Isotope Effect in the Gas Phase Reaction of Pyrene-d_{10} with Nb$^+$ Ions*

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The deuterium isotope effect in the gas phase ligation of niobium (Nb) monocations by a mixture of pyrene and perdeutero pyrene was studied in a FTMS instrument. The attachment of pyrene (pyrene-d_{10}) is followed by a rapid release of hydrogen (deuterium) from the Nb-pyrene (Nb-pyrene-d_{10}) cation, respectively. The dehydrogenated product formation depends on the experimental conditions in the reaction chamber. A 1,2-elimination of H$_2$ (D$_2$) from the ligation product is proposed.

INTRODUCTION

The kinetics of gaseous metal ion chemistry[1] (or, more generally, organometallic chemistry in the gas phase)[2] in which the ion reacts with organic ligands were subjected recently to mass spectrometric investigation.[3] Unfortunately, because of difficulties in determining ligand concentrations in the gas phase, only relative reaction rates could be determined. Srzić *et al.*[4] overcame this difficulty and were able to determine the gas phase concentration of a polycyclic aromatic hydrocarbon (PAH) within the spectrometer by means of the equilibrium

$$Pn^+ + Pn \rightleftharpoons Pn_2^+$$
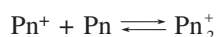
for which the thermodynamic parameters are known.[5] This approach generated second-order rate constants for the gas phase ligation of metal monocations (M$^+$) with pyrene (Pn).

Most metal ions ligate consecutively by simple addition of two Pn molecules. Some metal ions ligate the first Pn with simultaneous loss of H$_2$. Some metal ions may also ligate three instead of just two Pn units. And, finally, metals with an ionization potential (IP) higher than that of Pn may undergo a charge-exchange reaction.

$$M^+ + Pn \longrightarrow M + Pn^+$$

An isotope effect, Pn-d_{10} *versus* Pn, was not evident in simple addition ligation,[6] indicating that such addition leads to a sandwich structure of the complex. We report here the results of Nb$^+$ ligation by Pn, which takes place almost exclusively by loss of H$_2$ in the first step. Ligation then proceeds as follows: i) formation of (NbPn$_2$ – H$_2$)$^+$ along with a small amount of ions which had lost 2H$_2$ and 3H$_2$; ii) formation of (NbPn$_3$ – 2H$_2$)$^+$ along with a small amount of ions formed by loss of 3H$_2$; and iii) formation of (NbPn$_4$ – 3H$_2$)$^+$ along with some ions

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which had lost $4H_2$. The first and second step products may be accompanied by small amounts of the 2nd step product with an added oxygen atom; these latter products appear only at longer reaction times and are produced by reaction with residual water in the instrument. Some Pn^+ is also produced by charge exchange and is in equilibrium with Pn_2^+. The complete set of reactions is, in fact, rather complicated, especially if one compares them with the reactions[7,8] of Ta^+. Here we wish to address the isotope effect observed when a Pn/Pn-d_{10} mixture is used to ligate Nb^+.

EXPERIMENTAL

Pyrene and its perdeuterated analog, were obtained from Fluka Chemie AG, Buchs, Switzerland. The mixture contained 64, 14, 6 and 16 % of d_{10}, d_9, d_8 and d_0, respectively. The Nb metal foil was 99.8 % pure (Aldrich, Milwaukee, WI, USA). All experiments were performed on an FT/MS 2001-DD Fourier transform mass spectrometer (Madison, WI, USA) equipped with a 3 T superconducting magnet, and a Nicolet 1280 data station. Positive ions were acquired at 2×10^{-9} Torr in the source compartment of a dual cubic trap. The trapping voltage was maintained at 2 V throughout the experiment. Single 1064 nm pulses of a Nd:YAG Quanta Ray DCR-11 laser (Spectra-Physics, Inc., Mountain View, CA, USA) were used to produce Nb^+ ions from Nb metal foil located behind the source trap plate. The Pn/Pn-d_{10} mixture of was administered by evaporating an alcoholic solution to the probe. Following metal ion formation, reaction times of 1 ms – 300 s were allowed before recording the gas phase products (Exp1) or, after a given time delay, all but the Nb^+ ions were removed and then their reaction with gas phase Pn was allowed to take place during another delay time before recording the spectrum (Exp2, Exp3, Exp4). This second procedure was supposed to ensure that all excited Nb^+ ions had relaxed before the reaction was monitored. The same Pn/Pn-d_{10} mixture was always used, the deuterium content being determined from a low energy (18 eV) electron impact mass spectrum.

RESULTS AND DISCUSSION

Mass spectra of Nb^+ ions after exposure to gas phase Pn and to the Pn/Pn-d_{10} mixture are compared in Figures 1a and 1b, respectively. The spectrum with Pn was recorded after a delay of 60 ms; it shows that Nb^+ is consumed and that formation of reaction products up to $(NbPn_4 - 4H_2)^+$ of *m/z* 893 does occur. It exhibits nearly exclusive formation of $(NbPn - H_2)^+$ of *m/z* 293 in the first step. However, the spectrum with the Pn/Pn-d_{10} mixture, after just 1 ms, shows the presence of a considerable amount of NbPn-d_{10}^+ of *m/z* 305 formed by simple addition (*i.e.*, without loss of D_2). Such a state of affairs is not surprising because one expects that two C–H bonds are easier to break than two C–D bonds; however,

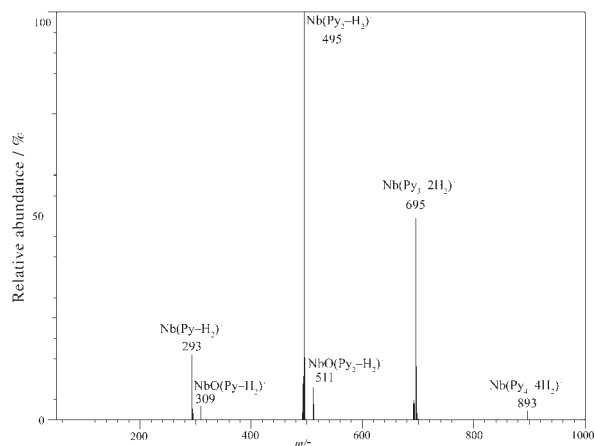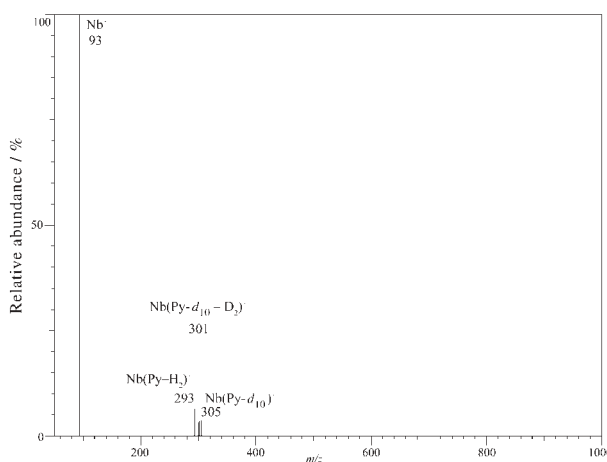Figure 1a. LD/I spectra of Nb^+ gas phase reactions products with pyrene after a 60 ms reaction time.

Figure 1b. LD/I spectra of Nb^+ gas phase reactions products with mixture of Pn and Pn-d_{10} (1:4) after 1 ms reaction time.

Ta, W, and Pt which also form $(MetalPn - H_2)^+$ ions react with Pn-d_{10} to produce $(MetalPn-d_{10} - D_2)^+$ ions only.

The temporal change of the $NbPn^+$ reaction products formed with the Pn/Pn-d_{10} mixture indicates that the relative importance of simple addition product formation increases for both analogues with the reaction time. This could be the result of:

i) more initial H_2/D_2 loss due to reaction of electronically excited Nb^+ ions;

ii) higher reactivity of the $(NbPn - H_2/D_2)^+$ ions in the next step, thus causing their depletion at longer delay times, or

iii) generally higher stability of $(NbPn-d_{10})^+$ as compared to $(NbPn)^+$.

To check these possibilities and to investigate the isotope effect, we measured the relative intensities of *m/z* 293, 295, 301 and 305 corresponding to $(NbPn - H_2)^+$, $NbPn^+$, $(NbPn-d_{10} - D_2)^+$ and $(NbPn-d_{10})^+$, respectively, in a series of experiments outlined below.

These experiments and their characteristics can be described as follows:

Exp1: 100 µs after the laser pulse, only the Nb^+ ions are retained and allowed to react for a given period of time (reaction time). This procedure provides the smallest chance for relaxation of electronically-excited Nb^+.

Exp2: After the laser pulse, all products except Nb^+ are expelled four times, each time with a pause of 1 ms between ejections; the residual Nb^+ is then allowed to react for a given period of time (reaction time). Most of the fast reacting Nb^+ ions and their products are removed by this tactic.

Exp3: Immediately after the laser pulse, only Nb^+ ions are retained and kept for a given period of time (cooling time) and then, four times in succession, all products except Nb^+ are expelled with a 100 µs pause between ejections. The final Nb^+ were allowed to react for 1 ms and the products recorded. Thus, since the Nb^+ ions were given various lengths of time to react and all resulting products were removed, this procedure measures the initial reaction products of the remaining Nb^+ (*i.e.*, after a very short but constant reaction time).

Exp4: N_2 gas was added after the laser pulse and then all but Nb^+ ions are expelled five times with a pause of 100 µs between ejections. The remaining Nb^+ ions were allowed to react for a given period of time (reaction time). The procedure is similar to Exp2 but the addition of N_2 helps to collisionally deactivate excited Nb^+.

For each procedure, the relative intensities $I(293)$ of m/z 293 expressed as

$$I(293) = (mass\ 293)/(mass\ 293 + mass\ 295)$$

and of m/z 301 expressed as

$$I(301) = (mass\ 301)/(mass\ 301 + mass\ 305)$$

were determined. Their ratio was used as a measure of the isotope effect (IE). These ratios for Exp1, Exp2, Exp3 and Exp4 were 1.17, 1.37, 1.37, and 1.25, respectively. The results for 4 typical reaction times are shown in Table I.

In all procedures, the initial intensity of m/z 295 was found to be 1/10 that of m/z 305 although, according to the Pn/Pn-d_{10} mixture composition, it should be 1/4. As noted above, both intensities rise with reaction time, but faster when Nb^+ is allowed longer relaxation times. However, the relative intensities $I(293)$ always remain greater than $I(301)$, (*i.e.*, the isotope effect, IE > 1). The lowest value of IE occurs in Exp1 indicating (i) the presence of

TABLE I. Intensities of product masses m/z 293 and 295 of pyrene and m/z 301 and 305 of pyrene-d_{10} dehydrogenation and addition reaction with Nb^+, their fractions $I(293) = 293/(293 + 295)$ and $I(301) = 301/(301 + 305)$ and corresponding isotope effects IE = $I(293)/I(301)$ for various reaction (cooling) times in milliseconds

Reaction (cooling) time/ms	293	295	301	305	$I(293)$	$I(301)$	IE
				Exp1			
1	4.77	0.29	15.96	2.94	0.942	0.844	1.12
30	8.52	0.53	26.97	5.49	0.941	0.831	1.13
70	16.70	1.20	63.08	10.50	0.933	0.857	1.09
100	23.07	1.85	83.31	15.50	0.926	0.843	1.10
				Exp2			
1	1.50	0.20	4.50	2.50	0.882	0.643	1.37
30	3.30	0.50	10.00	5.80	0.868	0.633	1.37
70	11.00	1.10	30.00	11.00	0.909	0.732	1.24
100	9.30	1.00	34.00	15.00	0.903	0.694	1.30
				Exp3			
1 (1)	4.50	0.50	11.20	5.50	0.90	0.671	1.34
1 (30)	4.00	0.50	10.00	5.20	0.889	0.658	1.35
1 (70)	3.90	0.50	9.70	5.90	0.886	0.622	1.43
1 (100)	4.50	0.60	10.70	6.30	0.882	0.629	1.40
				Exp4			
1	4.10	0.35	11.60	4.00	0.921	0.744	1.24
30	14.80	1.60	40.70	14.40	0.902	0.739	1.22
50	21.80	2.10	62.30	22.00	0.912	0.739	1.23
100	34.70	4.20	100.00	43.00	0.892	0.699	1.28

excited Nb^+. The ratio of addition/dehydrogenation products is also highest in this case: 15 for Pn and 5 for Pn-d_{10} in contrast to 10 and 2, respectively, when the relaxation procedures of Exp2, Exp3 and Exp4 were used. The value of IE is highest and practically the same for Exp2 and Exp3. Since Exp3 gives early reaction products for always the same reaction time of 1 ms but in dependence of increasing cooling time the comparison with Exp2 shows that (ii) higher reactivity of the (NbPn – H_2/D_2)$^+$ ions in the next step is not operative because the ratios of the products in Exp2 and Exp3 are the same. It does not exclude (iii) the higher stability of NbPn-d_{10}.

In the MS–MS experiment where, after reaction time long enough for Nb^+ and Pn-d_{10} to form sufficient *m/z* 305, all other ions were expelled and additional reaction time ensued to permit reaction of this latter ion species, the sole product was *m/z* 301. Hence because *m/z* 305 does not react further by addition of another Pn this indicates that the isotope effect is connected with the removal of hydrogen from the first addition product, which removal is easier for H_2 than D_2. Concerning the mechanism of the reaction and the origin of the deuterium effect, we know that the reaction is driven by the energy which the Nb^+ received in the ionization process. This energy in the case of Nb-metal is 6.88 eV, close to the IP of 7.42 eV for Pn. The first addition product NbPn$^+$ is assumed to form by Beauchamp's[9] mechanism
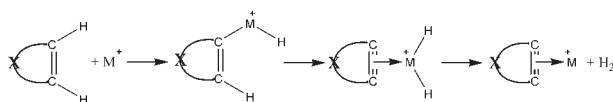
in which each step is energetically preferred for C–H vs. C–D and Nb$^+$–H *vs.* Nb$^+$–D bonds. The overall dependence constitutes the isotope effect. For Ta, because of its IP of 7.88 eV, the surplus of energy is so high that the addition product and therefore the isotope effect is not observed. According to previous results, we anticipate that dehydrogenation is a 1,2-process but this still needs to be proven. Such work is in progress.

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SAŽETAK

Izotopni efekt u reakciji pirena-d_{10} s Nb$^+$ ionima u plinskoj fazi

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Analiza deuterijskoga izotopnoga efekta ligacije Nb$^+$ s pirenom (Pn) u plinskoj fazi pri kojoj se molekula vodika brzo otpušta iz NbPn$^+$ pokazuje da efekt pri stvaranju dehidrogeniranoga produkta zavisi o eksperimentalnim uvjetima i iznosi 1,2–1,4. Predložen je tentativni reakcijski mehanizam.