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The niobium and tantalum riddle: gas-phase monocation reactions with pyrene and pyrene-D_{10}

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This paper is dedicated to Professor John Beynon whom we admire and respect. If we do not succeed in solving the riddle referred to in our title, we hope our efforts will spur others to do so

Abstract

Metal monocation gas-phase reactions with pyrene (Py) have been investigated. Of those cations which bind Py by abstraction of two hydrogen atoms, there are two subgroups of which Nb^+ and Ta^+ are the most striking and puzzling representatives. The Ta^+-like group binds three Py units consecutively, each by expulsion of two hydrogen atoms, whereas the Nb^+ group binds four Py units; however, in this latter case, the second Py attachment occurs without the expulsion of any hydrogen. When perdeuterated Py-D_{10} is used, the Ta^+ group behavior is unaffected, but the Nb^+ group now exhibits a considerable degree of Py attachment in which no deuterium atoms are lost in the first reaction step. We will attempt to explain this behavior by using the results of reactions of Nb^+ and Ta^+ with Py in a Fourier transform mass spectrometer (FTMS).
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1. Introduction

Freiser and co-workers [1] published a seminal work on the gas-phase reactions of Nb^+ and Ta^+ with alkanes and alkenes. They showed that both react similarly and that they are by far the most reactive metal ions toward C–H bond activation ever reported. However, the same ions behave quite differently in their reactions with polycyclic aromatic hydrocarbons (PAHs), such as pyrene (Py). In a continuation of the early experiments of Wu and Brodbelt [2], who investigated the ligation of metal monocations with mono- and bidentate nitrogen heterocyclic ligands using Py as a basal indicator, we have initiated a new study of the ligation of PAHs and their heteroanalogues.

We have been interested in the gas-phase reactions of unipositive metal ions with Py, as studied by Fourier transform mass spectrometry (FTMS), for quite some time [3–8]. We find that the following reaction types can be distinguished:
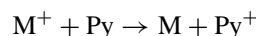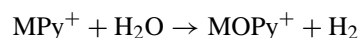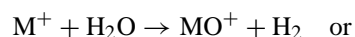
(a) simple addition (attachment)

$$M^+ + Py \rightarrow MPy^+ + Py \rightarrow MPy_2^+ + Py \rightarrow \cdots$$

(b) substitution (attachment with loss of hydrogen)

$$M^+ + Py \rightarrow (MPy - H_2)^+ + H_2$$

(c) charge exchange

$$M^+ + Py \rightarrow M + Py^+$$

(d) oxidation (by traces of H_2O present in the system)

$$M^+ + H_2O \rightarrow MO^+ + H_2 \quad \text{or}$$
$$MPy^+ + H_2O \rightarrow MOPy^+ + H_2$$

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(e) hydrogenation (by traces of hydrogen present in the system)

    We did not investigate (d) and (e) because these usually take place only at longer reaction times. Reaction (c) is important only if ionization potential IP(M) is higher than IP(Py) or when excited M^+ ions are present. And, if significant amounts of Py^+ are present at longer reaction times, a dimerization equilibrium

(f) $Py^+ + Py \rightleftharpoons Py_2^+$
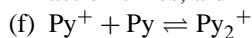
may be observed. Reaction (f) may be used [5,6] to determine the gas-phase concentration of neutral Py.

Most M^+ ions bind two Py by reaction (a). Reactions with deuterated Py exhibited no isotope effect [8], indicating that neither C–H bond cleavage, elongation, or hybridization change is involved in the rate-determining step. We conclude that these compounds are of sandwich-type or, in the standard language of gas-phase organometallics, C–C bond activated [9–15].

On the other hand, a small number of M^+ ions (e.g., Hf^+) are extremely prone to oxidation and it is difficult to determine all the various reaction paths. However, the oxidation products never exceed the maximum coordination number for a given M^+ (i.e., if the coordination number is 2 then only M^+ and MPy^+ are observed in oxidized form and if the coordination number is 3 then M^+, MPy^+, and

MPy_2^+ can be oxidized). However, the oxidized species in turn, may then be ligated up to the coordination number (but not exceeding it).

Finally, those M^+ ions which cause a loss of H_2 from Py in the first step, may be divided into two groups: (i) Nb^+, Re^+, and Zr^+ and (ii) Ta^+, W^+, and Pt^+. We present here the characteristics of the reactions of Nb^+ and Ta^+ with Py and point up their striking differences. These differences constitute the riddle we would like to solve.

2. Experimental

2.1. Compounds

Pyrene (Py) and its perdeuterated analogue (Py-D_{10}) were obtained from Fluka Chemie AG, Buchs, Switzerland. The Nb and Ta metal foils were of high purity (99.8%; Aldrich, Milwaukee, WI, USA).

All experiments were performed on a FT/MS 2001-DD Fourier transform mass spectrometer (Finnigan, Madison, WI, USA) equipped with a 3 T superconducting magnet and a Nicolet 1280 data station. Positive ions were produced at 2×10^{-9} Torr in the source compartment of the dual cubic trap. The trapping voltage was maintained at +2 V during the experiment. Single 1064 nm laser pulses, Nd:YAG
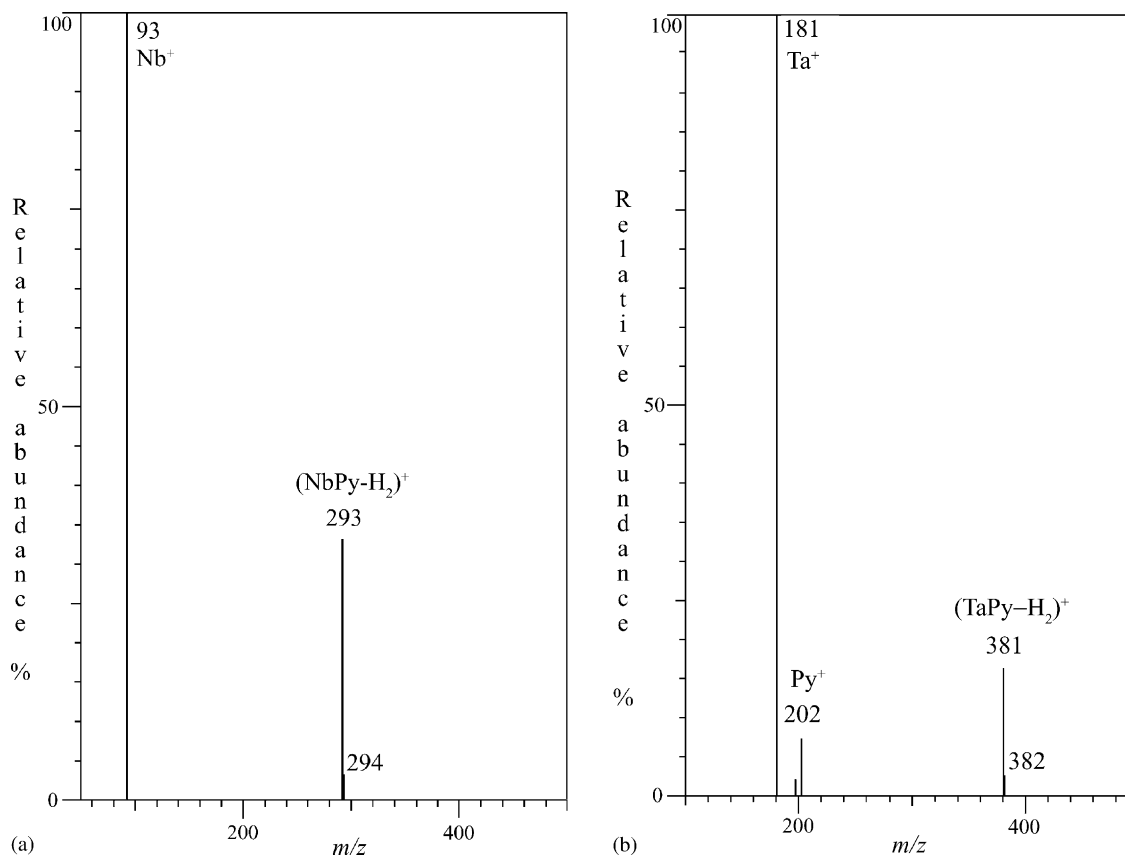

Fig. 1. LD/I spectra of (a) Nb^+ and (b) Ta^+ gas-phase reactions products with pyrene after a few milliseconds reaction time.

laser Quanta Ray DCR-11 (Spectra-Physics, Inc., Mountain View, CA, USA) were used to produce Nb^+ or Ta^+ ions by impingement on the appropriate foil. The probe and the foil were located behind the source trap plate. Py (or a mixture of it and its perdeuterated analogue) was introduced

into the gas phase by evaporating an alcoholic solution at the probe. Following metal ion formation, (i) reaction times of 1 ms to 300 s ensued before the spectrum was recorded; or (ii) after a given delay, all but the M^+ ions (or one of some higher product ions) were removed and the reaction
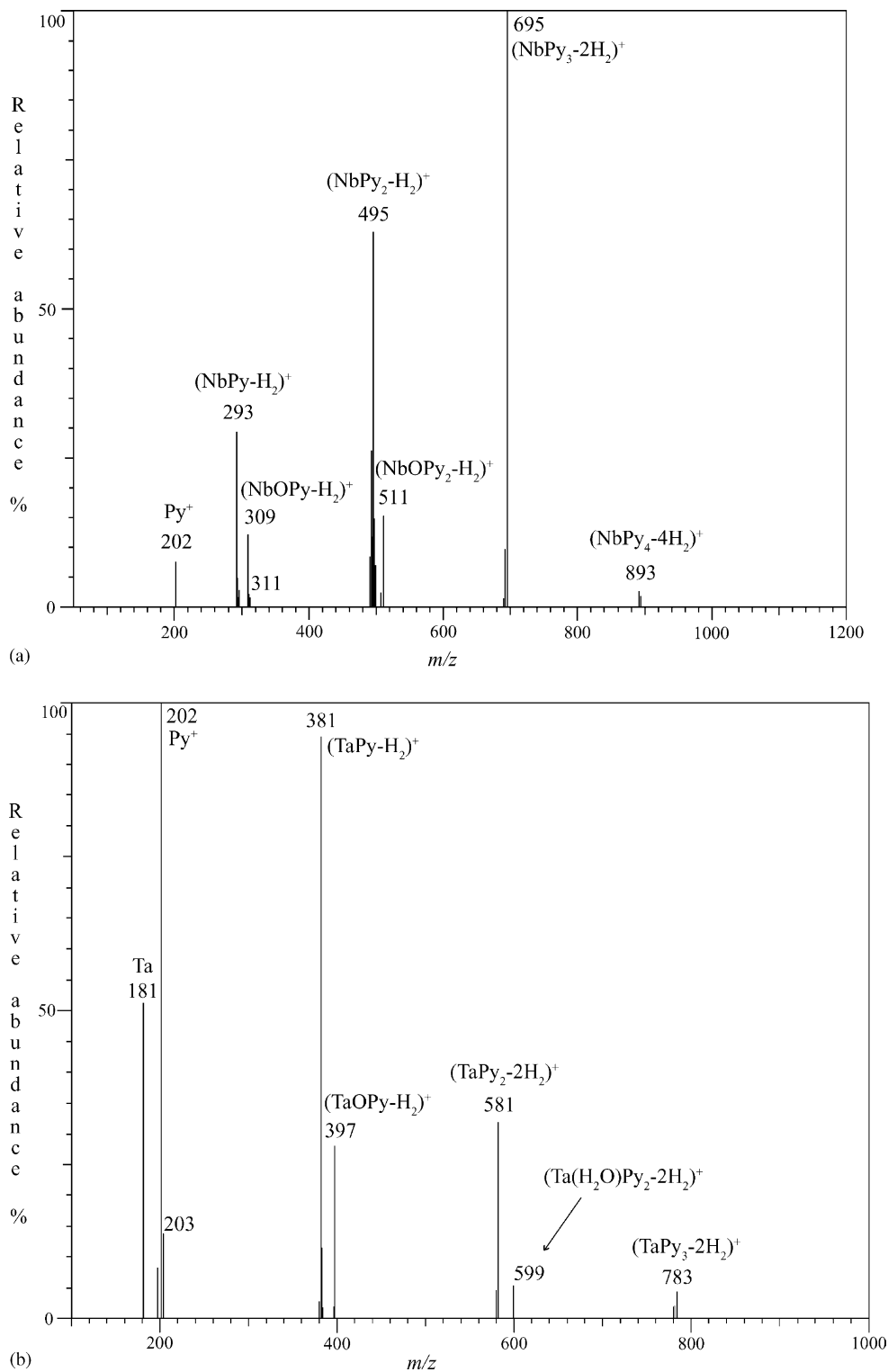

Fig. 2. LD/I spectra of (a) Nb^+ and (b) Ta^+ gas-phase reactions products with pyrene after a several hundred milliseconds reaction time.

with gas-phase Py was allowed to proceed for a specified time before the spectrum was recorded. It was supposed that the second procedure would permit excited M^+ (and whatever other species might be present) to relax before starting to monitor the reaction or to pick up differences that might have occurred relative to the first procedure. Since Py is already present in the gas phase as the M^+ are being formed, there is no efficient way to ensure relaxation of all excited states; consequently, the results may reflect mixtures of excited and ground state cation reactions. However, the results are reproducible and, especially in the long time range, they certainly do not involve excited states. Consequently, we will not address their presence further. An excellent review on importance of electronically excited states in metal ion chemistry has been given by Armentrout [16].
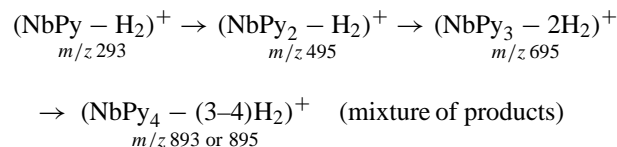
The deuterium content of the Py/Py-D_{10} ratio was fixed and was determined by the low energy (18 eV) EI mass spectrum as Py-D_{10}:Py-D_9:Py-D_8:Py-D_0::64:14:6:16.
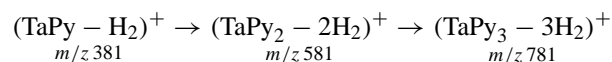
3. Results and discussion

FTMS spectra of the products of Nb^+ and Ta^+ reactions with gas-phase Py after a few and several hundred milliseconds are shown in Figs. 1a, b, 2a and b, respectively. It is found that Ta, whose IP of 7.88 eV is somewhat larger than that of Py at 7.43 eV, produces a considerable amount of Py^+ by process (c). On the other hand, Nb (IP = 6.76 eV) should

not exchange charge with Py when ionized. However, even here, after long reaction times, some Py^+ is present indicating that excited states of Nb^+ may have been involved in the reaction. Both metals, but Ta^+ even at very short times, form oxidized products.
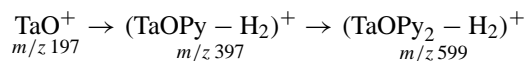
The main reaction products for Nb^+ are:

$$(NbPy - H_2)^+ \rightarrow (NbPy_2 - H_2)^+ \rightarrow (NbPy_3 - 2H_2)^+$$
$$m/z\,293 \qquad m/z\,495 \qquad m/z\,695$$

$$\rightarrow (NbPy_4 - (3–4)H_2)^+ \quad \text{(mixture of products)}$$
$$m/z\,893\ \text{or}\ 895$$

Those for Ta^+, besides Py^+ of m/z 202, are:

$$(TaPy - H_2)^+ \rightarrow (TaPy_2 - 2H_2)^+ \rightarrow (TaPy_3 - 3H_2)^+$$
$$m/z\,381 \qquad m/z\,581 \qquad m/z\,781$$

Oxidation products are also observed:

$$TaO^+ \rightarrow (TaOPy - H_2)^+ \rightarrow (TaOPy_2 - H_2)^+$$
$$m/z\,197 \qquad m/z\,397 \qquad m/z\,599$$

$(TaOPy - H_2)^+$, the next oxidation product, is not observed presumably because it loses H_2O to yield m/z 784 which, in the late stages of the reaction, becomes the base peak. The surprising result is that Nb^+ binds more of the rather large Py ligands than does Ta^+ which is certainly bigger and should better be able to accommodate them. It is also surprising that, unlike $(TaPy - H_2)^+$ in the second step, $(NbPy - H_2)^+$ binds Py without loss of H_2.
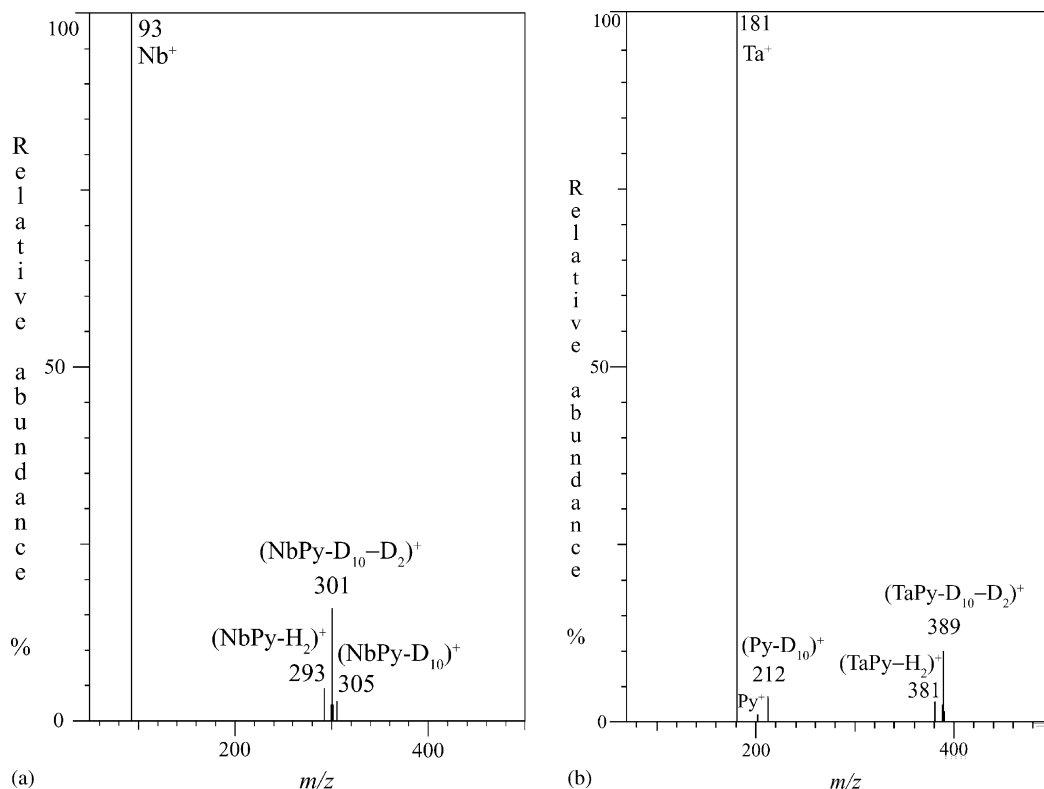

Fig. 3. LD/I spectra of (a) Nb^+ and (b) Ta^+ gas-phase reactions products with mixture of Py and Py-D_{10} (1:4) after short reaction time.

Although the majority of the gas-phase reactions of M^+ with organic molecules involves C–H bond rupture, reports on deuterium isotope effects are scarce. For isotope effect to be operative, theory requires that the bond rupture, elongation, rehybridization, or other energy consuming process occurs as part of the rate-determining step (transition state) of the reaction [17]. Identical experiments with Nb^+ and Ta^+ using a mixture of Py and Py-D_{10} reveals an effect on the first step of the reaction with Nb^+ but not with Ta^+ (Fig. 3a and b). Ta^+ binds Py exclusively by expulsion of H_2 and, against expectation, no isotope effect is observed when Py

and Py-D_{10} are compared. However, the very small fraction of reaction (a) observed in the first step of the Nb^+ reaction with Py forming m/z 295 becomes significantly larger with Py-D_{10} and increases as the reaction proceeds. At some point, the (NbPy-D_{10})$^+$ of m/z 305 becomes as intense as the (NbPy-D_{10} − D_2)$^+$ of m/z 301. An analysis of several reaction runs under different conditions was performed by calculating the increase of m/z 295 as:

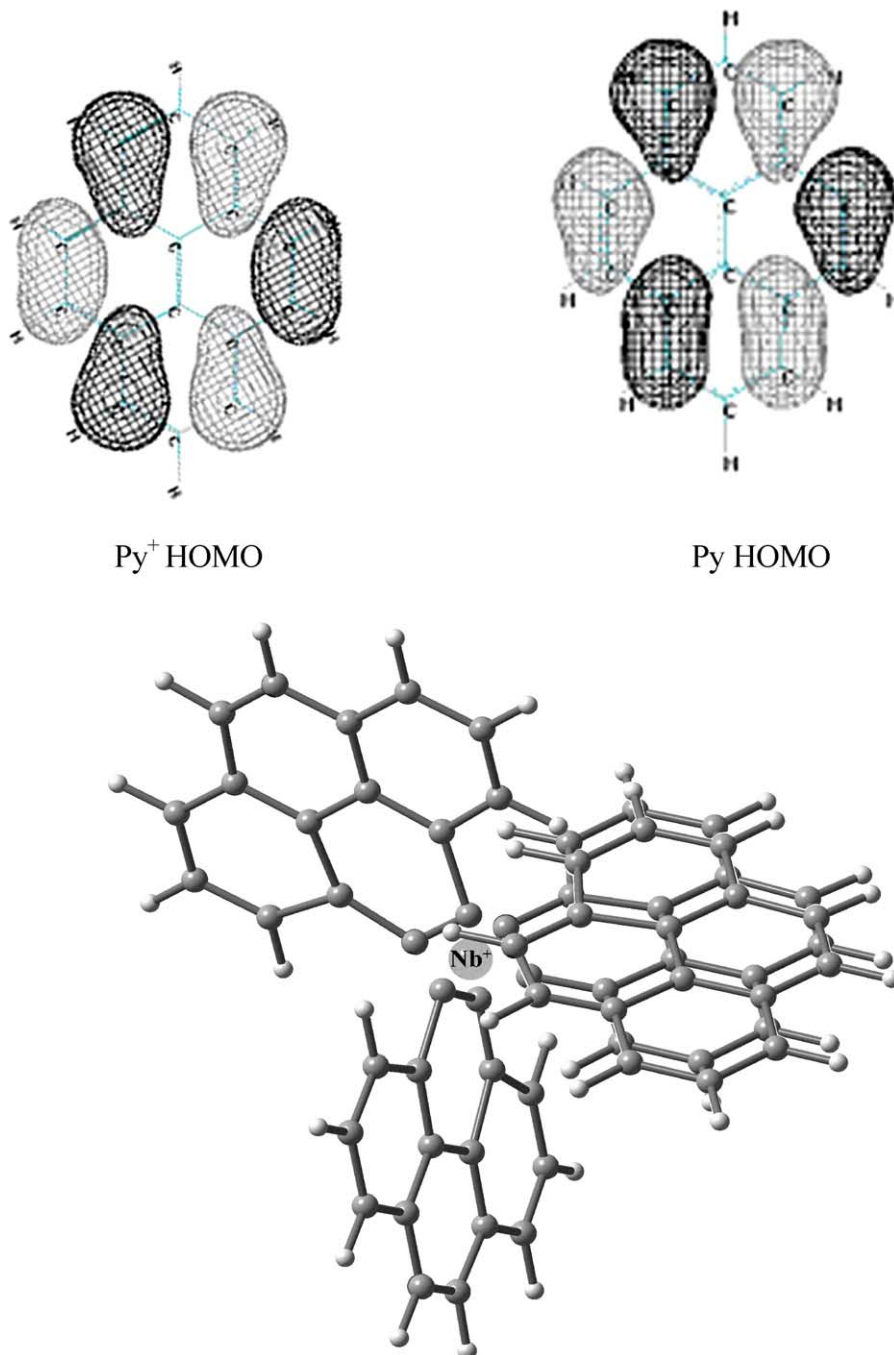$$A = \frac{I(\text{mass } 295)}{I(\text{mass } 293) + I(\text{mass } 295)}$$

Py$^+$ HOMO

Py HOMO

Fig. 4. Tentative structure of (NbPy$_4$ − 3H$_2$)$^+$.

and that of m/z 305 as:

$$B = \frac{I(\text{mass } 305)}{I(\text{mass } 301) + I(\text{mass } 305)}$$

where I is the mass intensity; it was found that the ratio B/A is rather constant at about 2.5 throughout the course of the reaction. Thus, the intensity of the deuterated addition complex rises 2.5 times faster than that of the nondeuterated. Since an isotope effect on reaction (a) most likely relates to the rate of stabilization of the metastable complex (either radiative or by collisions) and an isotope effect in reaction (b) most likely relates to effects on the transition state, very different situations may exist. In a radiative association, deuterium substitution can affect the kinetics of the attachment reaction by changing the rate of radiative decay of the complex. This, of course, differs radically from the reasons for isotope effects on substitution channels and represents an interesting example of a kinetic isotope variant in the gas-phase complex chemistry [18].

An explanation for the fact that the second Py ligand adds without loss of hydrogens and for the coordination number 4 for Nb^+ is still elusive. We suppose that in this case a strong bond of the first (dehydrogenated)Py ligand and the Nb^+ exists, in which the 3,4-dehydropyrene (or 3,4-pyryne) [19,20] transfers one of its π-electrons to the metal. The product, a Nb-dehydropyrene cation may be presumed to be positively charged at the Py surface, which then permits another Py to attach in parallel (see HOMO diagrams of Py and Py^+) on top of it, much as in the charged pyrene dimer, $Py_2{}^+$. The next two Py ligations then proceed by reaction (b), again at the metal center by C–H bond activation and H_2 release. The final step, which yields the products $(NbPy_4 - (3–4)H_2)^+$, may have the structure of a Nb^+-centered octahedron with three $(Py - H_2)$ units on the edges, one being a loose dimer with a neutral Py (see Fig. 4).

In conclusion, while not particularly confident that we have solved the riddle, we are certain that our set of assumptions will goad others to do so.

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