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Fragmentation and reactivity of energy-selected ferrocenium ions

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While investigations on the reactivity of excited bare metal ions ("state-selective reactivity") has been a significant advance in gas phase organometallic chemistry [1], little is known about the dependence of fragmentation and reactivity of ionic metal complexes with their internal energy. In this study, we present results concerning the dissociation of state-selected ferrocenium ions ($(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^+$ commonly called Cp_2Fe^+ , as well as their reactions with methanol and ethanol. It is interesting to get more information about the thermochemistry and the reactivity of ferrocene Cp_2Fe and derived ions for different reasons: first it is known to be a very efficient smoke inhibitor in flames [2,3], secondly the Cp (cyclopentadienyl) ligand, widely used in organometallic chemistry, might vary its complexation mode (5, 3 or 1 atoms) with internal energy.

In this study parent ions Cp_2Fe^+ are produced by VUV photoionization of neutral ferrocene using synchrotron radiation (Super-ACO, Orsay), and selected in internal energy by threshold photoelectron-photoion coincidences (CERISES experimental setup [4,5]). Briefly, the apparatus is divided into three differentially pumped regions: the source, the reaction and the detection zones. In the source, state-selected parent ions are formed and can be selected in mass by a first quadrupole filter. State-selected ions are then injected in the second zone which is a RF octopole ion guide where reactions can occur in a collision cell filled with the target gas. In the third zone, either fragment ions or reaction product ions are mass analysed by a second quadrupole filter and detected by microchannelplates. In addition, the long flight time in the octopoles (several hundreds of microseconds) allows studying long-lived metastable ions.

In the study of ferrocenium ion dissociation, several kinds of measurements were performed.

- First, total mass spectra were recorded at different photon energies.

The fragmentation channels are summarized in the Table, as well as the percentage of the observed fragments in the total mass spectrum at a photon energy of 13.75 eV. In addition to the main CpFe^+ and Fe^+ fragments, several minor fragments are detected such as $\text{C}_{10}\text{H}_{10}^{2+}$, which reflects the formation of a C-C bond between the two Cp ligands. Losses of CH_3 , C_2H_2 and C_4H_4 also indicate that important structure rearrangements take place before cleavage.

- The appearance energies of each mass-selected fragment ion were measured by recording fragment ion yields as a function of photon energy. Surprisingly, all fragments were found to have the same energy onset, i.e. 13.2 eV photon energy, except for $\text{C}_3\text{H}_3\text{Fe}^+$ (m/z 95). For Fe^+ ions, a sharp increase was observed at 17 eV, above the thermochemical onset of $\text{Fe}^+ + 2 \text{Cp}$. The 13.2 eV appearance energy of Fe^+ is thus assigned to the formation of $\text{Fe}^+ + \text{C}_{10}\text{H}_{10}$. The thermochemistry of the ferrocenium ion is not well established; the $\text{CpFe}^+ - \text{Cp}$ bond energy is evaluated to 3.7 eV [6] or 3.9 eV [7]. The CpFe^+ ion experimental onset at 13.2 eV is at 6.55 eV above the Cp_2Fe IP, i.e. about 2.5 eV above the estimated thermochemical onset. This important difference may be attributed either to a dissociation barrier or to kinetic shift.

- In order to evaluate the kinetic shift, coincidence mass spectra have been measured in two different time ranges, by using either the quadrupole mass filter mounted at the exit of the source (detection time in tens of μs) or the quadrupole mass filter mounted after the octopole ion guide (detection time in the hundreds of μs). A shift of the crossing points of the breakdown curves clearly demonstrates the presence of long-lived metastable ions. Figure 1

shows the breakdown curve recorded by the second quadrupole mass filter for the major ions. In this diagram, parent ion lifetimes can be derived in the considered energy range. Results are reported in Figure 2, as well as lifetimes measured from time-of-flight spectra.

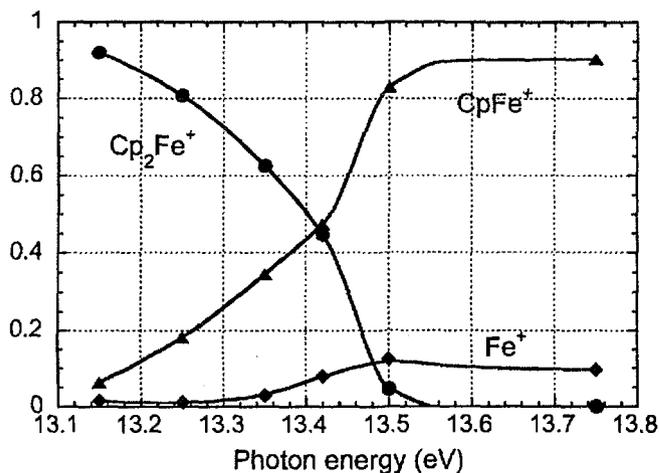


Figure 1 : Breakdown curve of $C_{10}H_{10}Fe^+$, restricted to the most important fragments $CpFe^+$ and Fe^+ .

Table : Major fragmentation products of ferrocenium ion.

Mass	Fragment ion(a)	Neutral loss	Appearance threshold (eV)	%, spec. mass 13.75 eV (b,c)	%, coincid. 13.75 eV(d)
186	$C_{10}H_{10}Fe^+$ (Cp_2Fe^+ , parent)	-	6.65	84.2	0
121	$C_3H_3Fe^+$ ($CpFe^+$)	C_5H_5	13.2	11.5	81
56	Fe^+	$C_{10}H_{10}$ $2 C_3H_5$	13.2, 17.0	1.9	8
171	$C_9H_7Fe^+$	CH_3	13.2	0.6	5
160	$C_8H_5Fe^+$	C_2H_2	13.2	0.5	3
134	$C_9H_6Fe^+$	C_4H_4 ?	13.2	0.2	3
130	$C_{10}H_{10}^+$	Fe	13.2	0.5	2
95	$C_3H_3Fe^+$	$C_3H_5 + C_2H_2$	17.3	0.1	0

(a) Very minor fragments are found at m/z 158 and 128; their relative intensity increases with increasing photon energy.

(b) Proportion of the considered ion in the mass spectrum, at photon energy $E_i = 13.75$ eV.

(c) For $E_i = 11.5$ eV (with LiF cutoff for photons > 12 eV), the parent is the only detectable ion.

(d) Proportion of the considered ion in coincidence with threshold electrons (relative to the sum of ions in coincidence with threshold electrons), at photon energy $E_i = 13.75$ eV.

- The $CpFe^+$ time-of-flight spectra exhibit two peaks, corresponding to the time-of-flight of the expected fragment and of the parent respectively. The latter corresponds to ions which

fragment during their pathway between the source and the detector. Let us note that dissociation lifetime measurements reported in the literature [6,8], also shown in Figure 2, have some ambiguity in the internal energy assignment.

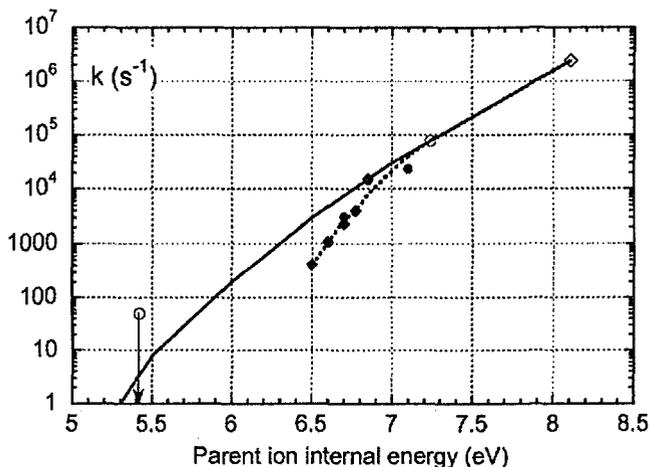


Figure 2: Fragmentation rate constant of Cp_2Fe^+ : ◆ from the fragmentation diagram, ● from the time-of-flight spectra, Literature: ○ [6] ◇ [8] — RRKM fit [6]

Besides the evidence of a kinetic shift, two arguments seem to indicate the presence of a barrier and a rearrangement prior to dissociation: all fragments have the same appearance energy within experimental errors, secondly fragments such as $\text{C}_{10}\text{H}_{10}^+$ demonstrate the recombination between the two Cp ligands.

The rate-determining step is thus most probably an isomerization of Cp_2Fe^+ , which implies that the Cp loss is not a simple bond cleavage as previously supposed [6,8]. Figure 2 shows a RRKM fit calculated by Faulk and Dunbar [6], assuming a loose transition state. It does not fit well our experimental data. Further RRKM modelling, as well as structure calculations for the transition state, are now necessary to understand the ferrocenium ion dissociation which appears to be much more complex than previously stated.

The reactivity of ferrocenium ion with methanol and ethanol has been investigated as a function of photon energy. It gave quite unexpected results. While no reaction occurs at lower photon energies, several reaction products appear at 13.0 eV photon energy, very close to the fragmentation threshold. It was checked that these ions are really products from the parent ion Cp_2Fe^+ , since reaction of each of the different mass-selected fragments with the alcohol leads to different products.

Only one product ion, m/z 201 ($[\text{Cp}_2\text{Fe}(\text{CH}_3)]^+$), comes from single collisions. It is formed in both reactions with methanol and with ethanol.

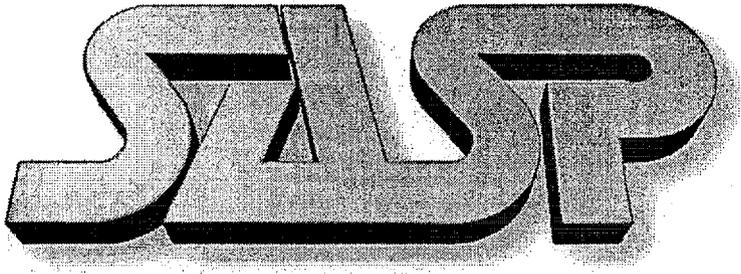
Several other products appear at the same threshold, mainly m/z 217 ($[\text{Cp}_2\text{Fe}(\text{OCH}_3)]^+$) for methanol and 231 ($[\text{Cp}_2\text{Fe}(\text{OC}_2\text{H}_5)]^+$) for ethanol. Their non-linear increase with increasing reactant gas pressure indicates that their formation involves several collisions.

The observed particular reactivity of the ferrocenium ion just below its fragmentation threshold seems to show that only metastable ions are reactive. It suggests that in order to

either dissociate or become reactive, ferrocenium ions have first to isomerize. In order to check this hypothesis, further work is necessary, in particular ab initio calculations of possible isomers.

References

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Poster B