Generation and Identification of Neutral $CpFeC_5H_4{=}X$ ($X = O, CH_2, CO$) Complexes in the Gas Phase by Tandem Mass Spectrometry[†]

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Received November 8, 1996[⊗]

Tandem mass spectrometry experiments were performed to generate and identify neutral FcX ($Fc = CpFeC_5H_4$; $X = O, CH_2, CO$) complexes having a formal 19-electron configuration. Neutralization−reionization mass spectra of FcX^+ ions showed recovery signals corresponding to the formation of their neutral counterparts. $FcO^•$ and $FcCH_2^•$ were also identified by means of the collision-induced (dissociative) ionization method as neutral products of the unimolecular fragmentation of molecular ions of the monosubstituted ferrocenes. Appearance energies of FcX ions and neutrals were measured. Activation energies for the $[FcX{-}R]^{•+}$ bond cleavage were significantly higher than those in similar aromatic systems, $PhXR^{•+}$. It was proposed that only a part of this energy was related to the FcX−R bond dissociation, the remainder being required for the intramolecular electron transfer from the ligand to the metal atom. The $Fc^+{-}CO$ bond dissociation energy in $[FcCO]^+$ ions was substantially lower than that in the benzoyl ion. The weakness of the (neutral) Fc−CO bond was considered to be the major reason for the poor survival of $FcCO^•$ radicals in the neutralization−reionization of $FcCO^+$ ions.

Introduction

Neutralization−reionization mass spectrometry (NR MS) has been successfully applied to the gas-phase generation of elusive organometallic complexes;[1] for example, the 19-electron rhodocene and its monosubstituted derivatives have been produced.[2] In the NR MS method,[3] a beam of mass-selected positively charged counterparts of the required neutral are prepared and then neutralized by kilo(electron volt) energy collisions with a target gas. All remaining ions are deflected away, and to identify their formation, the corresponding neutral molecules or radicals are collisionally reionized. The observation of a signal having the same *m/z* ratio as that of the starting ion indicates that the corresponding neutral was produced in the experiment and that it was stable on the microsecond time scale.

The aim of the present study was to attempt the generation of formally 19-electron cyclopentadienyliron complexes of the general formula $FcX^•$, where $Fc = CpFeC_5H_4$ and $X = O$, CH_2, and CO. The complex of CpFe with benzene has been described,[4] and it showed a moderate stability in both the crystalline and liquid phases. It has also been characterized by electron impact (EI) mass spectrometry.[5] The formation of its isomer having a fulvene ligand bound to the CpFe moiety might take place in some transformations of ferrocenylmethyl derivatives, but no convincing spectral evidence has been brought forward to show the existence of this species. Complexes having a polysubstituted cyclopentadienone ligand bound to a transition-metal atom have been described elsewhere,[6] but the unsubstituted ferrocenoxyl radical has never been characterized. Neutral $FcCO^•$ was also unknown, and its generation has not yet been attempted.

In this work two mass spectral methods were used to produce and characterize $FcX^•$ complexes. In addition to the NR MS experiments, neutral $FcX^•$ species were also generated directly by the fragmentation of metastable ionized ferrocene derivatives FcXR. This method, collision-induced dissociative ionization (CIDI), has been employed to identify various neutral molecules and radicals in ion fragmentation processes.[7] The electron-transfer step of NR experiments, which usually results in neutrals having high internal energies, is thus eliminated, giving the neutrals a better chance to produce stable ions after their collisional ionization. Appearance energy (AE) measurements were performed to characterize the energetics of reactions resulting in FcX ions and neutrals.

Experimental Section

All ferrocene derivatives and $CpFe(\eta^5\text{-}C_6H_6C_5H_5)$ were provided by the Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow, Russia).

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[†] Dedicated to the memory of Prof. Mark E. Vol'pin.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

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S0276-7333(96)00951-X CCC: $14.00

The NR and CIDI experiments were carried out on a modified triple-sector (BEE) VG ZAB-2F instrument (VG Analytical, Manchester, U.K.). The general description of the two techniques has been published elsewhere.[1,3,7] The neutralization of the ions of interest, FcX^+, generated by the electron impact ionization of the corresponding ferrocene derivatives, FcXR, was performed with dimethylamine as a collision gas. The pressure of Me_2NH in the collision cell was set to provide a transmission of ca. 50% of the main ion beam (50% T). Oxygen was used for the ionization of neutrals and in the collision-induced dissociation (CID), NR, and CIDI experiments. Its pressure reduced the main ion beam by ca. 30%. The best NR mass spectra (in terms of the recovery signal intensity) were observed in the third field-free region (3-FFR) with a short distance (2 cm) between the collision cells.

In the triple mass spectrometry experiments, FcX^+ ions produced by NR or CIDI in the 2-FFR were mass-selected and transmitted to the 3-FFR and then collisionally activated (O_2, 70% T). The resulting CID mass spectra were compared with the CID mass spectra of the ion source generated species in order to examine their structural similarity.

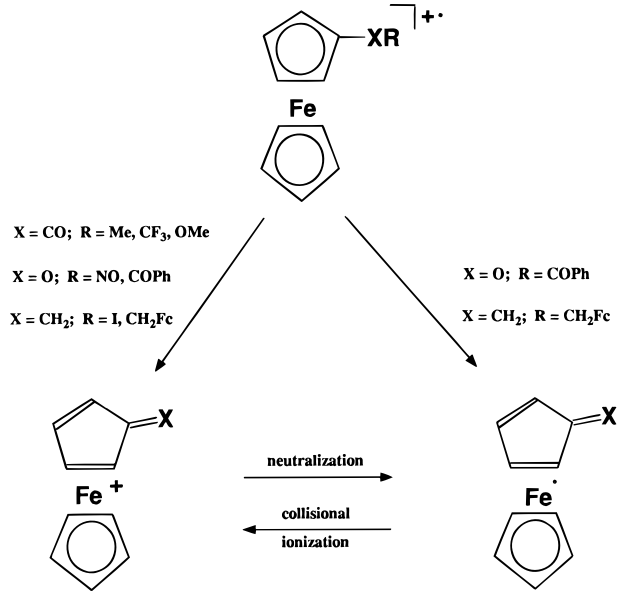
Kinetic energy release (KER) measurements were performed on the same mass spectrometer at sufficient energy resolution to reduce the main ion beam width at half-height to ca. 4 V. The KER values (from the half-height widths of metastable peaks, $T_{0.5}$) and kinetic energy release distributions (KERD) were calculated using established methods. The reproducibility of $T_{0.5}$ values was better than 10%.

Ionization energies (IE) of molecules and AE values of fragment ions were measured on an AEI MS9 (U.K.) instrument using the procedure described in ref 8. The ionization energy of methyl acetate was used as a standard in the EI measurements. Because of the large difference between the ionization energies of AcOMe (10.27 eV[9]) and ferrocenes (~7 eV[10]) the error in the experimental values could be as much as 0.2 eV. The AE values of Ac^+ ions generated in the ion source (~11 eV) or from metastable $AcOMe^{\bullet+}$ ions (10.94 eV[8]) were used as standards in the AE measurements. Appearance energies of ion source generated FcX^+, Fc^+, or $PhCO^+$ ions and those originating from the metastable molecular ions of the corresponding substituted ferrocenes were indistinguishable within experimental error (0.15 eV).

Results and Discussion

The electron impact ionization of the appropriate ferrocene derivatives was used in order to generate FcX^+ ions for NR MS investigations or to produce $FcX^\bullet$ as a neutral fragment (Scheme 1). The $FcCH_2^+$ ion is a common fragment of various ferrocenylmethyl derivatives, $FcCH_2R$,[11,12] including $FcCH_2CH_2Fc$.[11,13] The metastable dissociation of the molecular ion of the latter compound gave rise to ionized *and* neutral $FcCH_2$. $CpFe^+C_6H_6$ ions were also studied and compared with their fulvene-containing isomers, which were generated by the ionization of the substituted cyclohexadienyl complex $CpFe^+C_6H_6C_5H_5$.

Scheme 1



Two ferrocene derivatives, $FcNO_2$ and FcOOCPh, were used to produce FcO^+ ions. The fragmentation of their molecular ions by the loss of NO and $PhCO^\bullet$, respectively, gave the ferrocenoxyl ion.[11] The metastable dissociation of $FcOOCPh^{\bullet+}$ resulted in $PhCO^+$, and so $FcO^\bullet$ was expected to be the neutral product (Scheme 1).

A variety of ferrocenylcarbonyl derivatives, FcCOR, were used to generate $FcCO^+$ ions. The dissociation of their molecular ions (R = Me, Et, CF_3, Ph, etc.) produced a high yield of $FcCO^+$.[11,14] No suitable precursors for neutral $FcCO^\bullet$ were found, and so for this reason only NR experiments were performed in the attempt to generate and detect this radical.

FcO^+ and $FcO^\bullet$. The NR mass spectrum of FcO^+ ions is shown in Figure 1. It displayed a weak but significant recovery signal, indicating that neutral $FcO^\bullet$ was successfully produced in the experiment. The NR mass spectrum was consistent with the CID mass spectrum of these ions (Figure 1), showing the same metal-containing fragment ions. The differences in relative abundances of ion peaks can be accounted for by the different internal energies of ions generated in the ion source and after neutralization−reionization.

The low intensity of the survivor ions can be attributed to significant geometry differences between the ion and neutral species, with the Fe−C_5H_4O bond likely to be the most affected. This bond is also the weakest bond in the FcO^+ ions, which is indicated by their CID (Figure 1) and MI mass spectra. Note that the loss of C_5H_4O was the only reaction of metastable ions and the most prominent collision-induced dissociation.

The CIDI experiments on $FcO^\bullet$ were performed in order to avoid the neutralization step that could produce

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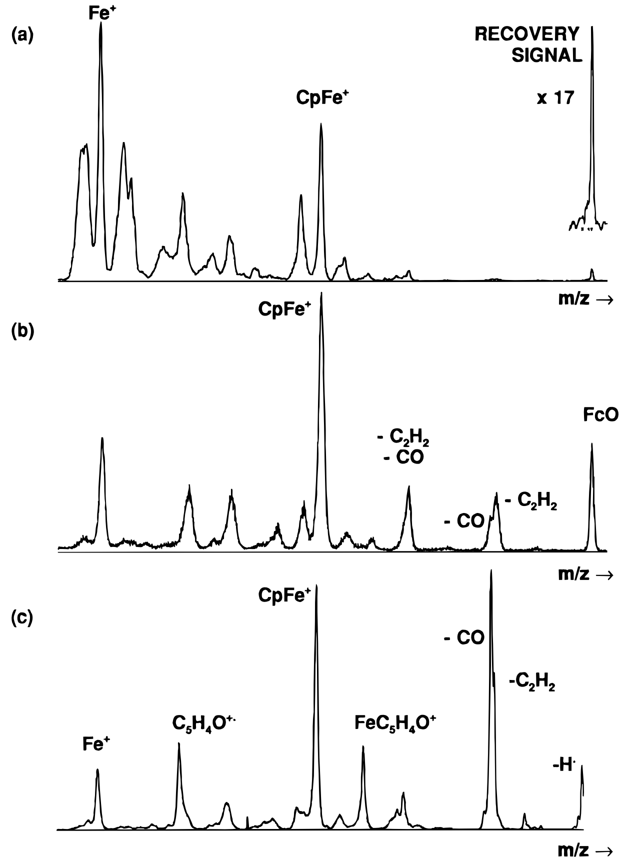

Figure 1. (a) Neutralization−reionization mass spectrum of FcO$^+$ ions, (b) collision-induced dissociative ionization mass spectrum of FcOOCPh, and (c) collision-induced dissociation mass spectrum of FcO$^+$.

highly excited and easily dissociating neutrals. The dissociation of metastable FcOOCPh$^{\bullet+}$ ions resulted in only the positively charged product, PhCO$^+$, and so this reaction could well involve the formation of neutral FcO$^\bullet$. Indeed, the CIDI mass spectrum of the ionized ferrocenyl benzoate showed a strong signal corresponding to FcO$^+$ ions (Figure 1). This result demonstrated that the radical was generated upon the dissociation of FcOOCPh$^{\bullet+}$ as shown in Scheme 1. The CIDI mass spectrum also displayed other ions, easily accounted for by the fragmentation of ionized FcO$^\bullet$, which moreover were the same as those in the CID and NR mass spectra of FcO$^+$ ions.

These experimental results demonstrated that neutral FcO$^\bullet$, having a lifetime of more than 1 μs, had been generated in the gas phase. They also showed that the neutralization of the ionic counterpart produced FcO$^\bullet$ radicals with high internal energy such that they barely survived the reionization process. Our results were in general agreement with the results for W(CO)$_n{}^+$ ions,[15] for which most of the internal energy deposited in the course of neutralization−reionization was accumulated during the neutralization event.

FcCH$_2{}^+$ and FcCH$_2{}^\bullet$. The results for FcCH$_2{}^\bullet$ were similar to those for FcO$^\bullet$. The NR mass spectra of FcCH$_2{}^+$, generated from molecular ions of various ferrocenylmethyl derivatives, showed a recovery signal (Figure 2) corresponding to the (intermediate) formation of the neutral cyclopentadienyl(fulvene)iron. This signal was weak, and the NR mass spectra were dominated by hydrocarbon ions. These ions originated mainly from the collision-induced (dissociative) ionization of fulvene produced in various stages of the experiment (metastable and collision-induced dissociation of ions before neutralization and after reionization as well as the dissociation of neutral CpFeC$_5$H$_4$CH$_2$).

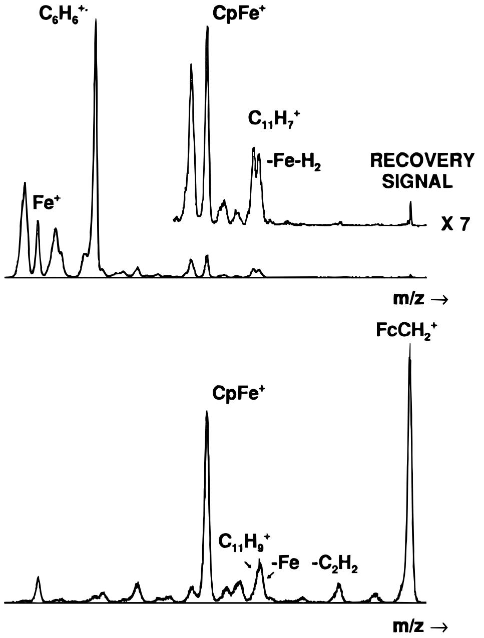

Figure 2. (a) Neutralization−reionization mass spectrum of FcCH$_2{}^+$ ions and (b) collision-induced dissociative ionization mass spectrum of FcCH$_2$CH$_2$Fc$^{\bullet+}$.

A better demonstration of the formation of stable neutral FcCH$_2{}^\bullet$ was provided by the CIDI experiments with FcCH$_2$CH$_2$Fc$^{\bullet+}$ ions. The latter species dissociated in the field-free region, producing the FcCH$_2{}^+$ ion, and the neutral product was clearly identified by its CIDI mass spectrum as FcCH$_2{}^\bullet$ (Figure 2). It was dominated by FcCH$_2{}^+$ and CpFe$^+$ ions. The first corresponded to collisionally ionized FcCH$_2{}^\bullet$; CpFe$^+$ ions could be produced both from the dissociation of FcCH$_2{}^+$ by the loss of C$_6$H$_6$ and from the collisional ionization of CpFe$^\bullet$ originating from the neutral FcCH$_2{}^\bullet$. In general, the CIDI mass spectrum of FcCH$_2$CH$_2$Fc$^{\bullet+}$ was comparable with the CID mass spectrum of the ion source generated FcCH$_2{}^+$, indicating that ions of similar structure were produced. In addition to CpFe$^+$ ions, both mass spectra displayed peaks for C$_9$H$_9$Fe$^+$, C$_{11}$H$_n{}^+$, C$_3$H$_n$Fe$^+$, C$_2$H$_n{}^+$, Fe$^{\bullet+}$, and other metal-containing or metal-free ions.

The rearrangement of hydrocarbon ligands in the coordination sphere of the metal ion is a common reaction for gas-phase organometallic ions,[16] and the isomerization of a fulvene ligand to a benzene ring in FcCH$_2{}^+$ ions has been proposed by several authors.[12] *Qualitative* differences in the unimolecular chemistry of these two structurally similar systems were not

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Table 1. Ionization Energies (IE) of Substituted Ferrocenes, Appearance Energies (AE) of Metastable Ions,[a] Associated Kinetic Energy Releases ($T_{0.5}$), and Activation Energies (E^a) for the X−R Bond Cleavage in $FcXR^{\bullet+}$ Ions and the Corresponding Aromatic Derivatives[b]

FcX−R	IE	AE(FcX^+)	AE(R^+)	$T_{0.5}$	$E^a{}_{FcXR}$	$E^a{}_{PhXR}$
FcO−COPh	6.7		10.7	0.03	4.0	1.0[c]
$FcCH_2$−I	6.5	7.8		0.03	1.3	0.4[d]
$FcCH_2$−CH_2Fc	6.5	10.8	(10.8)	0.03	4.3	1.9[e]
FcCO−Me	7.0	11.8		0.15	4.8	0.8,[f] 0.63[c]
FcCO−CF_3	7.4	11.8		0.16	4.4	1.3[f]
Fc−CO		12.5,[g] 12.7[h]		0.10	0.7,[g] 0.9[h]	3.0[f]

[a] All values are in eV. [b] The results for ions generated in the ion source and from the metastable precursors were indistinguishable within experimental error (±0.15 eV); this rules out any major kinetic shift for these processes. [c] From: Elder, J. F., Jr.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1976**, *11*, 415. [d] From: Yeo, A. N. H.; Williams, D. H. *J. Chem. Soc. D* **1970**, 886. [e] For $PhCH_2CH_2Ph$; from: McLafferty, F. W.; Wachs, T.; Lifshitz, C.; Innorta, G.; Irving, P. *J. Am. Chem. Soc.* **1970**, *92*, 6867. [f] From: Majer, J. R.; Patrick, C. R. *Trans. Faraday Soc.* **1963**, *59*, 1274. [g] For ions generated from $FcCOMe^{\bullet+}$. [h] For ions generated from $FcCOCF_3{}^{\bullet+}$.

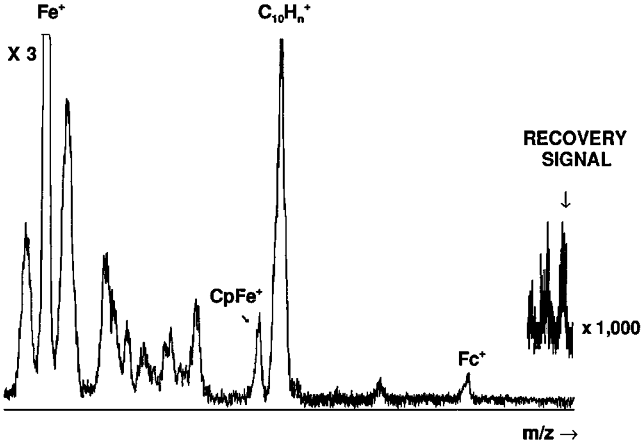

Figure 3. Neutralization−reionization mass spectrum of $FcCO^+$ ions.

expected, but the *quantitative* characteristics of their mass spectral behavior could be isomer-dependent. In order to examine the possible $FcCH_2{}^+$ to $CpFe^+C_6H_6$ transformation, their CID mass spectra were compared. However, they were indistinguishable, indicating that isomerization may well have taken place among energy-rich $FcCH_2{}^+$ species from the ion source.

Unlike the CID mass spectra of the ion source generated ions, the collisional activation of $FcCH_2{}^+$ and $CpFe^+C_6H_6$ ions produced from their *metastable* precursors ($FcCH_2CH_2Fc^{\bullet+}$ and $CpFe^{\bullet+}C_6H_6C_5H_5$, respectively) displayed differences. The loss of C_6H_6 was the dominant fragmentation in both cases. In addition to the $CpFe^+$ ion peak, the CID mass spectrum of $FcCH_2{}^+$ (as well as the CIDI mass spectrum of $FcCH_2{}^{\bullet}$ from $FcCH_2CH_2Fc^{\bullet+}$, Figure 2b) showed significant signals due to $C_9H_9Fe^+$ and $C_{11}H_{11}{}^+$ ions. The loss of the metal atom can be rationalized by ligand coupling and may indicate a significant electron spin density at the CH_2 group. Note that a similar process involving the formation of a bond between two even-electron ligands has been observed for other transition-metal-containing ions. For example, the dissociation of the ferrocenium ion to the $C_{10}H_{10}$ ion and neutral species has been identified by several authors.[10g,h,11,17] The results for ions having low internal energies demonstrated that two $CpFe^+(C_6H_6)$ isomers exist[18] and that $FcCH_2{}^+$ and its neutral counterpart are stable species in the gas phase.

$FcCO^+$ and $FcCO^{\bullet}$. The NR mass spectrum of $FcCO^+$ ions is shown in Figure 3. The recovery signal was very weak, but its presence indicated the (intermediate) formation of neutral $FcCO^{\bullet}$. The low intensity of survivor $FcCO^+$ ions can result from a relatively weak Fc^+−CO bond. This was indicated, for example, by appearance energy measurements (see Table 1). The Fc−CO bond should also be the weakest bond in neutral $FcCO^{\bullet}$, and the excess internal energy for most of the intermediate neutrals exceeded the dissociation limit. This may be indicated by the strong Fe^+ signal in the NR mass spectrum of $FcCO^+$ (Figure 3). The loss of a neutral Fe atom, which would result in $C_{11}H_9O^+$ ions, did not occur directly from the collisionally excited $FcCO^+$. For Fc^+ ions, however, the loss of Fe was the only metastable and the most significant collision-induced dissociation. Thus, the observation of abundant $Fe^{\bullet+}$ ions in the NR mass spectrum must (at least partially) be attributable to the fragmentation of *neutral* $FcCO^{\bullet}$ followed by the CIDI of $Fc^{\bullet}$.

Thermochemistry of the $[FcX{-}R]^{\bullet+}$ Bond Dissociation. The thermochemistry of the dissociation of ionized ferrocene[10a,b,f−i] and some derivatives[19] has been examined by electron impact and photoionization mass spectrometry with the aim of characterizing the metal−ligand bond cleavage. The appearance energies (AE) of some ions resulting from halogen atom loss and the migration of Cl and Br atoms from the cyclopentadienyl ring(s) to the metal atom have been reported,[19] but bond dissociation energies (BDE) in *the substituent* at the ferrocenyl group are unknown.

In the present work the AE of FcX^+ ions and their neutral analogues, originating from the dissociation of molecular ions of the corresponding substituted ferrocenes, $FcXR^{\bullet+}$ (Scheme 1), were measured. The results are shown in Table 1. The ionization energies of these molecules were also determined. In all cases they were very close to those of the unsubstituted ferrocene[10] and its derivatives[19,20] studied before. Low ionization energies of these complexes are associated with the removal of an electron from the metal atom's d levels.

The activation energies for the dissociation of FcX−R bonds in ionized FcXR were calculated from the differ-

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(18) The third $[C_{11}H_{11}Fe]^+$ isomer was identified. The ions generated by the consecutive loss of CH_3CO and CO from the molecular ion of 1,1′-diacetylferrocene showed a significant peak corresponding to the loss of CH_3. This indicated the migration of the methyl group to the metal atom prior to the loss of CO. Hence, the $[(C_5H_4)_2Fe^+CH_3]$ structure represents this ion better than $C_5H_4Fe^+C_6H_7$, proposed originally in: Sheley, C. F.; Fishel, D. L. *Org. Mass Spectrom.* **1972**, *6*, 1131.

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ence between the AE and the IE (Table 1). Moderate kinetic energy releases ($T_{0.5} \approx 30$ meV) were observed for the fragmentation of metastable $FcCH_2I^{•+}$ and $FcCH_2CH_2Fc^{•+}$ ions to $FcCH_2^+$ and for the fragmentation of $FcOOCPh^{•+}$ to $PhCO^+$ (Table 1). Similar results were obtained for metastable dissociations of other Fe-containing ions.[11,21] This indicated that the reverse reactions may have only small energy barriers and that the measured activation energies were close to the thermochemical limit for the corresponding dissociations.

The latter was unlikely for $FcCO^+{-}^•Me$ and $FcCO^+{-}^•CF_3$ bond cleavages. Both reactions were accompanied by significant KER (Table 1). Moreover, their KERD's showed that the metastable peaks were composite. Thus more than one mechanism was involved in the loss of $Me^•$ and $CF_3^•$. The component associated with a high $T_{0.5}$ value dominated the KERD's. At least for this dissociation channel, a substantial reverse activation barrier may exist. It should also be noted that these ions inhabit deep potential wells, 4−5 eV, and so kinetic shift effects cannot be discounted. A similar proposal can be made for the fragmentation of $FcCO^+$ to Fc^+. The KER for this reaction was also high (Table 1), ruling out a process with no or an insignificant barrier for the reverse reaction. The corresponding metastable peak had a Gaussian shape, showing a single channel for the loss of CO.

Energies for the $FcX^+{-}^•R$ and $FcX^•{-}R^+$ bond dissociations were very high relative to those for similar reactions in ionized benzene derivatives (Table 1). Some of them were even greater than the corresponding *homolytic* bond strengths in analogous organic molecules; e.g., for $PhCH_2{-}CH_2Ph$ and $PhCO{-}Me$ they are 2.8 and 3.1 eV, respectively.[9] To rationalize the experimental results for $FcXR^{•+}$ ions, we propose the formal involvement of two processes in their dissociation. The first step is the generation of an ion with the charge on the ligand. This may involve the intramolecular electron transfer from the π-system of the cyclopentadienyl ring or O-atom of the substituent. The latter can be achieved via direct interaction between the carbonyl group of the acetyl or benzoyloxy substituent with the positively charged metal atom. Similar reactions, resulting in the migration of the anion (or radical) from the side chain of the substituent in the cyclopentadienyl ligand to the Fe atom, are common for the dissociation of substituted ferrocenes.[11,12,14,19a] The energy requirements for this electron transfer are determined by the difference in ionization energies of the corresponding molecular orbitals. For example, the difference between the ionization energy on the ligand π-system or an O-atom in 1,1′-diacetylferrocene and that on the metal atom is ∼1.8 eV.[18] Hence, only a portion of the measured activation energies (Table 1) belongs to the *dissociation* of the FcX−R bond. The remaining portions of the activation energies are close to those for similar aromatic systems. Note also that $FcXR^{•+}$ ions with the positive charge on the ligand can arise from the ionization of neutral complexes. The existence of two routes to such species may result in two dissociation channels for the same fragmentation, as was observed for the acetyl- and (trifluoroacetyl)ferrocenes.

The absence of reliable data on the heats of formation of the substituted ferrocenes studied in the present work and the lack of well-established substituent effects on the thermochemistry of Cp_2Fe did not permit the calculation of heats of formation of FcX^+ or their neutral analogues. However, the appearance energies obtained in this study will be useful when $\Delta H_f°[FcXR]$ values have been determined by theory or experiment.

Acknowledgment. J.L.H. thanks the Natural Sciences and Engineering Council of Canada for continuing financial support. D.V.Z. acknowledges the Institute of Organometallic Compounds, Russian Academy of Sciences (Moscow, Russia), for the samples of substituted ferrocenes.

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(21) Kinetic energy releases of similar value ($T_{0.5} = 25{-}45$ meV) were observed for many other metastable dissociations of Fe-containing ions studied by the authors, independently of the type of process and ion origin.