



The reactivity of ferrocenylalkyl azoles under the conditions of electrospray ionization

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ABSTRACT

Under the conditions of electrospray ionization of ferrocenylalkyl azoles FcCH(R)X ($\text{Fc} = \eta^5\text{-C}_5\text{H}_5\text{Fe-}\eta^5\text{-C}_5\text{H}_4$, $\text{R} = \text{H, Me, XH} = 2\text{-methyl imidazole, pirazole}$) the processes of oxidation, protonation, fragmentation and ferrocenylalkylation to form, molecular ions $[\text{M}]^+$, protonated molecules $[\text{M+H}]^+$, ferrocenylalkyl cations $[\text{FcCHR}]^+$ and bisferrocenylalkyl azole cations $[(\text{FcCHR})_2\text{X}]^+$, respectively, take place. Using special experimental techniques (deuterated solvents, saturation of ionic source of an ESI mass-spectrometer by the vapors of solvents, the experiments under the “inverse” ESI conditions when the solvent is subjected to electrospray in the presence of ferrocenylalkyl derivative vapours) and quantum-chemical calculations at the level of the B3LYP/LanL2DZ theory the scheme of the formation of these ions in a gas phase according to the mechanism of “activating protonation” was suggested. It was found that all these ions are formed through the protonation stage, which is taking place mainly in a gas phase. The key stage is the exothermic process of the protonation of the initial compounds by hydroxonium ions giving rise to protonated $[\text{M+H}]^+$ molecules which further oxidize and alkylate ferrocenylalkyl azoles to form molecular radical cations and bisferrocenylalkyl azole ions $[\text{FcCH(Me)-X-CH(Me)Fc}]^+$. The decomposition of protonated ions with the elimination of the azole molecule gives rise to ferrocenylalkyl cations $[\text{FcCHR}]^+$ capable in turn of oxidizing and alkylating the initial compounds.

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1. Introduction

It has been shown recently by us [1,2] that under the conditions of ionization electrospray (ESI) ferrocenylalkyl azoles FcCH(R)X ($\text{Fc} = \eta^5\text{-C}_5\text{H}_5\text{Fe-}\eta^5\text{-C}_5\text{H}_4$, $\text{XH} =$ the derivatives of imidazole, pirazole, triazole and their benzo analogs, $\text{R} = \text{H, Me, Et, Ph}$) along with the processes typical of this ionization method, such as oxidation, protonation, fragmentation and dimerization to form, respectively, molecular ions $[\text{M}]^+$, protonated molecules $[\text{M+H}]^+$, ferrocenylalkyl cations $[\text{FcCHR}]^+$ ($[\text{A}]^+$), ions of dimer $[\text{2M}]^+$ and its protonated form $[\text{2M+H}]^+$, the ferrocenylalkylation known in the chemistry of solutions [3] giving rise to bisferrocenylalkyl azole cations $[(\text{FcCHR})_2\text{Az}]^+$ ($[\text{MA}]^+$) also takes place (Fig. 1).

The mechanism of ion-formation on electrospray ionization of non-polar substances, unable to form charged species in solution, is still speculative [4]. A concept according to which the ESI ion source is considered as an electrochemical unit and ions in such an ion source result from the redox processes taking place in solution and/or at the solution-capillary interface surface [5–7] is the most widespread. At the same time, the protonation of the analyte neutral molecules under the conditions of ESI may occur in gas phase in the

course of ion-molecular reactions. So Amad et al. [8] showed, that on electrospraying of clean water the protonated water clusters $(\text{H}_2\text{O})_n\text{H}^+$ ($n = 1\text{--}4$) are formed. However, on admission of vapors of methanol having higher proton affinity than water to the ion source, the peaks of water cluster ions disappear from the ESI mass-spectrum and the peaks of protonated methanol cluster ions $(\text{MeOH})_n\text{H}^+$ ($n = 1\text{--}4$) appear, i.e. in this case the protonation of methanol in a gas phase is fulfilled by hydroxonium ions. Recently, [9] it has been discovered by us that the ferrocene molecular ions are formed under the “inverse” ESI conditions when the ferrocene vapors are situated in the ion source, and only clean acetonitrile is subjected to electrospraying. By the help of quantum-chemical calculations it has been found, that under these conditions the ferrocene oxidation occurs in the gas phase according to the scheme of activating protonation, when the protonated molecule is the oxidizer of the initial ferrocene molecule, and the role of electrochemistry in the process of the electrospraying consists in generation of hydroxonium ions, which protonate the ferrocene molecules in the gas phase [9].

2. Results and discussion

In this article, the results of the investigation of mechanisms of ionoformation of 1-ferrocenylmethyl-1H-pirazole FcCH_2Pz (**1**), 2-methyl-1-(1-ferrocenylethyl)-1H-imidazole FcCH(Me)Im (**2**), ferrocenylmethyldimethylamine (**3**) and ferrocenylmethanol FcCH_2OH

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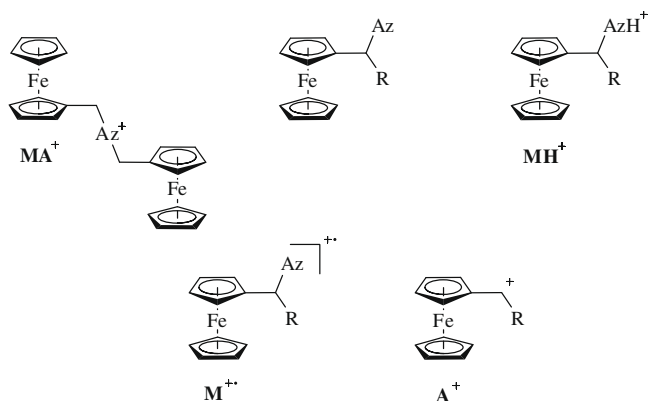
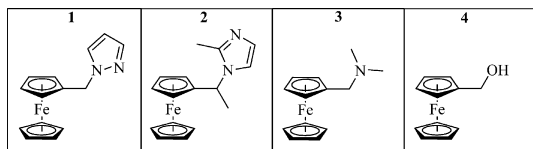


Fig. 1. The ions, formed on the electrospray ionization of ferrocenylalkyl derivatives.

(4) under the conditions of the ESI using experimental techniques and quantum-chemical calculations are given. The ESI mass-spectra of the compounds **1** and **2** in acetonitrile solutions (ACN), ACN/H₂O (1:1 w/w) and ACN/D₂O (1:1 w/w) as well as on saturation of ionic source by H₂O, D₂O and CD₃OD vapors were obtained (Table 1). In the last case, the vessel with the corresponding solvent was placed into the ion source.



Recently, we have discovered, that the shape of the ESI mass-spectra of ferrocenylalkyl azoles and ferrocenylalkanols essentially depends upon the conditions of the experiment (the analyte concentration, the solvent phase flow rate, solvent, temperature, electric potential) [1,10]. Thus in order to preserve the same ionization conditions the mass-spectra of an equimolar mixture of the compounds **1** and **2** was registered. Under the ESI each of these compounds forms four basic ions: molecular ions [M]⁺, protonated molecules [M+H]⁺, ferrocenylalkyl cations [FcCHR]⁺ ([A]⁺) and bisferrocenylalkyl azole cat-

ions [(FcCHR)₂Az]⁺ ([MA]⁺) (Fig. 2, Table 1; subscript indices 1 and 2 define the compounds **1** and **2**, respectively).

Unlike in the control experiments) when the vessel with H₂O was present in the ion source (experiment 2), in the ESI mass-spectra (Table 1), obtained in the presence of D₂O or CD₃OD vapors in the ion source (experiments 3 and 4) the peaks of ions of the protonated molecules [M₁+H]⁺ (*m/z* 267) and [M₂+H]⁺ (*m/z* 295) was partially shifted for one unit in the direction of higher masses, that is, *m/z* 268 and *m/z* 296, respectively, i.e. along with the protonation the deuterium addition takes place. The analysis of the intensity ratio of these peaks showed, that the deuterium occurs for more than 85%. Other ions do not comprise deuterium. Using the mixture ACN/D₂O (1:1 w/w) as a solvent but in the absence of D₂O vapors (experiment 6) also brings to the enrichment of protonated molecules by deuterium [M₁+H]⁺ and [M₂+H]⁺ for 72.5% and 87.5%, respectively. However, in the presence of H₂O vapors (experiment 7) the part of ions [M₁+D]⁺ and [M₂+D]⁺ reduces to 4.6% and 18.6%, respectively, and once more increases to 80.5% and 92.5% in the presence of D₂O vapors (experiment 8, Table 1).

Two alternative explanations of these results can be suggested: (1) the protonation occurs in solution, and the isotope change of hydrogen takes place in the ions [M₁+H]⁺ in the gas phase; (2) protonation takes place mainly in the gas phase.

In order to elucidate the possibility of protonation in a gas phase the experiment was made in the “inverse” ESI conditions, when only a solvent was subjected to electrospraying, and the vessel with ferrocenylmethylpyrrolidine was placed in the ion source. In this case, the set of ions formed was the same as was observed in the ESI mass-spectrum, obtained under the usual conditions on electrospraying of solution of this compound (Table 2). However, because of the low volatility of ferrocenylmethylpyrrolidine the intensities of the peaks of these ions were not more than 50 times higher than a background and were two orders lower, than in the spectrum, obtained under usual conditions on electrospraying of solution of this compound in acetonitrile (1 μl of solution with the concentration of 3 × 10^{−5} mol/l). Thus for more reliable confirmation of the fact of protonation of ferrocenylalkyl derivatives in a gas phase we used the compound ferrocenylmethyldimethylamine **3** as a model possessing higher volatility in comparison with ferrocenylalkyl azoles.

On electrospraying of acetonitrile mixtures with H₂O and D₂O (1:1 w/w) in the presence of ferrocenylmethyldimethylamine vapors the set of ions was reliably registered. The same set was observed in the ESI mass-spectrum, obtained under usual

Table 1

The peak intensities (%Σ) and the percentage of deuterated ions on the registration of the ESI mass-spectra of the equimolar mixture of 1-N-(ferrocenylmethyl)pyrrolidine FcCH₂Pz (**1**), 1-N-(ferrocenylethyl)-2-methyl imidazole FcCH(Me)Im (**2**) in solutions MeCN, MeCN/H₂O (1:1 w/w) and MeCN/D₂O (1:1 w/w), and also in the presence of vapors of H₂O, D₂O and CD₃OD in the ion source. C = 3 × 10^{−5} mol/l, V = 50 ml/min, T = 90 °C, U = 4.5 kV, solvent phase MeCN.

Ion	Solvent vapor <i>m/z</i>	ACN	ACN			ACN/H ₂ O	ACN/D ₂ O	ACN/D ₂ O	
			H ₂ O	D ₂ O	CD ₃ OD			H ₂ O	D ₂ O
		1	2	3	4	5	6	7	8
[A ₁] ⁺	199	0.94	0.77	0.87	6.46	1.13	0.64	0.32	0.44
[A ₂] ⁺	213	3.07	1.24	1.49	1.13	3.91	3.46	1.14	1.14
[M ₁] ⁺	266	0.30	1.37	0.93	1.90	0.47	0.22	0.48	0.20
[M ₁ +H] ⁺	267	0.37	12.13	1.37	0.02	3.47	0.64	4.25	0.38
[M ₁ +D] ⁺	268	0.00	0.00	9.47	0.15	0.00	1.68	0.20	1.54
%D		0.00	0.00	87.35	88.20	0.00	72.51	4.56	80.45
[M ₂] ⁺	294	1.72	1.13	0.80	1.26	1.08	1.36	2.01	1.23
[M ₂ +H] ⁺	295	50.30	45.67	5.04	6.97	63.86	8.68	59.71	4.95
[M ₂ +D] ⁺	296	0.00	0.00	36.79	40.40	0.00	60.60	13.68	61.54
%D		0.00	0.00	87.96	85.29	0.00	87.47	18.64	92.55
[M ₁ A ₁] ⁺	465	11.74	1.52	0.17	0.00	0.27	1.08	0.35	13.17
[M ₂ A ₁] ⁺	493	14.60	21.94	26.92	24.14	0.33	0.82	0.32	0.39
[M ₂ A ₂] ⁺	507	16.96	14.23	16.13	17.60	25.49	20.82	17.54	15.02
TIC/6		12.7	18.4	10.9	5.1	23.5	23.9	39.0	38.1

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