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Gas Phase Ligation Kinetics of Metal Monocations with Pyrene*

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The gas-phase ligation of M^+ ions with pyrene is reviewed. The M^+ (M = Al, K, V, Cr, Fe, Co, Ni, Cu, Nb, Mo, Ru, Ag, Sn, Ta, W, Re, Pt, Au, Hg, Pb, Bi and U) were produced by a single laser shot. Gaseous pyrene was already present in the Fourier transform mass spectrometer (FTMS). The reaction proceeded by consecutive ligations, sometimes accompanied by expulsion of a part (usually H_2) of the ligand. Charge transfer (when the neutral metal has a higher ionization energy than the pyrene), pyrene dimerization, oxidation by residual oxygen, and protonation by ubiquitous water in the instrument may also take place. Reaction progression was followed by varying the delay time between the shot and the mass-spectrometric assay of the ions. If electronically-excited M^+, which might have been produced by the laser pulse, was interfering with the reaction, these ions and their products were swept out of the FTMS chamber prior to initiation of the time delay specified above.

INTRODUCTION

Gas-phase ligation of metal monocations by organic compounds is an extensively investigated field.[1–6] Metal ions are powerful catalysers of numerous important chemical reactions; the gas-phase results provide intrinsic reactivities, ones bereft of the influences of the solvent and surfaces, which make direct connection to theory.[7–9] Mass spectrometry in combination with metal ion chemistry holds an exceptional promise of getting an insight into organometallic, catalytic and biological chemistries.[6] The experimental data for reactions with saturated and unsaturated hydrocarbons, possibly because of their importance to the petroleum industry, is especially rich. There are also numerous investigations on reaction products and reaction mechanisms and thermodynamics with various classes of molecules. Much less data exists on reactions with polycyclic aromatic hydrocarbons (PAH), which are much less reactive and, apparently, less important.[5,10–14] We began our investigations of pyrene, some related molecules, and their heteroanalogs some years ago,[15–22] at a time when few or no such investigations existed. The most informative one was published in 1995 by Wu and Brodbelt.[23] Curiously enough, this situation has not changed much. The results of our studies are somewhat surprising and, even though our work is still incomplete, we believe it is an appropriate time to give an overview of the reaction products and reaction routes of metal monocations and pyrene in the gas phase.

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* Dedicated to Dr. Edward C. Kirby in happy celebration of his 70th birthday.

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EXPERIMENTAL

Compounds

Pyrene (Py) was obtained from Fluka Chemie AG, Buchs, Switzerland. Metal ions were produced from foils of high 99.8 % purity (Aldrich, Milwaukee, WI, USA) or from alloys (stainless steels, coins) or from salts (Na, K). The use of alloys and coins (which are also alloys of a given composition) enables one to deduce relative metal-ion reaction rates and if an absolute rate is available for one of the metals in the alloy, one can immediately obtain absolute rates for all of them.

All experiments were performed on a 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 the dual cubic trap. Trapping voltage was maintained at +2 V during the experiment. Single 1064 nm laser pulses from a Nd:YAG laser Quanta Ray DCR-11 (Spectra-Physics, Mountain View, CA, USA) were used to produce metal ions from the samples by laser desorption ionization (LDI). The probe and the foil were located behind the source trap plate. Pyrene was previously administered by evaporating an alcoholic solution on the probe. After the laser shot (*i.e.*, after metal ion formation), reaction times of 100 μs – 30 s were allowed to elapse before the chemical assay (*i.e.*, before recording the spectrum). If the possibility of the presence of M^+ ions existed, all reaction products were removed shortly after the laser shot, and it was then assumed that only ground-state M^+ was present. The reaction of the remaining M^+ ions with gas phase Py was then allowed to take place for a period of 100 μs – 30 s before recording the spectrum. It was supposed that the second procedure would make it possible to relax electronically excited M^+ and remove their preformed reaction products.

RESULTS AND DISCUSSION

Some of our results for the reaction of metal monocations with pyrene in the gas phase were reported previously. Reactions of Cr, Fe, Ni, Nb, Ta, and U monocations were investigated in some detail. Reaction rate constants, probable structures of the products as deduced from isotope studies with perdeuterated pyrene, and tentative mechanisms of products formation were reported. For all other metals, only their ionization potentials, which are indicative of the probability of charge transfer between the metal ion and pyrene, and the extent of ligation (coordination number) were usually given. The available data set is given in Table I. An excellent review of electronic state-specific transition metal ion chemistry was given by Armentrout.[24]

Because of the high ionization energies of metals Pt, Au and Hg, one expects that their cations will simply and exclusively remove an electron from pyrene and that no adducts will form. This is true for Au and Hg. However, with Pt^+ (the Pt foil contained some Ru), a small fraction of $(PtPy–H_2)^+$ and even $(PtPy_2–H_2)^+$ formation was observed (Figure 1). The reason for this anomaly could well be a fast loss of hydrogen from the pyrene, which then permits the addition to compete with the initially-preferred charge exchange reaction; however, it should not be forgotten that Pt has the lowest ionization energy of the three metals. Surprisingly, with long time delays, the formation of $NaPy^+$ (*m/z* 225) was observed even though no Na-salt or compound was intentionally introduced! The Py^+ ion forms a dimer with neutral Py and enters a temperature-dependent equilibrium with Py_2^+ (*m/z* 404); the intensity ratio of Py^+/Py_2^+ permits determination of the neutral Py concentrations and the absolute ligation rate constants in the gas phase.[16–18]

Of the five main groups (non-transition) metals Al, K, Sn, Pb and Bi, the first two have ionization potentials clearly below that of Py, namely, 7.426 eV. As a consequence, they do not produce Py^+; they also ligate only one Py. Ionization potentials for the other three metals lie slightly above that of pyrene, by approximately 0.15 eV and, as a result, they do yield some Py^+ by charge exchange in addition to the main processes – slow consecutive ligations of two Py units. In the case of Sn^+, it seems that a third Py will attach; however, the time delay required to confirm this definitively is too long for a satisfactory assay. On the other hand, the monocations of the first-row transition metals V, Cr, Fe, Co, Ni and Cu quickly bind two Py units without any loss of hydrogen in either step. According to the metal ionization potentials (Table I), only V^+ and Cr^+ should not exchange charge with Py but, because of the rapidity of the ligation process, the fraction of charge exchange is significant only with Fe^+. Fe^+ is the slowest ligator in both steps, with absolute rate constants $k_2(Fe^+) = 3.4 \times 10^{10}$

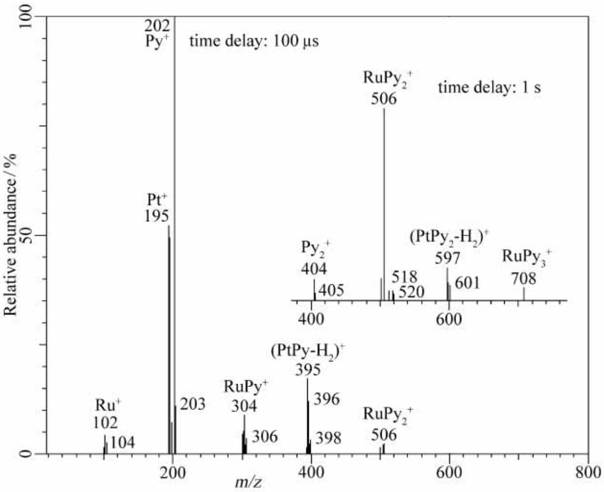

Figure 1. LDI-FT mass spectra of the reaction products of Pt^+ and some Ru^+ ions with pyrene (Py) after 100 *μ*s (below) and after 1 s (above) of reaction time.

and $k_3(FePy^+)$ = 3.3 × 10^9 $dm^3mol^{-1}s^{-1}$ for the $FePy^+$ and $FePy_2^+$ formation, respectively, whereby for both steps (k(Cr) = 2 k(Fe)).[18] Based on the fact that all these metal ions bind only two Py units and that for Cr, Fe and Ni no isotope effect was found when perdeuterated Py was used, one can conclude that they react through C-C

TABLE I. Some characteristics of the investigated metals and their monocations in the gas phase reactions with pyrene (Py) of the latter

Metal ion	Atom ionization energy / eV	Electron configuration of metal ion	Charge exchange	Py ligation steps (expulsion)			
				1st	2nd	3rd	4th
Al^+ *m/z*: 27 (100 %)	5.98	$[Ne]3s^2$	No	+	–	–	–
K^+ *m/z*: 39 (100 %), 40 (0.02 %), 41 (7.22 %)	4.34	$[Ne]3s^23p^6$	No	+	–	–	–
V^+ *m/z*: 51 (100 %)	6.74	$[Ar]3d^4$	No	+	+	–	–
Cr^+ *m/z*: 52 (100 %), 53 (11.3 %), 54 (2.8 %)	6.76	$[Ar]3d^5$	No	+	+	–	–
Fe^+ *m/z*: 56 (100 %), 54 (6.4 %), 57 (2.3 %)	7.87	$[Ar]3d^64s$	Yes	+	+	–	–
Co^+ *m/z*: 59 (100 %)	7. 86	$[Ar]3d^8$	Yes	+	+	–	–
Ni^+ *m/z*: 58 (100 %), 60 (38.5 %), 62 (5.3 %), 61 (1.7 %), 64 (1.4 %)	7.63	$[Ar]3d^9$	Yes	+	+	–	–
Cu^+ *m/z*: 63 (100 %), 65 (44.6 %)	7.72	$[Ar]3d^{10}$	Yes	+	+	–	–
Nb^+ *m/z*: 93 (100 %)	6.88	$[Kr]4d^4$	No	+ (H_2)	+	+ (H_2)	+ (H_2)
Mo^+ *m/z*: 92 (61.5 %), 94 (38.3 %), 95 (66.0 %), 96 (69.1 %), 97 (39.6 %) 98 (100 %) 100 (39.9 %)	7.10	$[Kr]4d^5$	Yes	+	+	–	–
Ru^+ *m/z*: 96 (17.6 %), 98 (5.9 %), 99 (40.4 %), 100 (39.9 %), 101 (54.1 %) 102 (100 %) 104 (59.0 %)	7.37	$[Kr]4d^7$	Yes	+	+	+	–
Ag^+ *m/z*: 107 (100 %), 109 (92.9 %)	7.57	$[Kr]4d^{10}$	Yes	+	+	+	–

TABLE I. Continued

Metal ion	Atom ionization energy / eV	Electron configuration of metal ion	Charge exchange	Py ligation steps (expulsion)			
				1st	2nd	3rd	4th
Sn$^+$ *m/z*: 112 (3.0 %), 114 (2.0 %), 115 (1.0 %), 116 (44.6 %), 117 (23.6 %), 118 (74.3 %), 119 (26.4 %), 120 (100 %), 122 (14.2 %), 124 (17.8 %)	7.34	$[Kr]4d^{10}5s^25p$	Yes	+	+	+	–
Ta$^+$ *m/z*: 181 (100 %), 180 (0.01 %)	7.89	$[Xe]4f^{14}5d^36s$	Yes	+ (H_2)	+ (H_2)	+ (H_2)	–
W$^+$ *m/z*: 180 (0.4 %), 182 (86.5 %), 183 (46.7 %), 184 (100 %), 186 (92.8 %)	7.98	$[Xe]4f^{14}5d^46s$	Yes	+ (H_2)	+	+ (H_2)	+ (H_2)
Re$^+$ *m/z*: 185 (59.7 %), 187 (100 %)	7.88	$[Xe]4f^{14}5d^56s$	Yes	+ (H_2)	+	+ (H_2)	+ (H_2)
Pt$^+$ *m/z*: 192 (2.3 %), 194 (97.5 %), 195 (100 %), 196 (74.6 %), 198 (21.2 %)	9.00	$[Xe]4f^{14}5d^9$	Yes	+ (H_2)	+ (H_2)	–	–
Au$^+$ *m/z*: 197 (100 %)	9.22	$[Xe]4f^{14}5d^{10}$	Yes	–	–	–	–
Hg$^+$ *m/z*: 196 (0.5 %), 198 (33.4 %), 199 (56.5 %), 200 (77.4 %), 201 (44.1 %), 202 (100 %), 204 (23.0 %)	10.44	$[Xe]4f^{14}5d^{10}6s$	Yes	–	–	–	–
Pb$^+$ *m/z*: 204 (2.7 %), 206 (46.0 %), 207 (42.2 %), 208 (100 %)	7.41	$[Xe]4f^{14}5d^{10}6s^26p$	Yes	+	+	–	–
Bi$^+$ *m/z*: 209 (100 %)	7.29	$[Xe]4f^{14}5d^{10}6s^26p^2$	Yes	+	+	–	–
U$^+$ *m/z*: 235 (0.7 %), 238 (100 %)	6.05	$[Rn]5f^36d7s$	No	+ (H_2)	+	+	–

bond activation and that the products may have a sandwich-type structure. Different behavior of metal ions from the above two groups is clearly visible in Figure 2. The Ni^+, Cu^+ and Pb^+ ions were produced by laser desorption from a US 10-cents coin (dime) with some lead metal on its surface. The reactants and products are shown after

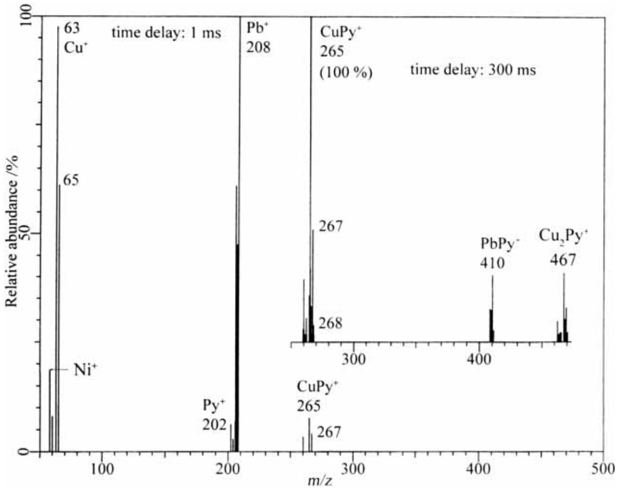

Figure 2. LDI-FT mass spectra of the reaction products of ions formed from a lead coated surface of a US 10-cents coin (dime) with pyrene (Py) after 1 ms (below) and after 300 ms (above) of reaction time.

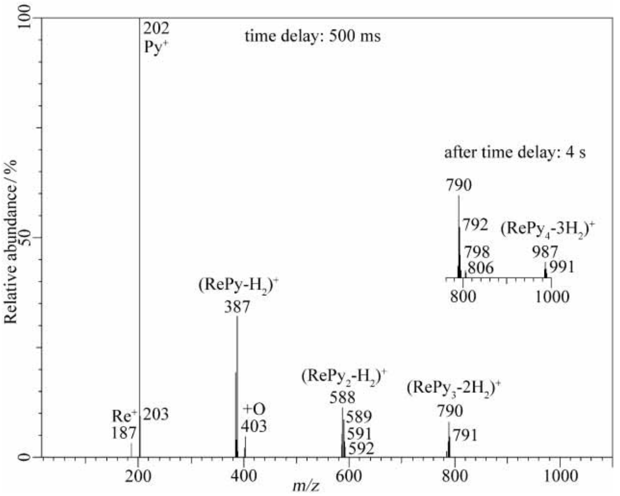

Figure 3. LDI-FT mass spectra of the reaction products of Re^+ ions with pyrene (Py) after 500 ms of reaction time. Insert shows products after 4 s of reaction time.

delay times of 100 μs (lower part) and 300 ms (upper part), indicating that Ni^+ and Cu^+ react much faster than Pb^+. Since Ni^+ was shown[25] to react somewhat faster than Cr^+ and also somewhat faster than Cu^+, it can be concluded that k(Cr) = k(Cu). Ligation of the second- and third-row transition metal monocations with Py is more difficult to understand. Unlike V^+, which shows a very clean addition of two units, Nb^+ ligates four (expelling H_2 in the first, third and fourth addition and nothing at all in the second), whereas Ta^+ adds three Py units with a loss of H_2 in all three steps. Mo^+ shows a neat addition of two units whereas W^+ adds four, again losing an H_2 in the first, third and fourth, but not in the second addition. Curiously, Ru^+ (Figure 1) adds three Py units. Re^+, which is not in the same group of the Periodic Table, ligates four, with an H_2 loss in the first, third and fourth ligation steps (Figure 3). In a previous paper, we considered this behavior to be a »riddle« and suggested that the second addition was not a true ligation but rather a dimerization of the first ligated Py unit (which behaved as a charged Py^+); this remains the only explanation available. Finally, Ag^+ seems to bind three Py units although after 100 s the corresponding *m/z* 713 and 715 peaks are still less than 10 % of the $AgPy_2^+$ base peak at *m/z* 513. U^+, which is very prone to oxidation by traces of water and oxygen in the instrument, ligates three Py units. Such oxidations also occur with other metals and can be traced, using +16 or +18 satellites, to the existing peaks in the spectra. They are especially abundant in the Hf^+ and Zr^+ experiments, which we will not discuss here because of lack of relevant data for Ti^+. Comparing the results of the second and higher row transition metal monocations with those of the first row and the main group elements, it is obvious that a change in the reaction mechanism takes place, which is reflected in C-H bond ruptures. This has been pointed out by classifying the reactions as the ones governed by C-H bond activation.[26–29] Although correct, the overall results show that within the various groups there are striking differences awaiting explanation. Our attempt to switch the Nb^+ C-H bond activation property to C-C activation by performing the ligation with perfluorinated PAHs naphthalene and anthracene (where the corresponding C-F bonds are shifted to high energies) showed surprisingly that no ligation but only NbF_4^+ or $(PAH–4F)^+$ formation could be observed.[29] A recent study on perfluorobenzene with 29 transition metal ions using inductively coupled plasma selected-ion mass spectrometry (ICP-SIFT) brought even more surprises.[31,32]

In conclusion, we feel that while providing some answers, we also raise numerous questions. Answers to these questions will require knowledge of the reacting electronic states and their properties. At this stage, it is best to consider this work as »research in progress«.

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SAŽETAK

Kinetike ligacije metalnih monokationa s pirenom u plinskoj fazi

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Istraživana je ligacija različitih metalnih monokationa M^+ s pirenom u plinskoj fazi. M^+ (M = Al, K, V, Cr, Fe, Co, Ni, Cu, Nb, Mo, Ru, Ag, Sn, Ta, W, Re, Pt, Au, Hg, Pb, Bi and U) nastaju pojedinačnim udarima lasera na metalne mete unutar spektrometra masa uz Fourierovu transformaciju (FTMS) u kojem je već prisutan piren u plinskoj fazi. Do ligacije dolazi konsekutivnim adicijama uz ili bez gubitka dijela (obično H_2) liganda. Ukoliko je energija ionizacije metala veća od energije ionizacije pirena dolazi do izmjene naboja. Također se opažaju reakcije dimerizacije, oksidacije s preostalim kisikom i protoniranje s prisutnom vodom u instrumentu. Napredovanje reakcija je praćeno snimanjem svih iona uz različita vremena zadržavanja u spektrometru nakon (i) udara lasera; (ii) dodatnoga izbacivanja trenutno stvorenih produkata s elektronički pobuđenim M^+.