Structure and Mechanisms of Formation of C₆H₈Fe⁺ Ions Produced by Electron Impact on η⁵-C₅H₅Fe(CO)₂CH₃

Dag Ekeberg, Georg Hvistendahl, Yngve Stenstrøm* and Einar Uggerud

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

Collisional activation (CA) mass spectrometry has been employed to show that C₆H₈Fe⁺ ions formed upon electron impact of dicarbonyl-(η⁵,2,4-cyclopentadienyl)-methyliron consist of a 1:1 mixture of fulvene-iron and benzene-iron structures. Analysis of daughter-ion spectra of the deuterium-labelled analogue shows that there exist two independent fragmentation routes leading to the different ion structures. These routes differ in the sequence in which the CO ligands and H₂ are lost from the molecular ion.

C₆H₈Fe⁺ ions are produced in the gas phase as the result of loss of H₂ and two CO ligands from energized C₆H₈Fe(CO)₂CH₃⁺ ions. The structure of C₆H₈Fe⁺ was for several years assumed to be a complex between Fe⁺ and benzene,¹ but in 1981 Müller and Lüdemann² raised the question of whether the structure of the C₆H₈ moiety is fulvene rather than benzene.

Nekrasov et al.³ have studied the formation of C₆H₈Fe⁺, undertaking deuterium-labeling experiments. Analysis of the electron ionization (EI) mass spectrum of C₆H₈Fe(CO)₂CH₃ (I, Scheme I) led these workers to conclude that the extent of dehydrogenation increases as coordination unsaturation of the metal atom. This conclusion was based on the fact that the number of carbonyl group (S = 0 for n = 2, S = 0.06 for n = 1 and S = 1.9 for n = 0). In addition, the EI spectrum of C₆H₈Fe(CO)₂CD₃ showed that HD loss in the predominant process with partial scrambling of H/D. The scrambling was found to increase with increased coordination unsaturation of the metal atom.

It is well known that molecular ions produced by 70 eV EI have a broad energy distribution and that a majority of the fragment ions are formed via high-energy processes.⁴ In order to gain information about the chemically more relevant low-energy processes it was necessary to perform experiments with ions which have energies close to the critical energy of each of the reactions under investigation. Equally important is high reaction specificity. Both requirements were achieved by studying the decomposition of long-lived metastable ions.⁵

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* Present address: Department of Biotechnological Science, Agricultural University of Norway, P.O. Box 40, N-1432 Ås-NLH, Norway.

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The purpose of the study described in this paper was to determine the molecular structure of the C₆H₈Fe⁺ ions and the reaction mechanism by which the ions are formed from C₆H₈Fe(CO)₂CH₃. By a systematic investigation of the fragmentation of metastable ions we wished to obtain reliable information about (a) in which sequence H₂ and the two CO ligands actually are lost and (b) the detailed mechanism of the loss of H₂. The latter point is closely related to the molecular structure of C₆H₈Fe⁺. Information about this structure will be obtained by comparison of the
collisional activation mass spectrum of the ion of unknown structure and corresponding reference ions with known structures.

**Experimental**

All spectra were recorded using a double focusing mass spectrometer of EB geometry (model 7070F VG Analytical Ltd. Manchester, UK). The samples were introduced to the ion source via a temperature-regulated direct insertion probe.

Daughter-ion spectra were recorded by linked scanning of the electric and magnetic sectors keeping the ratio B/E constant. Collisionally induced decomposition (CID) was achieved using He as the collision gas. Before the CID spectrum was taken, the He pressure in the collision cell was increased until the primary ion beam was attenuated by 80%.

The synthesis of C₆H₅Fe(CO)₃CH₃ was performed using standard methodology as previously described for acyl compounds. Addition of CH₃I or CD₃I to a suspension of C₆H₅Fe(CO)₃K⁺ in THF followed by evaporation and flash chromatography (silica gel 230–400 mesh, hexane) gave the σ complexes in 66 and 68% yields, respectively.

The purity of the two methyl compounds were ascertained by ¹H NMR spectroscopy. The degree of deuteriation was confirmed to be >99% corresponding to the deuteration of the starting CD₃I, both by ¹H NMR and MS. Ferrocenylmethanol (6) was made according to the literature. Ethoxymethylferrocene (5) was made using the literature procedure except that 95% EtOH was used and the compound was purified by flash chromatography (silica gel 230–400 mesh, ethyl acetate–hexane 5:95 v/v) to give (5) in 85% yield. The spectroscopic data were in accordance with the literature. Compound 4 was made according to Wilkinson’s procedure; the spectroscopic data were consistent with those previously reported. Compound 7 was made using a modification of the procedure for preparation of η₅-cyclopentadienetricarbonyl iron. Freshly prepared methylcyclopentadiene and Fe₅(CO)₁₅ were refluxed in diethyl ether overnight. Evaporation and flash chromatography (silica gel 230–400 mesh, ethyl acetate–hexane 5:95 v/v) gave 7 in 67% yield as a mixture of regioisomers as seen from the complex NMR spectra. Experimental details will be published in due course.

**Results and discussion**

The EI mass spectrum of η₅-C₆H₅Fe(CO)₃CH₃ (1) is reproduced in Fig. 1(a). The molecular ion, M⁺, was found at m/z 192. Loss of one and two CO ligands gave rise to peaks at m/z 164 and m/z 136, respectively. The base peak at m/z 121 corresponds to loss of both CO ligands together with the methyl group. The peak at m/z 177 corresponds to loss of the methyl group from M⁺, and further loss of CO gives rise to a peak at m/z 149. The C₆H₅Fe⁺ ion at m/z 134 is formed from the molecular ion upon loss of both CO ligands and H₂. The peak at m/z 56 corresponds to the naked iron ion. The fragmentation processes are summarized in Scheme 2. Fig. 1(b) shows the mass spectrum of the corresponding trideuteriomethyl analogue.

![Scheme 2](image)

The first step in establishing the reaction mechanism was to determine in which order the two CO ligands and H₂ are lost.
containing one CH₃ and one C₅H₅ group: (a) loss of both hydrogen atoms from the cyclopentadienyl ligand; (b) loss of one hydrogen atom from the cyclopentadiene ligand and one from the methyl group; (c) loss of both hydrogen atoms from the methyl group. These mechanisms can only be distinguished by deuterium labelling.

The daughter-ion spectrum of metastable C₅H₅Fe(CO)₂⁺CH₅⁺ ions (m/z 195) is shown in Fig. 3(a). The only process observed was loss of CO and formation of C₅H₅Fe(CO)CD₂⁺ (m/z 167). The major process observed in the daughter-ion spectrum of metastable C₅H₅Fe(CO)CD₃⁺ ions [Fig. 3(b)] was loss of HD. Only a minor peak corresponding to loss of H₂ is observed. The other major peak observed corresponds to loss of CO. Fig. 3(c) shows the daughter-ion spectrum of metastable C₅H₅Fe(CO)CD₄⁺ ions (m/z 139). This spectrum shows that loss of H₂, HD and D₂ occur in the ratio (0.42:0.47:0.11) which is close to the theoretical distribution obtained if we assume complete randomization of the eight hydrogens (0.36:0.54:0.10).

The important conclusions to be drawn from the isotope-labelling experiments are that loss of H₂ from

Fig. 2. Daughter-ion spectrum of the metastable ions C₅H₅Fe(CO)CH₂⁺ (m/z 192) (a), C₅H₅Fe(CO)CH₃⁺ (m/z 164) (b) and C₅H₅FeCH₄⁺ (m/z 136) (c).

The daughter-ion spectrum of metastable C₅H₅Fe(CO)₂⁺CH₅⁺ ions is shown in Fig. 2(a). The major process observed was CO loss which gave C₅H₅Fe(CO)CH₃⁺ (m/z 164). Loss of CH₂O, or more probably CO + H₂, was much less abundant, only 2% relative to loss of CO. No loss of CH₃ was observed. Metastable C₅H₅Fe(CO)CH₃⁺ ions (m/z 164) lose both CO and H₂ [Fig. 2(b)]. The two reactions are almost equally abundant, indicating that the two competing reactions have nearly identical critical energies. The daughter-ion spectrum of metastable C₅H₅FeCH₄⁺ ions (m/z 136), the result of two successive CO losses, is shown in Fig. 2(c). Only one peak corresponding to the loss of H₂ is observed.

From these data we conclude that there are two parallel routes for the formation of C₅H₅Fe⁺ from C₅H₅Fe(CO)₂CH₃⁺. One route is the following sequence of losses: −CO, −H₂, −CO, and the other route corresponds to the sequence: −CO, −CO and −H₂.

There are in principle three distinct mechanisms for the specific elimination of a hydrogen molecule from an ion

Fig. 3. Daughter-ion spectrum of the metastable ions C₅H₅Fe(CO)CD₂⁺ (m/z 195) (a), C₅H₅Fe(CO)CD₃⁺ (m/z 167) (b) and C₅H₅FeCD₄⁺ (m/z 139) (c).
C₅H₅Fe(CO)CH₃⁺ occurs largely via mechanism (b) (one hydrogen is lost from the methyl group and one from the cyclopentadienyl ring). H₂ loss from C₅H₅FeCH₃⁺ probably occurs via a different mechanism which involves full randomization of the hydrogens, probably by migration of the methyl group to the cyclopentadienyl ring.

The second part of the investigation concerns the structure of the C₅H₅Fe⁺ ion (m/z 134). Although several structures may be formulated, we considered only the two most probable, the fulvene-iron complex (2) and the benzene-iron complex (3). These reference ions were generated via independent routes.

Benzene-iron ions (3) were produced by electron impact of C₅H₅FeC₂H₂ (4) via loss of H and C₂H₂. Fig. 4(d) shows the CA spectrum of (3). The spectrum is clearly structure indicative. Loss of benzene is the dominant fragmentation reaction, while loss of H and subsequent losses of acetylene give rise to the peaks at m/z 133, 107 and 81.

The reference spectrum of what is believed to be the fulvene-iron ion 2 can be formed in two different ways.

The most direct approach was to use [η⁵-C₅H₅CH₂X]Fe-(η⁵-C₅H₅) X = OH (6), OC₅H₅ (5), the idea being that successive losses of C₅H₅ and X would lead C₅H₅CH₂Fe⁺ upon EI of the mother compound. This would most likely be successful for X = OH, which is a better leaving group than OH.

The other approach started with η⁴-C₅H₅C₅H₅Fe(CO)₃ (7). Electron impact of this compound resulted in successive elimination of three CO ligands and H₂. The weakness of this approach is that 7 exists in three isomeric forms, which may complicate the reactions leading to the desired C₅H₅Fe⁺ isomer. However, this argument is less relevant as can be seen from the experimental results (vide infra).

The CA spectrum obtained for C₅H₅Fe⁺ from (C₅H₅CH₂, CO₅H₅)Fe(C₅H₅) (5) [Fig. 4(c)] is significantly different from the corresponding benzene-iron ion spectrum [Fig. 4(d)]. In addition to the peaks found in the benzene-iron spectrum, there are peaks at m/z 119 corresponding to loss of C₂H₄ and m/z 94 corresponding to loss of C₅H₅.

The CA spectrum obtained for C₅H₅Fe⁺ from (C₅H₅)
$\text{CH}_2\text{XFe(C}_2\text{H}_5)\text{ for } X = \text{OH (6) [Fig. 4(e)] is different from the spectrum obtained from } X = \text{OC}_2\text{H}_5\text{ [Fig. 4(c)]. This may be attributed to the fact that OH is a poorer leaving group than OC}_2\text{H}_5\text{. The rather close resemblance between the spectra of Fig. 4(e) and 4(d) indicates a high degree of isomerization to the benzene–iron structure during ionization/dissociation of 6.}$

The CA spectrum of $\text{C}_6\text{H}_4\text{Fe}^+\text{ from } \eta^6\text{CH}_2\text{C}_6\text{H}_4\text{Fe(CO)}_2^+$ (7) is shown in Fig. 4(b). Except for small intensity differences the spectrum is identical with the spectrum of the assumed fulvene–iron ion [Fig. 4(c)]. The intensity variations may be attributed to differences in internal energy of the $\text{C}_6\text{H}_4\text{Fe}^+$ ions produced via the two independent routes.

When we compare the CA spectrum of $\text{C}_6\text{H}_5\text{Fe}^+$ produced from $\text{C}_6\text{H}_4\text{Fe(CO)}_2\text{CH}_3\text{ [Fig. 4(a)] with the two references [Fig. 4(c) and 4(d)] it is obvious that it is different. However, there are great similarities in all three; almost 100% fit is achieved if one assumes that the $\text{C}_6\text{H}_5\text{Fe}^+$ generated from $\text{C}_6\text{H}_4\text{Fe(CO)}_2\text{CH}_3^+$ consists of a 1:1 mixture of benzene–iron and fulvene–iron.}$

**Conclusions**

The results from this work have been summarized in Scheme 3. There exist two independent routes for formation of $\text{C}_6\text{H}_5\text{Fe}^+$ from $\text{C}_6\text{H}_4\text{Fe(CO)}_2\text{CH}_3^+$, both via routes from the common intermediate $\text{C}_6\text{H}_4\text{Fe(CO)}_2\text{CH}_3^+$.

Ions which first lose $\text{H}_2$ and then $\text{CO}$ produce $\text{C}_6\text{H}_5\text{Fe}^+$ ions which most probably have the fulvene–iron structure. This is because $\text{H}_2$ is lost specifically in the sense that one of the hydrogen atoms originates from the $\text{CH}_3$ group and the other from the $\text{CH}_3$ group. The loss of $\text{H}_2$ either precedes the formation of the $\text{C}−\text{C}$ of the fulvene moiety or it occurs simultaneously.

The second route applies to ions which first lose $\text{CO}$ and then $\text{H}_2$. In this mechanism the methyl group migrates to the $\text{CH}_3$ ligand prior to $\text{H}_2$ loss. This can be deduced from the fact that all eight hydrogens are randomized prior to loss of $\text{H}_2$. The product formed by this mechanism most probably has the benzene–iron structure.

**Acknowledgments.** This work was supported by VISTA (Statoil and the Norwegian Academy of Science and Letters).

**References**


Received April 11, 1991.