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Original Scientific Paper

Gas Phase Kinetics of Metal Ion Ligation by Pyrene*

Tomislav Cvitaš,[a] *Saša Kazazić,*[a] *Snježana Kazazić,*[a] *Nenad Kezele,*[a]
Leo Klasinc,[a,]** *Dunja Srzić,*[a] *and Herbert Budzikiewicz*[b]

[a]*Laboratory for Chemical Kinetics and Atmospheric Chemistry,*
Ruđer Bošković Institute, 10002 Zagreb, Croatia

[b]*Institut für Organische Chemie der Universität zu Köln, D-50939 Köln, Germany*

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Investigation of simple ligation reactions of metal M^+ ions with pyrene (Py) within the ICR FT mass spectrometer indicates relatively fast consecutive formation of MPy^+ and $MPy_2{}^+$ ions, and if $E_i(M^+) > E_i(Py)$ accompanied also by formation of Py^+ due to charge exchange. The much slower reaction and equilibrium $Py^+ + Py \rightleftharpoons Py_2{}^+$, for which the thermodynamic parameters are known, makes it possible to determine the concentration of Py during the ligation reactions and to calculate the second order rate constants from the set of pseudo first order constants obtained by iterative nonlinear least square fitting of experimental »snapshot« mass spectral data with the proposed kinetic scheme.

Key words: ligation reaction, charge exchange reaction, gas phase kinetics, iron(+), chromium(+), pyrene, pyrene(+), dipyrene(+), gas phase equilibrium.

INTRODUCTION

Ligation of metal ions in solution has been investigated extensively over most of the 20th century. Although the first ideas of inorganic reaction mechanisms can be found in the papers of the 1913-Nobel-Prize-winner A. Werner, such reactions were at that time too fast for kinetic studies. Modern techniques of fast reaction measurements allow determination of reaction

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

** Author to whom correspondence should be addressed. (E-mail: klasinc@joker.irb.hr) rate constants, *e.g.* for the exchange rate of water in octahedral aqua-complexes of metal ions which vary over 16 orders of magnitude;[1] thus, much is known about the kinetics and reaction mechanism of coordination compounds in solution. Studies of gas phase reactions of metal ions with organic ligands using mass spectrometry are rather recent.[2,3] As for their kinetics, it has so far been possible only to deduce relative rates because of the difficulties in determining the ligand gas phase concentration. We have recently suggested how to determine the gas phase concentration of a polycyclic aromatic hydrocarbon (PAH) in the mass spectrometer.[4] Here, we report the determination of reaction rate constants of simple ligation reactions of metal M^+ with pyrene (Py) in the gas phase using laser desorption to produce M^+ ions and »snapshot« spectra from a Fourier transform mass spectrometer, in which a determinable concentration of Py was held constant during the experiment.

EXPERIMENTAL

A constant steady state concentration of Py was achieved in the FT mass spectrometer by sublimation at a given temperature from a film obtained by evaporation of an alcoholic pyrene solution, previously applied and dried on the probe head. A metallic target close to this film was exposed to a single pulse from Nd:YAG Quanta Ray DCR-11 laser (Spectra Physics, Inc. Mountain View, CA, USA) operating at 1064 nm. The product FT mass spectra were recorded on a FT/MS 2001 DD Fourier-transform mass spectrometer (Finnigan, Madison, Wisconsin, USA) after different time delays ranging from 100 μs up to 300 s.

RESULTS AND DISCUSSION

Single charged metal ions produced in a mass spectrometer by pulsed laser impingement on metal surfaces react readily, if present in the gas phase, with PAH or their heterocyclic analogs. The reaction, where M^+ denotes the metal ion and L the neutral PAH or heterocyclic ligand molecule can be described as a series of consecutive ligation reactions

$$M^+ \xrightarrow[\text{-X}']{+\text{L}} (\text{ML} - \text{X}')^+ \xrightarrow[\text{-X}'']{+\text{L}} (\text{ML}_2 - \text{X}' - \text{X}'')^+ \xrightarrow[\text{-X}''']{+\text{L}} \ldots \qquad (1)$$

$$\text{X}', \text{X}'', \text{X}''' = \text{nil or some part of L}$$

If the ionization energy of the metal is higher than that of the ligand

$$E_\text{i}(\text{M}^+) > E_\text{i}(\text{L})$$

the charge exchange reaction

$$M^+ + L \rightarrow M + L^+ \tag{2}$$

may also be observed. Because of the excess of ligand molecules in the gas phase, all reactions exhibit a pseudo-first order kinetic behavior.

We were interested in the rates of the ligation reaction of various metals with a pyrene (Py) ligand. Pyrene as ligand has three advantages: (i) pyrene binds to most metal ions by simple attachment; (ii) sublimation of pyrene at low temperatures maintains a constant, sufficiently high concentration of gas phase molecules in the mass spectrometer for long periods of time; (iii) the concentration of neutral pyrene molecules in the mass spectrometer can be determined reliably.

Namely, PAH cations and neutral molecules exist in the gas phase[5] in the equilibria

$$(PAH)^+ + (PAH) \rightleftharpoons (PAH)_2^+ \tag{3}$$

The equilibrium constant for pyrene in the above reaction

$$K_p = \frac{p(Py_2^+)}{p(Py^+) \cdot p(Py)} \tag{4}$$

and the intensity ratio $I(Py_2^+) / I(Py^+) = p(Py_2^+) / p(Py^+)$ enable determination of the partial pressure of neutral pyrene $p(Py)$ in the mass spectrometer. Using the thermodynamic data for the dimer dissociation reaction obtained by Meot-Ner[5] and reversing the sign to be applicable to reaction (3) as $\Delta_r H^o = -79.9$ kJ mol^{-1} for the reaction enthalpy and $\Delta_r G^\circ = -34.3$ kJ mol^{-1} for the reaction Gibbs energy at 390 K and $p^\circ = 1$ atm, the equilibrium constants (4) for the experimental conditions and hence the partial pressures of neutral pyrene

$$p(Py) = \frac{I(Py_2^+)}{I(Py^+)} \cdot \frac{1}{K_p} \tag{5}$$

can be calculated. The standard (or thermodynamic) equilibrium constant is related to the pressure based constant (4) by

$$K^o = \exp\left(-\frac{\Delta_r G^o}{RT}\right) = K_p \cdot p^o \tag{6}$$

The temperature dependence is taken care of by the van't Hoff equation

$$\ln K^\circ(T_2) = \ln K^\circ(T_1) - \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7}$$

yielding the expression

$$p(\mathrm{Py}) = \frac{I(\mathrm{Py}_2^{\,+})}{I(\mathrm{Py}^+)} \frac{p^\circ}{\exp\left[-\frac{\Delta_r G^\circ}{RT_1} - \frac{\Delta_r H^\circ}{R}\cdot\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]} \tag{8}$$

for determination of the neutral pyrene partial pressure in experiments at temperature T_2. It is, however, necessary that the $I(\mathrm{Py}_2^+) / I(\mathrm{Py}^+)$ should remain constant over a sufficiently long period of time while the ligation reactions are investigated (Figure 1). Experiments showed that, after an initial period of 15–20 minutes, this ratio and hence the $p(\mathrm{Py})$ remain constant for about half an hour if measured at a 100 s delay after the laser pulse.

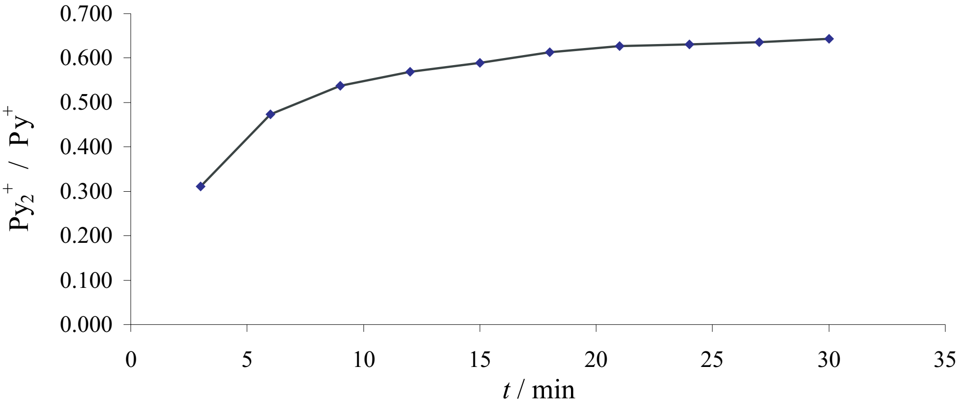


Figure 1. Determination of $I(\mathrm{Py}_2^+) / I(\mathrm{Py}^+)$ ratio after 100 s delay in the reaction of chromium (Cr^+) with pyrene (Py) at 25 °C.

Ligation reactions are much faster and are completed within seconds. As an example, we show spectra of metal ions Cr^+, Fe^+ and Ni^+ from stainless steel with pyrene after 100 μs and 100 ms from the laser pulse (Figure 2). To monitor ligation reactions, the mass spectra are recorded at different time delays after the laser pulse. The »snapshot« spectra allow it to follow the disappearance of M^+ and the formation of MPy^+, MPy_2^+ and Py^+ products.

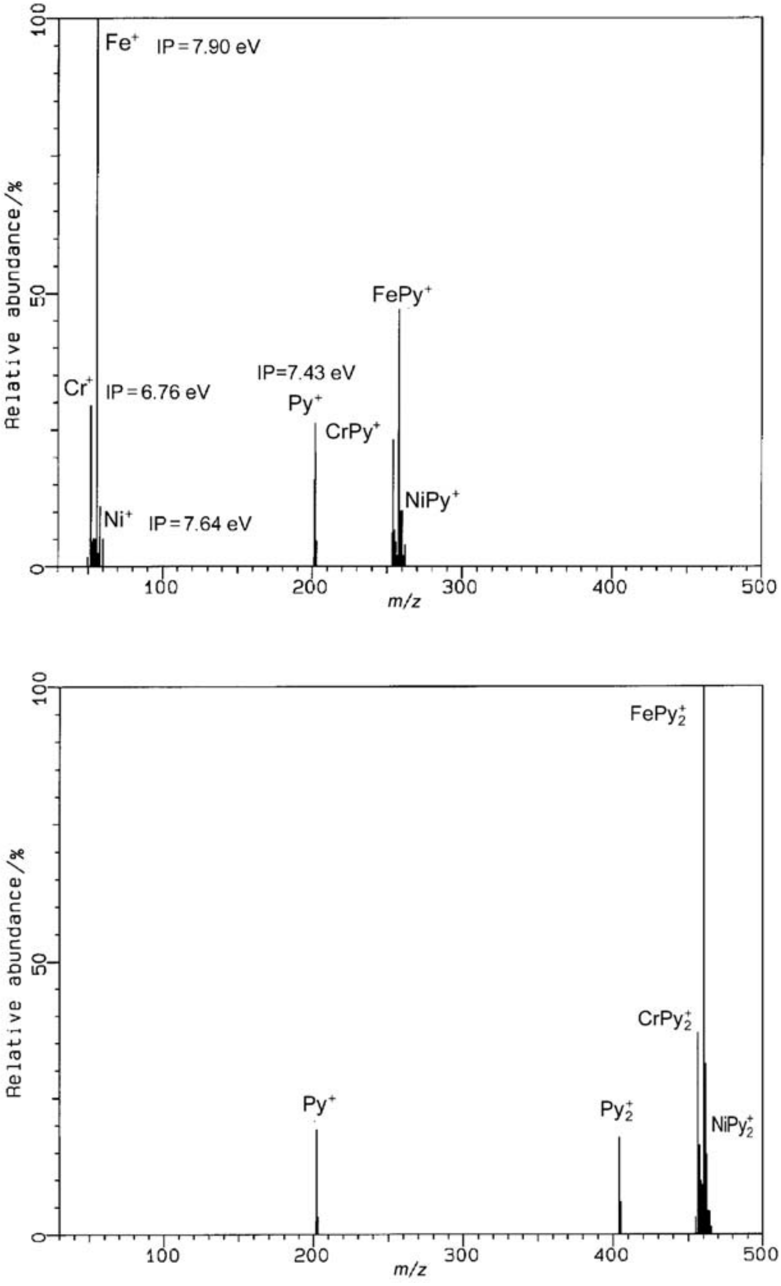
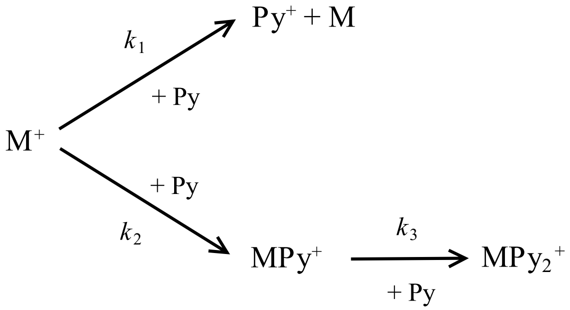


Figure 2. Spectra of stainless steel ($Fe^+ : Cr^+ : Ni^+ = 3 : 1 : 0.4$) 100 ms after starting the reaction with pyrene and with 100 s delay after the reaction is finished. $Py_2{}^+$ resulting from the equilibrium between Py^+ and neutral Py is observed in the latter. Py^+ is formed initially from Fe^+ and Ni^+ ions by charge exchange, since $E_i(M) > E_i(Py)$.

For each of these spectra, the sum of ion abundances is normalized to 100. We are concerned with a system of differential equations describing the pseudo-first order reaction scheme



which is easily integrated to give

$$[M^+]_t = [M^+]_{t=0}\, e^{-(k_1+k_2)t}$$

$$[Py^+]_t = \frac{k_1[M^+]_{t=0}}{k_1+k_2}(1-e^{-(k_1+k_2)t})$$

$$[MPy^+]_t = \frac{k_2[M^+]_{t=0}}{k_3-(k_1+k_2)}(1-e^{-(k_1+k_2)t} - e^{-k_3 t})$$

$$[MPy_2{}^+]_t = \frac{[M^+]_{t=0}}{k_3-(k_1+k_2)}(k_3(1-e^{-(k_1+k_2)t}) - (k_1 + k_2)(1-e^{-k_3 t})$$

These equations allow it to calculate the concentration of each reaction partner at any time, provided the starting amount of M$^+$ and the rate constants k_1, k_2 and k_3 are known. We have fixed the initial M$^+$ concentrations at 100 and, from the normalized mass spectra at given times, we can determine the distribution of charged reaction partners in the above scheme. If these is a sufficient number of such »snapshot« spectra, the unknowns k_1, k_2 and k_3 can be determined iteratively by minimizing the sum of squares of the differences between the observed, y_i, and the calculated, $f_i(k_1, k_2, k_3)$, amounts of reaction species.

$$\Phi = \sum_{i}^{\substack{\text{all spectra and}\\ \text{reaction partners}}} (y_i - f_i(k_1,k_2,k_3))^2 = \min$$

Because we want to approach k_1, k_2 and k_3 iteratively, we define them as

$$k_1 = k_1{}^0 + x_1,\ \ k_2 = k_2{}^0 + x_2,\ \ k_3 = k_3{}^0 + x_3$$

where the x_1, x_2, x_3 are the corrections at particular iterative stages.

Using the Taylor expansion

$$\begin{array}{ccccc} f(k_1,k_2,k_3) = f(k_1{}^0,k_2{}^0,k_3{}^0) & + \dfrac{\partial f}{\partial k_1{}^0}x_1 & + \dfrac{\partial f}{\partial k_2{}^0}x_2 & + \dfrac{\partial f}{\partial k_3{}^0}x_3 \\ \Downarrow & \Downarrow & \Downarrow & \Downarrow \\ F & P & Q & R \end{array}$$

we obtain

$$\Phi = \sum (y_i - f_i(k_1,k_2,k_3))^2 = \sum (y_i - F_i - P_i x_1 - Q_i x_2 - R_i x_3)^2$$

which, when minimized according to

$$\frac{\partial \Phi}{\partial x_i} = 0$$

yields

$$\begin{pmatrix} \Sigma P & \Sigma PQ & \Sigma PR \\ \Sigma PQ & \Sigma Q^2 & \Sigma QR \\ \Sigma PR & \Sigma QP & \Sigma R^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} \Sigma yP - \Sigma FP \\ \Sigma yQ - \Sigma FQ \\ \Sigma yR - \Sigma FR \end{pmatrix}$$

In this way, one calculates the set x_1, x_2 and x_3 and, therefrom, the new set of k-values $k_1{}^0$, $k_2{}^0$ and $k_3{}^0$, which are the feedstock for the next iteration. This iterative process continues until the sum of squares is minimized. FORTRAN programs for the partial derivatives, P, Q and R, in which we have used a 1% increase approximation

$$(i.e., \quad \frac{\partial f}{\partial k_i} = \frac{f(k_i + 0.01k_i) - f(k_i)}{0.01k_i} \;)$$

provides satisfactory results (Table I).

Using the observed $Py_2{}^+/Py^+ = 0.51$, which corresponds to $[Py] = 2.54 \times 10^{-10}$ mol dm^{-3}, at 25 °C, we obtain

$$k_2 = k_2' / [Py] = 7.13 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_3 = k_3' / [Py] = 7.09 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

For Fe^+, the following rate constants were found at 25 °C:

TABLE I

Reaction of chromium (Cr^+) with pyrene (Py) at 25 °C

Time / s	$[Cr^+]$		$[CrPy^+]$		$[CrPy_2^+]$	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.0001	98.0	99.8	0.0	0.2	0.0	0.0
0.0005	95.7	99.1	15.4	0.9	0.0	0.0
0.0200	69.1	69.5	44.6	30.0	0.0	0.5
0.0500	42.9	40.2	61.8	57.1	0.0	2.7
0.1000	18.8	16.2	80.7	75.6	0.0	8.2
0.1500	8.7	6.5	89.8	79.0	0.0	14.5
0.2000	0.0	2.6	91.4	76.6	7.1	20.8
0.2500	0.0	1.1	83.1	72.1	12.0	26.8
0.4000	0.0	0.1	62.7	57.5	33.2	42.5
0.5000	0.0	0.0	44.8	48.9	44.9	51.0
0.6000	0.0	0.0	32.5	41.7	56.0	58.3
0.7000	0.0	0.0	21.5	35.4	69.0	64.6
0.9000	0.0	0.0	8.4	25.7	80.8	74.3
1.0000	0.0	0.0	6.0	21.8	96.4	78.2
2.0000	0.0	0.0	0.0	4.3	94.0	95.7
…	…	…	…	…	…	…
100.00	$I(Py_2^+)/I(Py^+) = 0.51 \Rightarrow [Py] = 2.54 \times 10^{-10}$ mol dm^{-3}					
	$k_2' = 18.1$ s^{-1}			$k_3' = 1.8$ s^{-1}		

$$k_1 = 2.55 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_2 = 6.61 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_3 = 3.18 \times 10^{9} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Analysis of errors for these rate constants indicates confidence limits of ±20% for them.

It follows that

$$k_2(Cr^+) \approx k_2(Fe^+)$$

$$k_3(CrPy^+) > 2\ k_3(FePy^+)$$

Concerning the mechanism of the reactions and product structures, there are indications that the binding between M^+ and pyrene takes place *via* the π-electrons of pyrene, leading to sandwich-type compounds. This explanation is supported by the findings that i) M^+ ligation by pyrene proceeds without loss of hydrogen, ii) only two pyrene ligands are bound, and iii) no deuterium isotope effect was observed[6] when a pyrene-$^2H_{10}$ / pyrene-$^1H_{10}$ mixture was allowed to compete for the metal ions. However, the last result could just mean that every qualified collision leads to ligation without involvement of an equilibrium.

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SAŽETAK

Kinetika ligacijske reakcije metalnih iona s pirenom u plinskoj fazi

Tomislav Cvitaš, Saša Kazazić, Snježana Kazazić, Nenad Kezele, Leo Klasinc, Dunja Srzić i Herbert Budzikiewicz

Istraživanje jednostavnih ligacijskih reakcija metalnih iona (M^+) s pirenom (Py) u ICR FT spektrometru masa, upućuje na razmjerno brzo susljedno nastajanje iona MPy^+ i MPy_2^+. Nastajanje Py^+ izmjenom naboja opaža se također kada je $E_i(M^+) > E_i(Py)$. Mnogo sporija reakcija i ravnoteža $Py^+ + Py_2^+ \rightleftharpoons Py$ za koju su poznati termodinamički parametri omogućuje određivanje koncentracije Py tijekom ligacijskih reakcija i računanje konstanti brzina reakcija drugog reda iz konstanti reakcija pseudoprvog reda, dobivenih nelinearnom regresijom eksperimentalnih podataka (iz spektara masa) prema pretpostavljenoj kinetičkoj shemi.