $4H_2$ loss is the dominant channel for all the isomers and, in fact, the only observed one for the m- and p-xylenes. All isomers react with the $n = 6$ clusters mainly with total dehydrogenation ($5H_2$ loss), with about 30% of the molecules exhibiting only $4H_2$ loss. For most cluster sizes with $n > 6$, total dehydrogenation and formation of $Nb_nC_8^+$ seems to be the dominant reaction for all three isomers:

$$Nb_n^+ + C_8H_{10} \rightarrow Nb_nC_8^+ + 5H_2$$
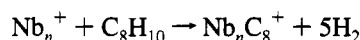
Interestingly, similar to the reactions with toluene, clusters in the range $n = 15-19$ behave "anomalously", and products resulting from partial dehydrogenation are detected:

$$Nb_n^+ + C_8H_{10} \rightarrow Nb_nC_8H_8^+ + H_2$$

$$\rightarrow Nb_nC_8H_6^+ + 2H_2$$
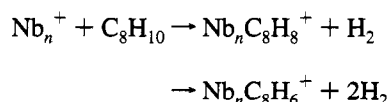
While all three isomers exhibit a reactivity gap in the same size range, it can be seen in Figure 1 that the reactivity patterns differ appreciably from isomer to isomer. For p-xylene, loss of a single H_2 is the dominant process in the entire range $n = 15-19$, and for $n = 18-19$ it is, in fact, the only observed process. No loss of $2H_2$ is observed. In o-xylene only $n = 15$ and $n = 18$ show predominantly single H_2 loss. For the $n = 16$ and 17 clusters total dehydrogenation is the major channel, but they
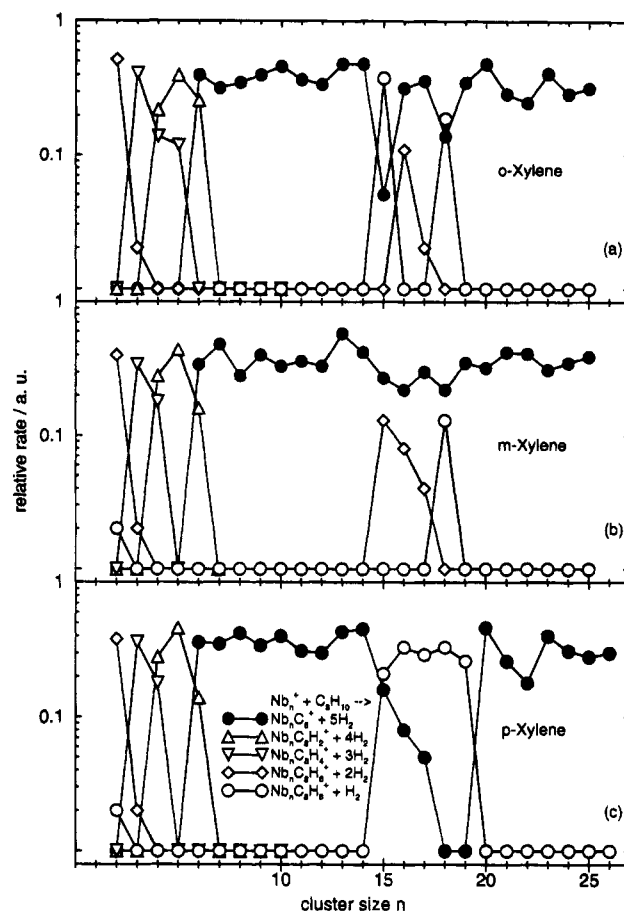

Figure 1. Relative rates for the reactions of Nb_n^+ with (a) o-, (b) m-, and (c) p-xylene. Total and partial dehydrogenation are indicated by filled and open symbols, respectively. Partial dehydrogenation does occur for cluster sizes $n = 15-19$. No loss of $2H_2$ is observed for p-xylene.

also exhibit a loss of $2H_2$. In m-xylene total dehydrogenation is the major process for all cluster sizes, but minor product with loss of $1H_2$ is observed for $n = 18$, while $n = 15$, 16, and 17 clusters also exhibit loss of $2H_2$. The $n = 19$ cluster which reacts only with a single H_2 loss with p-xylene, dehydrogenates completely both the o- and m-isomers.

3.2. Reactions with Mesitylene. Besides toluene and xylene, we have also investigated mesitylene, sym-trimethylbenzene (C_9H_{12}). Similar to the other two compounds studied, total dehydrogenation and formation of $Nb_nC_9^+$ clusters is the major process. In interpretation of the mesitylene results there might appear to be some ambiguity, since the products of total dehydrogenation, $Nb_nC_9^+$ have the same nominal mass as the also possible products $Nb_{n+1}CH_3^+$. This possibility can, however, be easily eliminated by high-resolution mass determination. It can also be ruled out by performing a variety of selective mass ejection experiments. For example, in an experiment where the Nb_{14}^+ cluster (m/z 1301) was selectively ejected out of an initial cluster distribution ranging from Nb_7^+ to Nb_{26}^+, the $Nb_{14}C_9^+$ product at m/z 1409 was found to be missing after the appropriate reaction delay. On the other hand, a product at m/z 1316 was still present, since it corresponds to $Nb_{13}C_9^+$ (product of Nb_{13}^+ reaction), and not to the $Nb_{14}CH_3^+$ (which would be due to Nb_{14}^+ reactions). The mesitylene results are summarized and compared with those obtained for toluene and xylene in Figure 2. Like the other two compounds, mesitylene also exhibits anomalous reactions with the $n = 15-18$ clusters. While other larger clusters dehydrogenate mesitylene completely with loss of six H_2 molecules, within this range partial dehydrogenation with single H_2 loss is the

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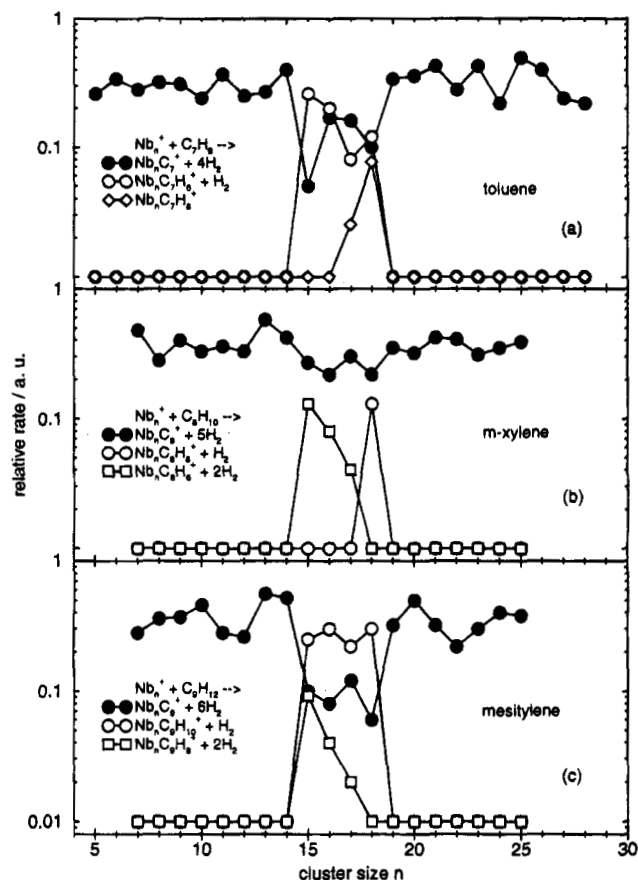*J. Phys. Chem., Vol. 99, No. 42, 1995* **15499**

Figure 2. Relative rates for the reactions of Nb_n^+ with (a) toluene, (b) *m*-xylene, and (c) mesitylene. In all three cases the very small niobium clusters as well as clusters in the range $15 < n < 19$ exhibit also a partial dehydogenation which is not found for clusters outside these ranges.

dominant reaction. In addition, similar to the reactions of *m*-xylene, for $n = 15-17$ also a minor channel with a $2H_2$ loss is detected.

3.3. Reactions with Deuterated Xylenes. An interesting question involves the origin of the eliminated hydrogens: Do they come from the aromatic ring or the aliphatic substituents? To address this question, we have performed experiments with deuterated and partially deuterated compounds. Reactions with perdeuterated *p*-xylene only confirmed the results obtained with normal xylene: total dehydrogenation for all clusters with $n \leq 14$ and $n \geq 20$ and mainly partial dehydrogenation for $n = 15-19$. For the cluster sizes for which branching between the total (loss of $5H_2$) and partial (loss of $1H_2$) dehydrogenation channels was observed ($n = 15$, 16, and 17), deuteration changes the branching ratio slightly in favor of the partial dehydrogenation.

The results of the isotopic studies are exemplified in Figure 3, which compares the product ions formed in the reactions of the Nb_{15}^+ and Nb_{18}^+ clusters with normal, methyl-deuterated *p*-xylene-d_6, and perdeuterated *p*-xylene-d_{10}. Particularly instructive are the results with the *p*-xylene-d_6, deuterated on the methyl groups, $(CD_3)_2C_6H_4$. In all the cases of partial dehydrogenation ($n = 15-19$), only loss of D_2 is observed. This clearly indicates that the partial dehydrogenation of *p*-xylene results from hydrogen loss from the aliphatic substituents.

4. Discussion

4.1. Comparison with Surface Studies. In the context of the studies with the isotopically substituted xylene it is interesting to mention several similar isotopic studies of dehydrogenation on metal surfaces. Similar to the present observation on
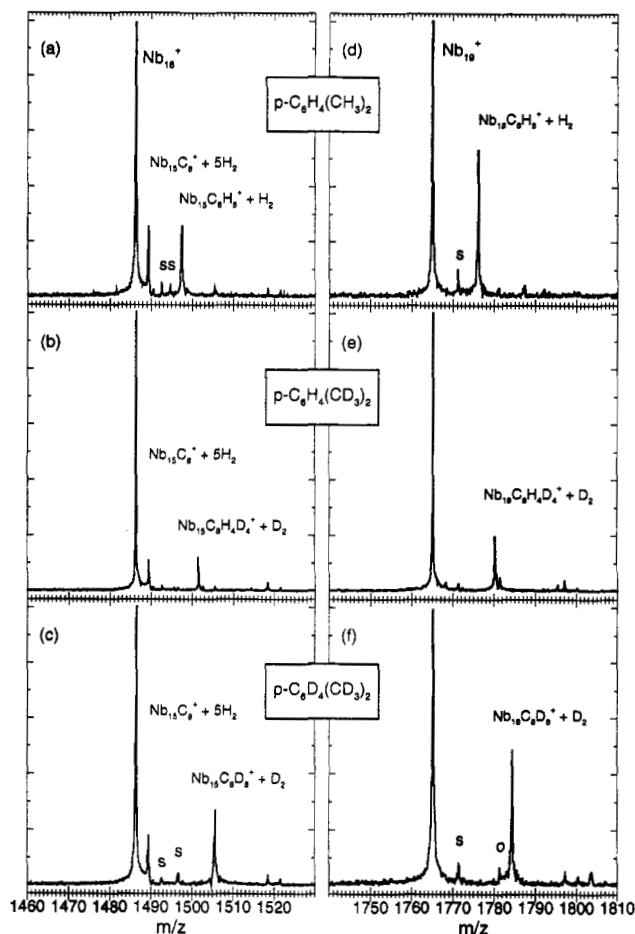

Figure 3. Part of product mass spectra for Nb_{15}^+ and Nb_{18}^+ reacting with (a)(d) *p*-xylene, (b)(e) *p*-xylene-d_6 ($(CD_3)_2C_6H_4$), and (c)(f) *p*-xylene-d_{10}, respectively. Niobium cluster oxides initially also present were ejected as completely as possible prior to reaction. The peaks labeled O are due to the remaining oxides; peaks labeled S are due to secondary products. Single-dehydrogenation products are indicative of purely aliphatic dehydrogenation.

Nb_n^+ clusters, thermal desorption of methyl-deuterated toluene adsorbed on Ni(111) and Ni(100)[16] as well as of partially deuterated *o*-, *m*-, and *p*-xylenes ($(CD_3)_2C_6H_4$) on Ni(111) and Ni(100)[17] surfaces showed that in all cases the first dehydrogenation step occurs at the methyl groups. This was also confirmed in a recent HREELS, LEED, and TPD study of the thermal decomposition of *p*- and *o*-xylene-d_6 ($(CD_3)_2C_6H_4$) on a Pt(111) surface.[18] In that study, mainly D_2 loss was observed upon annealing the adsorbed samples to 350 and 345 K, respectively. This again indicated that the methyl groups are involved in the bonding to the metal surface. Similar to our study, these experiments do not answer conclusively the question of whether the loss from xylene occurs in all cases by elimination of H_2 from the same methyl group or one atom is lost from each of the two methyls, perhaps with formation of quinone-like structure. This question could, of course, be answered unambiguously using xylene samples with one normal CH_3 and one CD_3 group. Similar studies with partially deuterated compounds would also be instructive in the case of *m*- und *o*-xylenes. As noted above, in these cases a loss of two H_2 molecules was also observed. Does this correspond to losing one H_2 from each of the methyl groups, or is one methyl completely dehydrogenated, with perhaps the fourth hydrogen originating from the aromatic ring? Here again, studies with xylenes selectively deuterated on one of the methyls would be useful. Such deuterated compounds could be relatively easily prepared, for instance, from the commercially available 2-,3-,
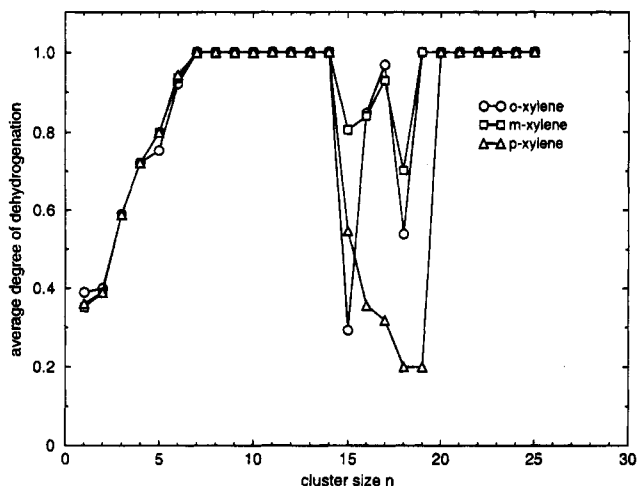
Figure 4. Comparison of the "average degree of dehydrogenation" of the *o*-, *m*-, and *p*-xylene isomers. This is defined as the average fraction of H atoms lost, summed over all product channels. Note that with very small clusters all isomers react similarly (n ≤ 6), while the partial dehydrogenation in the range $n = 15-19$ is strongly isomer specific.

and 4-bromotoluenes, and we are currently considering such experiments.

4.2. Dependence of Reactivity on Cluster Size. Particularly interesting and difficult to interpret is the size dependence of cluster reactivity. The first thing to note is that the overall reactivity pattern is very similar for all three methyl-substituted benzenes studied. The complete dehydrogenation can be viewed as the major reaction channel, with two ranges exhibiting anomalous reactivity: clusters with less than seven Nb atoms and the clusters in the range $15 \le n \le 19$, which dehydrogenate the hydrocarbons only partially. This can best be seen in Figure 1, as well as in a slightly modified form in Figure 4, which compares the "average dehydrogenation degree" of the three xylene isomers as compiled from the relative rate constants. In reaction with very small clusters all three xylene isomers behave very similarly and exhibit incomplete dehydrogenation. This incomplete dehydrogenation and the increase of the degree of dehydrogenation with the cluster size can perhaps be understood. The driving force behind the dehydrogenation and the breakage of a larger number of C−H bonds is the highly exothermic formation of the Nb−C bonds (D^0(Nb−C) = 564 ± 13 kJ/mol).[21] The number of such bonds which can be formed is, of course, limited for the clusters with very small numbers of Nb atoms, and only incomplete dehydrogenation results. For larger clusters the highly exothermic formation of stoichiometric "niobium carbides" is possible and liberates enough energy to evaporate all of the hydrogen.

Much more difficult to understand, and more interesting, is the "reactivity gap" in the cluster size range $n = 15-19$. As can be seen in Figure 4, in this range one again observes partial dehydrogenation, but unlike for the very small clusters, the reactivity pattern is strongly isomer specific. As noted above, the formation of multiple Nb−C bonds, and of the interstitial niobium carbide, is a strongly exothermic process. On the other hand, Nb−H bonds are relatively weak (D^0(Nb⁺−H) = 222 kJ/mol[19]), and pairwise desorption of H₂ from the cluster is a nearly thermoneutral process (D^0(H₂) = 432 kJ/mol[20]). It is therefore fairly clear that total dehydrogenation is energetically possible for all of the larger niobium clusters. The formation of partially dehydrogenated products is thus undoubtedly due to the presence of a kinetic barrier, rather than to thermodynamic stability of the partially hydrogenated products. It is, of course, interesting to speculate why such behavior, and a barrier to

complete dehydrogenation, should specifically occur for clusters in the range $n = 15-19$.

It is interesting to note that for a closely packed structure a cluster with $n = 13$ would be the smallest one with one "interior" atom and that it could form a closed icosahedral structure. It is conceivable that clusters with $n = 15-19$ represent a similar, relatively stable, closed structure, with a few oddly fitting additional atoms "adsorbed" on their surface, which then exhibit reactivity similar to very small niobium clusters. One can view the initial step in the reaction with very small clusters essentially as breakage of one of the aliphatic C−H bonds and formation of a radical bound to one of the "surface atoms" via the methyl substituent. This places the phenyl ring, as well as possibly other substituents on the phenyl, sufficiently far from the surface, so that further reactions do not occur. It may be noted that unlike mesitylene, or *o*- and *m*-xylenes, the *p*-isomer eliminates by partial dehydrogenation only one H₂. In mesitylene and the other two xylene isomers the remaining methyl substituents of the surface radical would be relatively close to the surface, so that a further reaction and elimination of a second H₂ could take place. It is well-known from surface studies that perfect crystals tend to be relatively unreactive. Kinks, steps, and other defects typically greatly enhance the overall reactivity.[2] As proposed above, perhaps one might postulate that the clusters in the sizes $n = 15-19$ resemble such a surface with defects. In other words, very small clusters as well as some larger clusters resembling "a surface with defects" are particularly reactive. They can react directly with the methyl substituent by breaking the relatively stable and unreactive aliphatic C−H bonds, resulting in an entity bound to the surface atom via the methyl group. Other cluster sizes are more reminescent of a smooth surface and are less reactive. Their reaction requires prior adsorption of the molecule on the cluster surface and attack on the phenyl ring. This then results in a formation of a number of Nb−C bonds, strong heating of the cluster, and eventually a complete breakdown of the hydrocarbon and complete evaporation of all hydrogen.

5. Summary

The reactions of several methyl-substituted benzene compounds with niobium metal cluster cations, Nb$_n^+$, $n = 2-26$, are found to be size dependent. The compounds studied exhibit very similar reactivity patterns. Most cluster sizes lead to complete dehydrogenation, with two ranges of "anomalous" reactivity. Very small clusters with $n < 7$, as well as clusters in the range $15 < n < 19$, exhibit also partial dehydrogenation, with elimination of one or two H₂ molecules. Studies with xylenes show that the reactions in this anomalous range are strongly isomer specific. Investigations with selectively deuterated xylenes show that the partial dehydrogenation results from reaction of the aliphatic C−H bonds and hydrogen loss from the methyl substituents.

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