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Charge separation (coulomb explosion) processes of doubly charged cations of sandwich compounds in the gas phase: evidence for the junction of two C_5H_5 units

Thomas Drewello, Carlito B. Lebrilla, Helmut Schwarz *

Institut für Organische Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12 (F.R.G.)

and Teodor Ast

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4/11, Belgrade (Yugoslavia)

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Abstract

The charge separation reactions (coulomb explosion) of the ferrocene, cobaltocene, and nickelocene dications, generated by electron impact ionization in the gas phase, are reported. These sandwich dications display a common behaviour in their unimolecular decomposition reactions, which are characterized by two distinct charge separation pathways. One corresponds to the reaction $[MC_{10}H_{10}]^{2+} \rightarrow [MC_5H_5]^+ + C_5H_5^+$, and the other to the generation of $C_{10}H_{10}^{+\cdot}$ and M^+ ($M = Fe$, Co, Ni). From the translational energy releases, associated with the charge separation processes, the intercharge distances of the exploding dications in their transition structures have been calculated. The results demonstrate that, irrespective of the nature of the transition metal ion M, the interchange distance for the formation of $[MC_5H_5]^+/C_5H_5^+$ is 5.0 Å and 6.2 Å for the generation of $C_{10}H_{10}^{+\cdot}$ and M^+.

Introduction

Although the chemistry of ferrocene and analogous sandwich compounds (Scheme 1) constitutes one of the most thoroughly studied subjects in the area of organometallic chemistry, relatively little is known about the stability and chemical reactivity of mono- and doubly-charged species [1*].

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* Reference numbers with asterisks indicate notes in the list of references.

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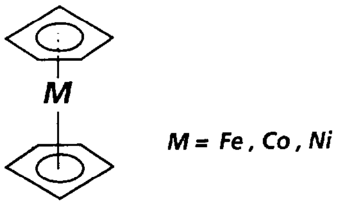
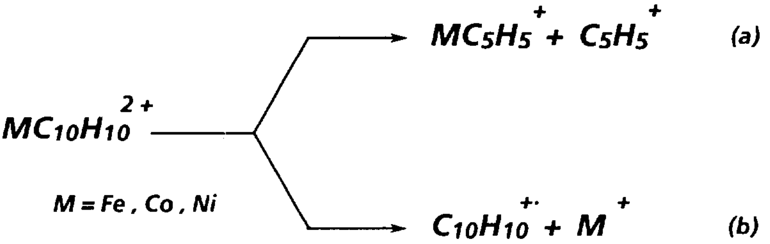


A qualitative MO analysis reveals the following sequence of the frontier orbitals of neutral ferrocene (M = Fe), cobaltocene (M = Co) and nickelocene (M = Ni), respectively: e_{2g} (bonding), a'_{1g} (non-bonding) and e^*_{1g} (anti-bonding). While the neutral ferrocene $FeCp_2$ ($Cp = C_5H_5$) with the electron configuration $(e_{2g})^4\ (a'_{1g})^2$ corresponds to a stable 18 valence electron shell, in the analogous $CoCp_2$ and $NiCp_2$ systems the additional one or two electrons are placed in anti-bonding orbitals, with the consequence that the 19 and 20 valence electron systems are expected to form via oxidation the "stable" 18 electron mono- and di-cations of $[CoCp_2]^+$ and $[NiCp_2]^{2+}$, respectively. In fact, cobaltocenium salts can be readily made from various precursors in solution, and the consecutive loss of two electrons to generate $[NiCp_2]^{2+}$ at very low temperature has also been reported [1].

$$NiCp_2 \rightleftarrows [NiCp_2]^+ \rightleftarrows [NiCp_2]^{2+} \qquad (1)$$

Owing to intermolecular reactions, a further characterization of $[NiCp]^{2+}$ could not be achieved in solution, nor was it possible to generate and characterize the analogous $[FeCp_2]^{2+}$ and $[CoCp_2]^{2+}$ species. It was recently reported [2 *], quite unexpectedly, that 70 eV electron impact ionization of $FeCp_2$ yields a dication of the same elemental composition. The gas phase behaviour (coulomb explosion) of this ion was monitored by ion kinetic energy spectroscopy of mass selected species (MIKES methodology, [3*]). It was observed that the charge separation (coloumb explosion) of $[FeC_{10}H_{10}]^{2+}$, generated from $FeCp_2$, gave rise to two reaction channels (eq. a and b), namely the formation of $[FeC_5H_5]^+/C_5H_5^+$ (reaction a) and, in competition, the reductive elimination of Fe^+ to generate $C_{10}H_{10}^{+\cdot}$ (reaction b).



In the present communication we describe the results of studies aimed at (i) the generation of the as yet unknown gas-phase dications of cobaltocene and nickelocene, and (ii) investigation of the effects of the transition metal M on the charge separation reactions described in eq. a and b.

Experimental

The experiments were performed using a Vacuum Generator triple-sector mass spectrometer (ZAB-HF-3F) which is of the configuration B(1)EB(2) (B stands for magnetic and E for electric sector). In the present study the second magnet is not used. Dications were generated by electron impact (70 eV) ionization of the commercially available compounds MCp_2 (M = Fe, Co, Ni). After acceleration to 4 kV, dications of the elemental composition $MC_{10}H_{10}$ were mass selected by B(1). The charge separation reactions ($m^{2+} \rightarrow m_1^+ + m_2^+$) occurring in the second field-free region of the instrument were recorded by scanning the ESA-voltage from the main

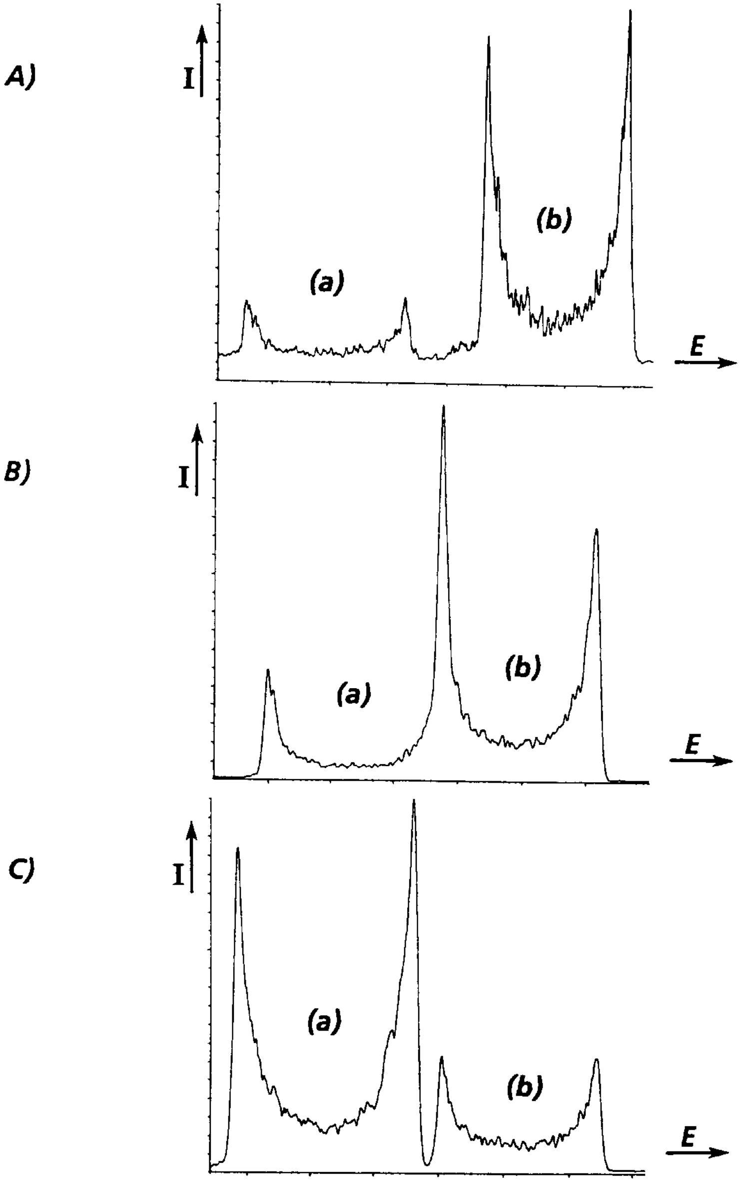


Fig. 1. Partial MIKE spectra of $[MC_{10}H_{10}]^{2+}$ dications generated from (A) ferrocene, (B) cobaltocene and (C) nickelocene, showing charge separation reactions (a) and (b) (see Scheme 2).

beam voltage E_0 to $2E_0$, thus allowing the detection of all singly charged ions having a larger m/z value than the one corresponding to the dications [4]. The resulting charge separation signals appear as broad dish-topped peaks, covering a mass range of several mass units (see Fig. 1).

As proposed earlier by Beynon et al. [3*,5] and demonstrated repeatedly [6*], the experimentally measured translational energy release T in the coulomb explosion of a dication $AB^{2+} \rightarrow A^+ + B^+$ may be equated to the intercharge distance r by the simple eq. 2. In this equation r corresponds to the distance between the "point charges" of A^+ and B^+ in the transition structure. As polyatomic dications are very often characterized by extensive charge delocalization, it is more appropriate to relate the r value to the distance between the two centres of positive charge at the moment of fragmentation. If the charge distribution in the fragmenting ion is not known, it is not possible to draw definitive structural assignments on the basis of r values alone. Nevertheless, certain structural characteristics can still be discerned; in numerous cases, for example, it was possible to distinguish between the ring and open-chain structures based on intercharge distance data. Furthermore, closely related structures can be compared on the basis of their r values, irrespective of the knowledge of the actual structures involved [7]. The error limits of the determination of T from the half-height peaks of the charge separation reactions are such that r is obtained with an uncertainty of ±0.3 Å.

$$T(\mathrm{eV}) = \frac{14.39}{r(\text{Å})} \qquad (2)$$

Results and discussion

As shown in Fig. 1, irrespective of the nature of the metal atom all the dications generated from MCp_2 (M = Fe, Co, Ni) give rise to the charge separation products shown in eq. a and b, either by loss of a $C_5H_5^+$ unit (reaction a) or by reductive demetallation to generate M^+ and $C_{10}H_{10}^{+\cdot}$ (reaction b). Reaction a clearly demonstrates that the dications of $[MCp_2]^{2+}$ retain (presumably intact [8*]) C_5H_5 units. Although the experiments do not reveal anything directly about the charge distribution in the non-reactive $[MC_{10}H_{10}]^{2+}$ species, the occurrence of process a leaves no doubt that in this reaction channel one charge unit goes with the C_5H_5 fragment and one stays with the $[MC_5H_5]^+$ part. From the translational energy release data, given in Table 1, we note that for all three metals the T values are, within the error limits, the same; they correspond to an intercharge distance of ca. 5.0 Å.

Perhaps more intriguing is the charge separation process b, which is also operative for all three metal complexes studied. In this reaction $[MC_{10}H_{10}]^{2+}$ falls apart to generate M^+ and a $C_{10}H_{10}^{+\cdot}$ unit. If in the dications, made from the sandwich compounds MCp_2, the two Cp units are still present as distinct units (which is also reflected in the formation of $C_5H_5^+$ and $[MC_5H_5]^+$), the generation of $C_{10}H_{10}^{+\cdot}$ leaves no doubt that charge separation accompanied with reductive demetallation brings about the junction of the two C_5H_5 units. This reaction, which has a formal precedent in the pyrolysis of nickelocene [9], gives rise to identical T values (2.32 eV measured at half peak-height); from this value an intercharge distance of 6.2 Å is derived. Based on the r values for the above two processes, the following conclusions can be drawn:

Table 1

Kinetic energy releases (T) and intercharge distances (r) for coulomb explosion processes of $(MC_{10}H_{10})^{2+}$ generated from ferrocene (M = Fe), cobaltocene (M = Co) and nickelocene (M = Ni)

M	$(MC_{10}H_{10})^{2+} \rightarrow (MC_5H_5)^+ + C_5H_5^+$ (a)		$(MC_{10}H_{10})^{2+} \rightarrow C_{10}H_{10}^{+\cdot} + M^+$ (b)	
	$T_{0.5}^{(b)}$ (eV)	r (Å)	$T_{0.5}^{(b)}$ (eV)	r (Å)
Fe [a]	2.82	5.1	2.32	6.2
Co	2.88	5.0	2.32	6.2
Ni	2.94	4.9	2.32	6.2

[a] Ast et al. (ref. 2a) obtained for $(FeC_{10}H_{10})^{2+}$ for reaction (a) a value of r 4.9 Å, and for process (b) a value of r 5.9 Å. [b] Translational energy release measured at half-height.

(i) Same structure(s) of the $[MCp_2]^{2+}$ ions are involved in all three compounds.

(ii) Reaction b involves the $[MCp_2]^{2+}$ ions in which the two C_5H_5 units are joined; however, none of the rings seems to be opened, since this would result in a much larger r value for the processes.

(iii) If reaction a were assumed to take place from the same rearranged structure as reaction b, an identical intercharge distance would be expected, since this would simply represent the breaking of the $C_5H_5^+$ end, rather than the M^+ end from the same structure. The fact that different r values are obtained suggests that different structures are involved. As one possibility, the original $[C_5H_5\text{–}M\text{–}C_5H_5]^{2+}$ type structure is consistent with the r value obtained.

(iv) On the basis of the qualitative MO analysis mentioned in the Introduction, $(NiCp_2)^{2+}$ would be expected to be the most stable of the three doubly charged molecular ions, since it involves an 18 valence electron system. Consequently, it would be predicted to show the lowest proportion of rearrangement leading to reaction b. The fact that this reaction has the lowest abundance for the Ni compound tends to support this conclusion.

Acknowledgements

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