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Original Scientific Paper

Deuterium Labeling Study of the Gas-phase Reaction of Fe^+/Cr^+ with Pyrene by FTMS*

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A ~ 10 : 1 mixture of deuterated with undeuterated pyrene was used to study the product composition in the reaction with various ratios of Fe^+ and Cr^+ (10 : 1 to 1 : 10) ions in a Fourier-transform mass spectrometer. None of the products $FePy^+$, $CrPy^+$, Py^+, $FePy_2{}^+$, $CrPy_2{}^+$ and $Py_2{}^+$ showed deviation from the statistically expected composition.

INTRODUCTION

We have recently observed that the gas phase reaction of positively charged metal ions, M^+, with neutral polycyclic aromatic hydrocarbons (PAHs) can be investigated in the Fourier-transform mass spectrometer over several minutes in terms of simple consecutive pseudo first order kinetic processes, provided that the concentration of PAH is kept constant.[1] This is achieved by allowing a certain amount of solid PAH to be present in the UHV environment, thus ensuring that by sublimation a steady state concentration exists in the instrument. The M^+ are produced by a single laser pulse and the development of the reaction is monitored by recording the mass spectra at certain time intervals after the laser shot. The variation of laser power in the shots is compensated by normalizing the obtained spectrum, *i.e.* by setting the sum of all measured ions in each spectrum (to 100%). It was possible to show that generally two molecules of PAH – phenanthrene or pyrene (Py) – bind to M^+ one after the other.[2] Parallel to the formation of these (sandwich-type) $MPy_2{}^+$ ions, one also observes the presence of Py^+ ions, which cannot be produced by laser ionization but must have been formed by charge electron transfer to the M^+. Such formed Py^+ react with neutral Py and, after some time, $Py_2{}^+$ ions are also observed in

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* Dedicated to the late Professor Stanko Borčić.

the mass spectrum. We decided to investigate this set of reactions by using the competition of two M^+, namely Fe^+ and Cr^+, for a mixture of undeuterated and perdeuterated Py-d_{10}, whereby also the existence of a (primary) isotope effect in these reactions may be revealed.

EXPERIMENTAL

All experiments were performed on an FT/MS 2001-DD Fourier-transform mass spectrometer (Madison, Wisconsin, 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, and the trapping voltage was maintained at ±2 V during the experimental sequence.

Single laser pulses on the same spot of a Nd:YAG laser Quanta Ray DCR-11 (Spectra-Physics, Inc., Mountain View, CA, USA) working at 1064 nm fundamental line were used for producing Fe^+/Cr^+ ions from the stainless steel probe, tip located behind the source trap plate. Pyrene (Fluka Chemie AG, Buchs, Switzerland) and its perdeuterated analogue (Fluka Chemie AG, Buchs, Switzerland) were also administered by evaporating an alcoholic solution to the probe. Following the metal ion formation, a 1 ms – 300 s delay was provided for the gas phase reaction of Fe^+/Cr^+ ions with pyrene. In various runs, the ratio of Fe/Cr was between 10 to 0.1. The deuterium content of always the same Py/deuterated Py mixture was determined from the low energy (10 eV) electron impact mass spectrum. In comparing the calculated (*i.e.* expected from the actual composition of the Py/deuterated Py mixture) with the observed spectrum, we took into account only the intensities of the MI-d_{10}, MI-d_9 and MI-d_0 in molecular ions (MI) containing one Py molecule, and of the MI-d_{20}, MI-d_{19}, MI-d_{10}, MI-d_9 and MI-d_0 in molecular ions (MI) containing two Py units, thus avoiding consideration of contributions from ^{54}Fe and ^{13}C.

RESULTS AND DISCUSSION

The composition of the employed Py/deuterated Py mixture is given in Table I. A typical spectrum of its reaction products with a Fe/Cr = 5 mixture recorded after a 2 s delay is given in Figure 1a and the resolved Py^+, $(Fe+Cr)Py^+$ and $(Fe+Cr)Py_2^+$ clusters therein in Figures 1b, 1c, and 1d, respectively.

TABLE I

The composition of Py/deuterated Py mixture

Compound	x
Py-d_{10}	0.64
Py-d_9	0.14
Py-d_8	0.06
Py	0.16

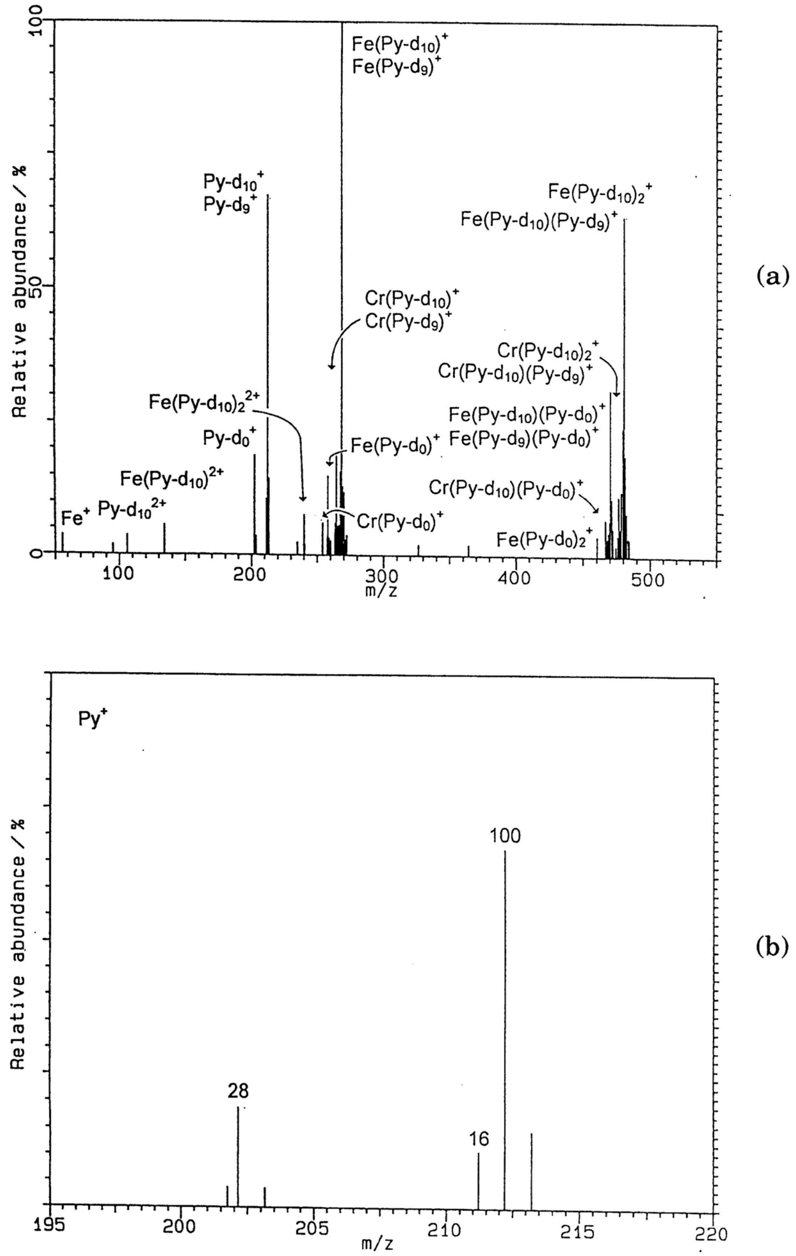

Figure 1. (a) LDI FTMS of Fe$^+$/Cr$^+$ (5 : 1) mixture at a 2 s delay time after the laser shot and reaction products with Py/deuterated Py mixture with (b) resolved Py$^+$, (c) (Fe+Cr)Py$^+$ and (d) (Fe+Cr)Py$_2$$^+$ clusters and the corresponding percentages therein (underlined for Cr species).

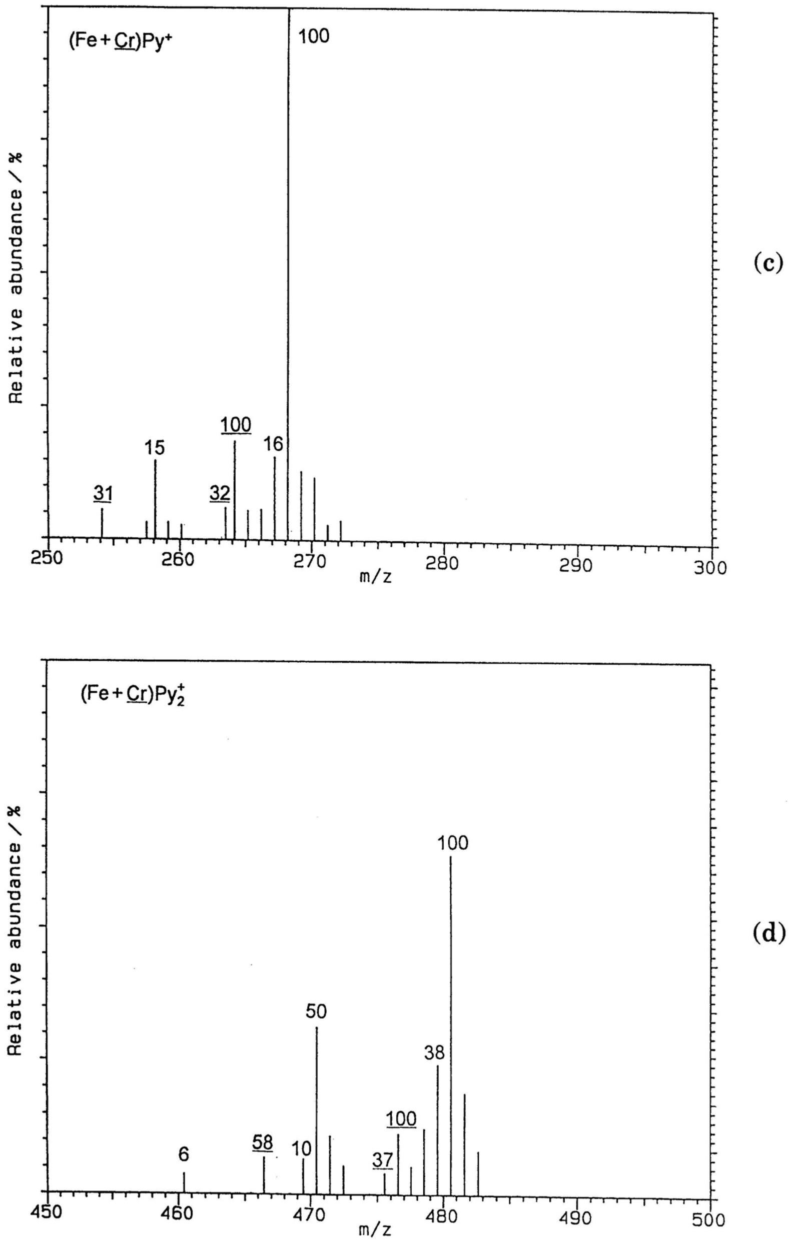

Figure 1. continued from p. 1451.

TABLE II

Calculated and observed relative intensities of MI-d_{10}, MI-d_9 and MI-d_0 in single pyrene and MI-d_{20}, MI-d_{19}, MI-d_{10}, MI-d_9 and MI-d_0 in two pyrenes containing molecular ions (MI)

	one – Py			two – Py				
	MI-d_{10}	MI-d_9	MI-d_0	MI-d_{20}	MI-d_{19}	MI-d_{10}	MI-d_9	MI-d_0
calc.	100	22	25	100	45	50	11	6
exp.	100	24 ± 6*	25 ± 4*	100	39 ± 6**	55 ± 9**	12 ± 3**	8 ± 2**

standard deviation: *n = 24, **n = 14.

The same composition was observed in the FTMS by inspecting the MI-d_{10}, MI-d_9 and MI-d_0 species of the Py^+, $CrPy^+$ and $FePy^+$ clusters indicating, as expected, that their formation is a result of statistical collisions. If this holds also for the addition of the second Py, then the product composition should be given by Newton's formula, *i.e.*

$$P_n(n_1, n_2, \ldots) = \frac{n!}{n_1!\, n_2! \ldots} p_1^{n_1} \times p_2^{n_2} \times \ldots \tag{1}$$

$$n_1 + n_2 + \ldots = n$$

Thus, n for Py_2^+, $CrPy_2^+$ and $FePy_2^+$ equals 2 and probabilities p_i are the molar ratios of Py species present in the mixture. The calculated composition for these ions according to (1) and the experimental one observed from the FT mass spectra for the inspected ions is given in Table II. On the basis of these results, we conclude that, within the error limits in all three reactions, the given Py molecules react statistically, *i.e.* without an observable isotope effect. This result speaks in favour of a sandwich-type structure for MPy_2^+ ions and/or for an irreversible attachment of both the first and the second Py molecules to the metal ion.

REFERENCES

1. D. Srzić, S. Kazazić, and L. Klasinc, *Rapid. Commun. Mass Spectrom.* **10** (1996) 688.
2. D. Srzić, S. Kazazić, and L. Klasinc, *J. Chem. Soc., Chem. Commun.*, submitted.

SAŽETAK

FTMS studij reakcija Fe^+/Cr^+ s pirenom u plinskoj fazi uz obilježavanje deuterijem

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Smjesa deuteriranog i nedeuteriranog pirena (~ 10 : 1) uporabljena je za proučavanje sastava produkata reakcije s Fe^+/Cr^+ (10 : 1 do 1 : 10) u FT spektrometru masa. Odstupanja od statistički očekivanog sastava nisu opažena kod produkata reakcije ($FePy^+$, $CrPy^+$, Py^+, $FePy_2^+$, $CrPy_2^+$ i Py_2^+).