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Kinetics of the gas phase reactions of the ion $C_5H_5Fe^+$ with substituted pyridines

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Abstract

The gas phase reactions between the ion $C_5H_5Fe^+$ and some substituted pyridines have been studied by ion trap mass spectrometry. Two different reactions have been observed: a simple addition process, found in almost all the cases, and a reaction with loss of HX found with the halogen substituted pyridines. The kinetics of these reactions has been studied and possible structures for the transition states are proposed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gas-phase chemistry; Ion–molecule reactions; Kinetics; Mass spectrometry

1. Introduction

The reactions of organometallic ions with neutral ligands have been thoroughly studied in gas phase in the last years and several aspects of their intrinsic reactivity and energetics of ligation have been elucitated [1–5]; also the cyclopentadienyl ions $C_5H_5Fe^+$ received some attention [6–11]. Recently, we initiated a study [12,13] to explore the efficiency of addition reactions of simple organic ligands to metal containing ions. It was found that the efficiency of such reactions is related to the thermodynamics of the reaction and to the activation entropy of the reaction.

Pyridines have been used as ligands in gas phase reactions with bare or ligated metallic ions to study the reaction kinetics [14] or to explore the relative affinity of the pyridines to the ions [15–18]; continuing our study on the gas phase kinetics we examined the reaction of substituted pyridines with the ion $C_5H_5Fe^+$. An interesting reaction with a direct interaction between the cyclopentadienyl ring and the halogenated pyridines was observed.

2. Results and discussion

2.1. The reactions

As already discussed [12,13] an appropriate choice of the experimental conditions reduces the number of reactions of the ion $C_5H_5Fe^+$ so that only those involving the pyridines are prominent. There are two possible reaction paths, reported in the Scheme 1, for the pyridines studied: reaction 1 gives the addition product $C_5H_5FePy^+$ and reaction 2, observed only with the halogen substituted pyridines, gives a product which results from the loss of HX from the adduct ion. The nature and position of the substituent determines the yield of the final products: the 2-fluoropyridine gives both the addition and the HF loss ions, the 3-fluoropyridine gives only the addition product, the 2-chloro- and 2-bromopyridine give only the HX loss ions, while the 3-chloro- and 3-bromopyridine give both the ions. Successive reactions are also possible and the isolation of the primary product ions and their successive reactions allows one to establish the complete reactions pathways as shown in the Scheme 1; a summary of the observed reactions is given in Table 1.

From the data reported above it is evident that the HX loss is favored when the substituent is in the two position and when the halogen is Cl or Br. After the addition reaction no other reaction occurs.

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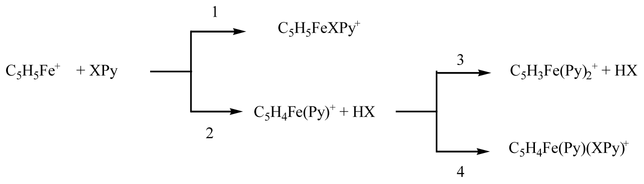
The use of perdeuterated ferrocene to generate the reacting ion $C_5D_5Fe^+$ gives a clear indication that in all the cases the H atom derives from the cyclopentadienyl ring. In every case indeed we observed only loss of DX so that we can estimate that any possible loss of HX should be less than 0.1% with respect to the loss of DX.

The reactions observed under the experimental conditions described above cannot proceed with an increase of enthalpy since after the formation of the encounter complex between the ion and neutral molecule, which of course imply a strong decrease in enthalpy, there is no way to gain energy to reach reaction products higher in energy than the reactants; however, a precise balance of the reaction energetics requires the knowledge of the halogen–carbon bond in the pyridines, of the hydrogen–carbon bond in the $C_5H_5Fe^+$ ion, of a carbon–carbon bond in the ion formed and of the H–X bond energy. In the absence of precise data we used known bond dissociation energies in similar compounds (halobenzenes for the C–X bond energy, and benzene for the H–C bond energy) to estimate roughly that the enthalpy variation for all the reactions should be comprised in about 5 kJ mol^{-1} range; it seems therefore, that the observed differences in reactivity are not to be ascribed to thermodynamic factors.



Scheme 1. Reaction scheme for the reaction of the ion $C_5H_5Fe^+$ with pyridines.

Table 1
Observed reactions of the ion $C_5H_5Fe^+$ with pyridines

Ligand	Reaction 1	Reaction 2	Reaction 3	Reaction 4
2-Fluoropyridine	Yes	Yes	Yes	
3-Fluoropyridine	Yes	No	No	
2-Chloropyridine	No	Yes	Yes	Yes
3-Chloropyridine	Yes	Yes	No	Yes
2-Bromopyridine	No	Yes	Yes	
3-Bromopyridine	Yes	Yes	No	Yes

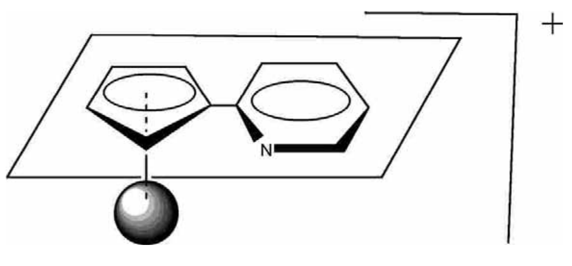


Fig. 1. Suggested structure for the ion obtained in reaction 2.

The application of a tickle frequency (up to 4 V for 5 ms), which increases the kinetic energy of the trapped ions so that they can gain energy from collision with the helium, to all the primary ions shows that they do not decompose so giving some evidence of their very high stability.

From the above data it seems therefore, that the reaction which leads to the loss of HX can occur only if the iron atom is available for the pyridine nitrogen atom. This suggests the structure shown in Fig. 1 as a possible structure for the ions obtained in reaction 2. In this structure the iron atom is free to accept another pyridine molecule to form the other products described above.

2.2. The kinetics

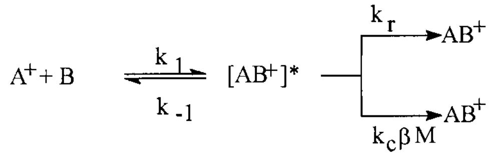
Under these experimental conditions, the disappearance of the ion $C_5H_5Fe^+$ must follow first order kinetics and this was found to be the case, so that a pseudo first order rate constant (k_{ps}) can be obtained from the semi-log plot of the relative abundance of the ion $C_5H_5Fe^+$ versus time. The pseudo first order constants should exhibit a linear dependence on the ligand pressure. In fact, this was always found. A typical plot is reported in Fig. 2 for the reaction of 3-fluoropyridine.

The experimental second order kinetic constants (k) obtained from the slopes of these plots are reported in the second column of the Table 2.

It is generally accepted [19] that the overall addition reaction between an ion and a neutral

$$A^+ + B \rightarrow AB^+$$

can be analyzed in terms of the following mechanism:



where k_1 is the bimolecular rate constant for the collisional complex formation; k_{-1} is the unimolecular redissociation rate constant; k_r is the unimolecular rate constant for the radiative stabilization reaction; k_c is the bimolecular rate constant for collisional stabilization of $[AB^+]^*$ by collision with neutral M and β is the collisional stabilization efficiency. In our system M is the buffer gas He and the ligand L. It was shown [12,13] that under these experimental conditions the experimental second order rate constants are equal to k_1 of the above scheme. A comparison of the experimental rate constants with calculated collision rate constants would be useful but the lack of data for the substituted pyridines does not allow these calculations

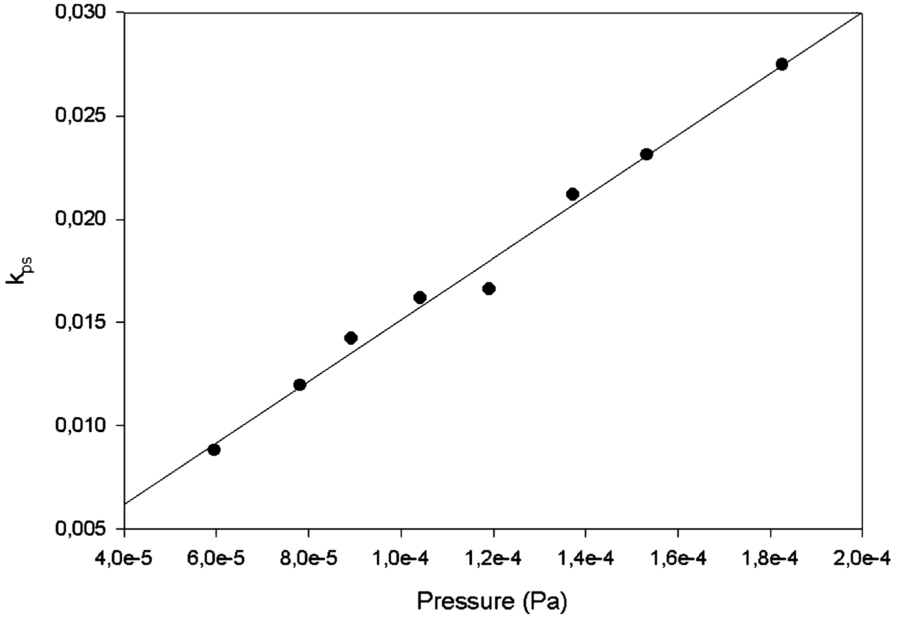


Fig. 2. Pseudo first order rate constants versus 3-fluoropyridine pressure.

except for pyridine itself. In this case, the collision rate constant, calculated according the method of Su and Chesnavich [20] is 1.7×10^{-9} cm^3 molecule^{-1} s^{-1} so that, in this case, the reaction efficiency is 68%.

As already discussed, these rate constants refer to an unique reaction for the pyridine, the methyl derivatives and the 3-fluoropyridine, but reflect two parallel reactions for the other compounds. For these last compounds from the analysis of the kinetic data it was possible to obtain the rate constants for the separate reactions; these rate constants are also reported in the Table 2; k_1 is the rate constant for the formation of the adduct ions and k_2 is that for the reaction with the HX loss. In the column of k_1, when appropriate, the data from the previous column are repeated.

We have previously found [12,13] that the rate constants for addition reaction of ligands to $C_5H_5M^+$ ions are correlated to the ionization energy of the ligand. In the present case the ionization energy of the substituted pyridines reflect ionization from the nitrogen lone pair or from the π system [21] so that this parameter is not appropriate; however, the proton affinities of the pyridines [22], which reflect the availability of the nitrogen lone pair to form a new bond, should be a good substitute [13,14,23]. Indeed a plot of the ln of k_1 versus the proton affinities (Fig. 3) gives a fair good linear correlation; the presence of this correlation extends the previous finding also to these ligands and in the meantime gives an indication that in this reaction there is a direct attack of the nitrogen atom on the iron atom.

A study of the temperature effect on the reaction rate constant was made for the reaction of 2-fluoropyridine; the results, shown in the Table 3 and also in the Fig. 4, indicate an *anti*-Arrhenius behavior for k_1 and a small, if any, influence of the temperature on k_2. This kind of rate constant dependence on the temperature is frequently found in gaseous phase ion molecule reactions studied in the low pressure regime [24–26], but our data have been obtained in the high pressure limit conditions so that, as already proposed [13] for other $MC_5H_5^+$ reactions, an activation entropy effect is present also in these reactions. The results are in line with the many studies on gaseous phase radical reactions. In these reactions, which proceed with very low or zero activation energies, *anti*-Arrhenius behavior [27–30] as well as negative activation entropy [31–33] are often observed.

The data indicate two different dependencies of the rate constant upon temperature, suggesting, but not proving, the presence of two different transition states.

Table 2
Rate constants (cm^3 molecule^{-1} s^{-1}) for the reaction of $C_5H_5Fe^+$ with pyridines

Ligand	$k \times 10^9$	$k_1 \times 10^9$	$k_2 \times 10^9$
2-Fluoropyridine	1.08 ± 0.48	0.69 ± 0.21	0.41 ± 0.08
2-Chloropyridine	0.99 ± 0.11		0.99 ± 0.11
3-Fluoropyridine	0.86 ± 0.12	0.86 ± 0.12	
3-Chloropyridine	1.13 ± 0.16	0.83 ± 0.1	0.31 ± 0.09
2-Bromopyridine	1.54 ± 0.67		1.54 ± 0.67
3-Bromopyridine	1.39 ± 0.20	0.82 ± 0.14	0.52 ± 0.10
Pyridine	1.16 ± 0.15	1.16 ± 0.15	
3-Picoline	1.56 ± 0.12	1.56 ± 0.12	
4-Picoline	1.41 ± 0.19	1.41 ± 0.19	
2-Picoline	1.52 ± 0.11	1.52 ± 0.11	

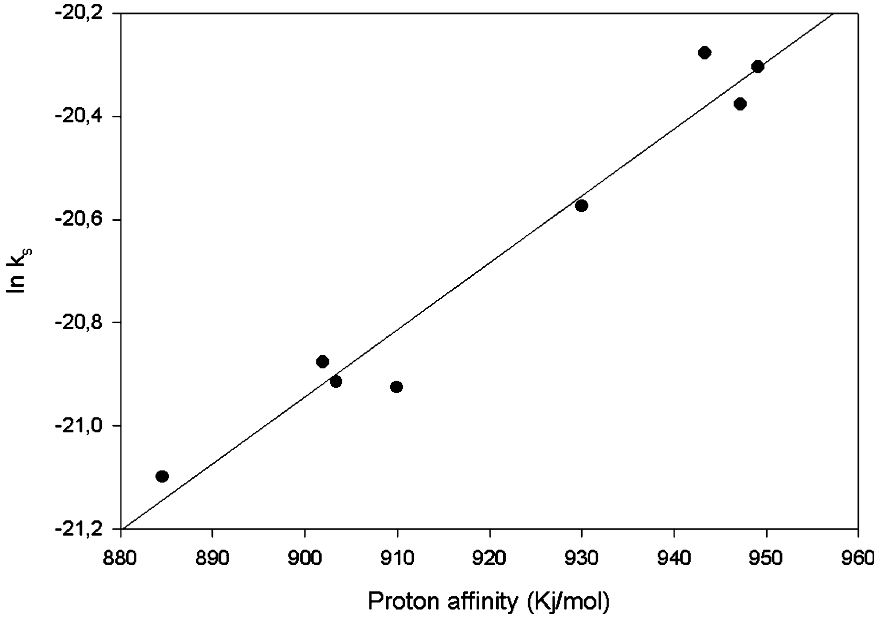


Fig. 3. ln k_1 versus pyridine proton affinities.

In principle, the interaction between the ion and the pyridine could happen via the nitrogen lone pair or via the π system of the pyridine ring; we exclude the attack via the π system because in this way the difference in reactivity between the two and three substituted pyridines is hard to explain; in addition a recent experimental and theoretical work [16] reports that the bare metal ions prefer to be bound to the nitrogen rather than the π cloud of the aromatic ring of pyridine. However, an interaction of the halogenated pyridines with the nitrogen lone pair should give too long a distance between the halogen and the hydrogen atoms to allow the loss of HX; for these reasons we suggest the transition states in Fig. 5 for the two cases. According to this hypothesis the formation of the adduct ion is due to an interaction between the iron and the nitrogen atom, transition state (a), while the reaction with the loss of HX derives from a transition state (b) in which there is interaction between these two last atoms and between the halogen and an hydrogen atom of the cyclopentadienyl ring.

The absence of the adduct ion as product in the reaction of the 2-Cl and 2-bromopyridine deserves some comment; the rate constants observed for the reaction 2 are not so great to completely repress the formation of the adduct ion whose rate constant can be deduced from the plot of Fig. 3.

We suggest that, due to a more favorable energy content of a transition state (b) involving both interaction between the iron atom and the nitrogen atom, and between the halogen atom and one of the hydrogen atoms of the ring, with respect to transition state (a), the reaction 2 is favored when the substituent in the pyridine ring is in the two position. This position should allow a better interaction respect to the position three and also the interaction should be favored with the larger halogen atoms.

Work is in progress to elucidate this point with the aid of theoretical calculations.

3. Experimental

Measurements have been done with a Finnigan Ion Trap Mass Spectrometer (ITMS). The general procedure to obtain kinetic data is as follows. Ferrocene is introduced in the ion trap via the direct insertion probe, while helium and the ligand (L) are introduced via two different standard gas inlet devices. The ferrocene pressure was usually around 8×10^{-5} Pa, the He pressure was kept constant at 3.5×10^{-2} Pa. The pressure of the ligands changed between about 4×10^{-5} and 3×10^{-4} Pa; the effective range for each ligand being determined by the reaction rate.

In a single experiment, at fixed ferrocene, ligand and helium pressure, the ITMS software managed the experiment loading the scan function and changing the

Table 3
Temperature effect on the rate constant (cm^3 molecule^{-1} s^{-1}) of the reaction of $C_5H_5Fe^+$ with 2-fluoropyridine

Temperature (K)	$k \times 10^9$	$k_1 \times 10^9$	$k_2 \times 10^9$
348	1.67 ± 0.26	1.14 ± 0.23	0.53 ± 0.08
383	1.39 ± 0.18	0.99 ± 0.19	0.45 ± 0.08
423	1.08 ± 0.48	0.69 ± 0.21	0.42 ± 0.08
463	0.47 ± 0.24	0.27 ± 0.11	0.2 ± 0.10

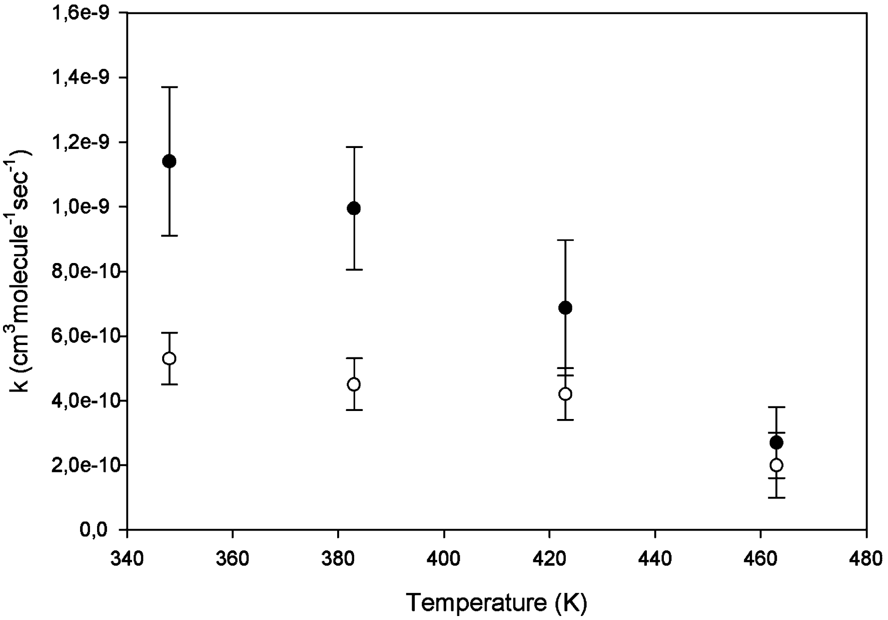


Fig. 4. Temperature effect on k_1 (closed dots) and on k_2 (open dots) for the reaction of 2-fluoropyridine.

reaction time; the scan function is shown in Fig. 6 and its functions are as follows: the ion $C_5H_5Fe^+$ was formed by electron ionization (70 eV) with an ionization time of 10 ms with the radio frequency set to a starting $m/z = 110$; in this way ions of lower mass are ejected from the ion source. The ion is then cooled for 50 ms and isolated, the reaction time was changed and two spectra were collected at each reaction time for a total of 24 spectra in a time range sufficient (typically between 0 and 100 ms) to reduce the relative intensity of the ion $C_5H_5Fe^+$ from 100% to about 10–5%. The high cooling time was necessary to assure the thermalization of the reacting ions; lower cooling time gave rise to first order kinetic plots with a marked upward curvature which is attributable to a non-homogeneous distribution in energy of the ions formed by electron ionization; this suggests that ions with a high energy content form encounter complexes which cannot efficiently dissipate the internal energy before redissociation.

To get the kinetic data, the relative intensity of the $C_5H_5Fe^+$ signal was calculated with respect to the total ion intensities. In the adopted experimental conditions the ligand pressure, in a single kinetic run, is constant so that the disappearance of the ion $C_5H_5Fe^+$ must follow first order kinetics. From the plots of the ln of its relative intensity versus reaction time, a pseudo first order rate constants is obtained.

The gas pressure was monitored with a Bayard–Alpert gauge; the corrections for the different gauge sensitivities have been determined with the method by Bartmess and Georgiadis [34] using a MKS Baratron. Measures at various temperatures have been achieved simply changing the temperature of the neutral inlet system and of the ITMS analyzer.

The kinetic data reported in the tables have been checked for homogeneity by using the F-test; the test was applied to at least three independent runs each of

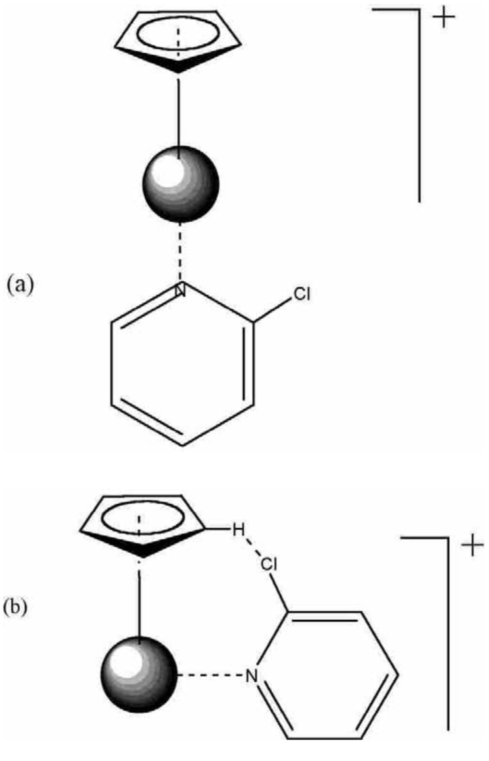


Fig. 5. Suggested transition states for the addition reaction (a) and for the reaction with HX elimination (b).

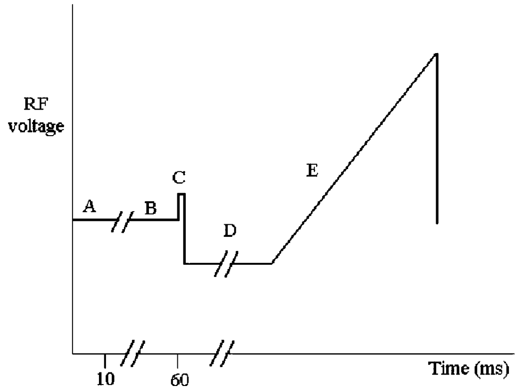


Fig. 6. Scan function employed in the kinetic study: (A) ionisation; (B) cool time; (C) isolation step; (D) reaction; (E) spectrum acquisition.

them containing seven or eight data points; the reported uncertainties in the tables are the standard errors [35]; those last values indicate the reproducibility of the measurements while the precision of the kinetic constant values strongly depends upon the pressure measurements and an uncertainty of about 25% is reasonable for the kinetic constants.

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