# 163. Generation of 'Bare' $FeF^+$ by C–F Bond Activation in the Gas Phase and Evaluation of Thermochemical Data

Short Communication

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The title compound $FeF^+$ has been generated in a *Fourier*-transform ion-cyclotron-resonance mass spectrometer *via* C–F bond activation by reacting hexafluorobenzene with bare $FeO^+$. Bracketing experiments provide a bond-dissociation energy (BDE) for $FeF^+$ of $86 < BDE < 101$ kcal/mol. High-level CAS-MCSCF pseudopotential *ab initio* calculations, including 501036 electronic configurations, predict a $BDE(Fe^+{-}F)$ of 100.9 kcal/mol.

**Introduction.** – The C–F bond is one of the least reactive bonds in chemistry. Due to this fact, fluorinated compounds are in widespread application in various fields of chemistry and technology [1]. Ther inertness of these compounds is not only due to the relatively high bond-dissociation energy (BDE) of the C–F bond (*e.g.* BDE(C–F) = 116 kcal/mol for $C_6F_6$) [2] but also results from its small polarizability, thus giving rise to large kinetic barriers. Even for transition-metal complexes¹), which often lower activation energies and in the presence of which catalytic reactions are feasible, C–F bond activation is rare in both the condensed [4] and the gas phases [5] [6]. In this communication, we report the generation of 'bare' $FeF^+$ in the gas phase by reacting $FeO^+$ with hexafluorobenzene. Both, experimental studies and high-level *ab initio* MO calculations are used to obtain thermochemical data on $FeF^+$, including the bond-dissociation energy for the process $FeF^+ \rightarrow Fe^+ + F\cdot$.

**Experimental and Theoretical Section.** – The experiments have been performed by using a *Spectrospin CMS 47X Fourier*-transform ion-cyclotron-resonance mass spectrometer²). Briefly, $Fe^+$ ions were formed by laser desorption/ionization in an external ion source, transferred into the analyzer cell, and trapped in the field of a superconducting magnet (*Oxford Instruments*), which has a maximum field strength of 7.05 Tesla. The isolation of the $^{56}Fe^+$ isotope, and all further isolations, have been performed by using FERETS [7], and ions have been thermalized by collisions with Ar at a pressure of $10^{-7}$ mbar. $FeO^+$ was formed by pulsed-in $N_2O$ [8], isolated, collisionally cooled, and subsequently reacted with hexafluorobenzene, which was introduced *via* a leak valve. For further ion-molecule reactions, $FeF^+$ was again isolated and allowed to react with different substrates.

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¹) For recent reviews on F-containing transition-metal complexes, see [3].

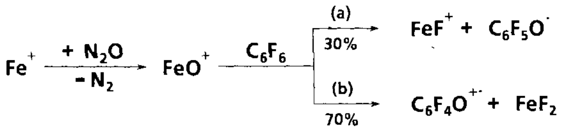
²) For a detailed description of the machine and the experimental set-up, see [6].

*Ab initio* SCF calculations have been carried out by using the GAMESS program package [9] including the pseudopotential method of *Durand* and *Barthelat* [10]. For the Fe-atom, we have employed a valence GTO basis in the contraction (6s, 3p, 8d//2111/111/32111) with a pseudopotential parametrized for the three lowest states of the neutral and cationic metal³). The F-atom is treated by using an all-electron basis (9s, 6p//42111/21111) contracted to a DZ basis, to which one d-polarization function ($\alpha = 0.65$) has been added. To account for the effects of correlation energy, the complete active valence space multiconfiguration SCF procedure (CAS-MCSCF) has been applied. The inclusion of the whole atomic orbital basis into the configuration space leads to a total of 501036 configuration for $FeF^+$. The optimal $Fe^+{-}F$ distance and the dissociation curve have been obtained by variation of the bond length of $Fe^+{-}F$ followed by a polynominal fitting.

**Results and Discussion.** – Cationic $MX^+$ ions (X = Cl, Br, I) can be formed by the reaction of the corresponding methyl halogenides with 'bare' $M^+$ in the gas phase, and the transfer of X to $M^+$ often occurs without an activation barrier [12]. However, $CH_3F$ does not react with ground-state $Fe^+$, thus setting an *upper* limit for the BDE($Fe^+{-}F$) of 113 kcal/mol [13] (*Eqn. 1*).

$$\mathrm{Fe^+ + CH_3F} \not\longrightarrow \mathrm{FeF^+ + CH_3^{\bullet}} \qquad \boxed{\mathrm{BDE(FeF^+)} \leq 113\ \mathrm{kcal/mol}} \tag{1}$$

In our experiment, $FeF^+$ has been formed from 'bare' $Fe^+$ by the reaction sequence depicted in *Eqn. 2*. In the first step, the highly reactive⁴) cationic metal-oxo species $FeO^+$ is formed from thermalized $Fe^+$ ions, which subsequently affords C–F bond activation of hexafluorobenzene to yield $FeF^+$⁵). This reaction permits the convenient generation of $FeF^+$ under the relatively well-defined conditions of an ion-molecule reaction, and thus will allow to study in the future the reactivity of $FeF^+$ with other substrates as well. Assuming the pentafluorophenoxy radical as the neutral product of *Reaction 2a*, a *lower* limit of 86 kcal/mol is obtained for the BDE of $FeF^+$⁶). The assignment of $C_6F_5O$ as a pentafluorophenoxy radical is supported by the generation of $C_6F_4O^+$ in *Reaction 2b* which clearly points to the formation of a C–O bond in the reaction of $FeO^+$ with $C_6F_6$.



$$\boxed{\mathrm{BDE(FeF^+)} \geq 86\ \mathrm{kcal/mol}} \tag{2}$$

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³) The full description of the computational details of the pseudopotential parametrization will be published separately, *cf.* [11].

⁴) 'Bare' $FeO^+$ is even capable of activating methane [14a, b]. There are four low-lying states for $FeO^+$ ($^4\pi$, $4\Delta$, $4\phi$, and '$\Sigma^+$'). An experimental assigment for which of the states is formed in the reaction of $Fe^+$ with $N_2O$ has not yet been reported [14c].

⁵) $FeO^+$ reacts with $C_6F_6$ almost at the collision rate, as the experimental value ($k_{exp.} = 1.1 \times 10^{-9} cm^3$ molecule$^{-1}$ s$^{-1}$) and the rate constant calculated for a *Langevin* collision process [15] are within the error bars (±25%) nearly identical ($k_L = 1.3 \times 10^{-9} cm^3$ molecule$^{-1}$ s$^{-1}$).

⁶) For relevant thermochemical data, see [2] [16].

In addition, $FeF^+$ has been found to react with $H_2O$ to form $FeOH^+$ and HF (*Eqn. 3*). From the thermochemistry of this reaction, an *upper* limit of 101 kcal/mol can be derived for BDE ($Fe^+$–F)[7]. While similar exchange reactions have been reported for $FeCH_3^+$ [18a] and $FeNH_2^+$ [18b], the iron halogenides $FeX^+$ (X = Cl, Br, I) do not react with $H_2O$ [18c]. Therefore, the reactivity of $FeF^+$ toward substrates is obviously more similar to that of $FeOH^+$ rather than that of the corresponding $FeX^+$ ions; actually, the latter are found to be much less reactive than $FeOH^+$ [5e][8].

$$\mathbf{FeF^+ + H_2O \longrightarrow FeOH^+ + HF} \qquad \boxed{\mathbf{BDE(FeF^+) \leq 101\ kcal/mol}} \qquad (3)$$

Additionally, we have performed high-level MCSCF *ab initio* calculations of $FeF^+$[9]. The BDE($Fe^+$–F) has been determined from the energy differences between the global minimum and a $FeF^+$ supermolecule with a Fe–F distance of 20.0 Å (see the *Fig.*). At the

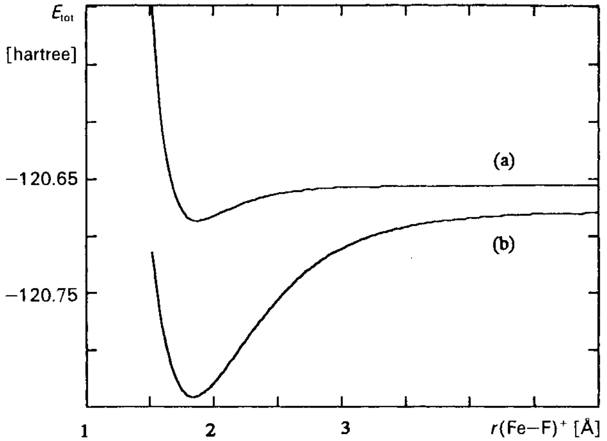

Figure. *Dissociation curve for $FeF^+$ ($^5\Sigma$ state) at* a) *the UHF level and* b) *after inclusion of electron correlation by CAS-MCSCF*

UHF level, a BDE($Fe^+$–F) of 38.5 kcal/mol has been obtained for the $^5\Sigma^+$ state of $FeF^+$; the Fe–F distance for the minimum corresponds to 1.872 Å. After inclusion of the effects of electron correlation by performing an MCSCF calculation using 501036 configurations of $FeF^+$, the BDE($Fe^+$–F) dramatically increases to a value of 100.9 kcal/mol; this number might become somewhat smaller, if the basis-set superposition errors are taken into account (*ca.* 5 kcal/mol) [22]. In line with a previous study [20] [21] of $MCl^+$ (M = V, Cr, Mn, Fe), the structure of $FeF^+$ can be described as a charge-transfer complex ($Fe^{2+}/F^-$) having a minimum bond length of 1.858 Å at the MCSCF level of theory.

The experimentally bracketed value of 86 kcal/mol < BDE($Fe^+$–F) < 101 kcal/mol and the calculated value of 100.9 kcal/mol agree well with a recent *Knudsen* cell measure-

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[7] For a recent value for the BDE($Fe^+$–OH), see [17].

[8] For a comparison of the reactions of $FeOH^+$ and $FeCl^+$ with simple alkanes, see [19].

[9] For a similar MCSCF computation of $CrCl^+$, see [20].

ment [22] of the thermochemistry of $FeF_2$, from which a value of BDE($Fe^+$–F) = 97 ± 8 kcal/mol can be derived; in earlier work a value of BDE($Fe^+$–F) = 94 ± 8 kcal/mol was reported [23] [24]. Further studies to explore the ion-molecule reactions of $FeF^+$ with various substrates are in progress, as well as a comparative, more detailed multi-reference configuration-interaction calculation of the iron halogenides $FeX^+$ (X = Cl, Br).

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