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Articles

C−F Bond Activation in Fluorinated Carbonyl Compounds by Chromium Monocations in the Gas Phase

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The Cr$^+$-assisted hydrolytic C−F bond activation in the gas phase reported recently for hexafluoroacetone applies also to other fluorinated carbonyl compounds. C−F bond hydrolysis is observed for monofluoroacetone, 1,1,1-trifluoroacetone, pentafluorobenzaldehyde, and 2,3,4,5,6-pentafluoroacetophenone. However, the diversity of the carbonyl group's substituents is paralleled by an increase of the hitherto small number of reaction channels, thus allowing for alternative ways of C−F bond activation as well. Both complexation and C−F bond activation of the organic substrates in the gas phase have been investigated by means of FT-ICR mass spectrometry.

Introduction

In a recent communication,[1] we reported the chromium-mediated C−F bond hydrolysis of hexafluoroacetone in the gas phase. This reaction is remarkable because hexafluoroacetone is not hydrolyzed in the condensed phase but forms stable sesqui- and trihydrates. Furthermore, “bare” chromium cations are generally unreactive in the gas phase,[2−6] and the C−F bond is known to be strong (the BDE (bond dissociation energy) is about 105−110 kcal mol^{-1} [7,8]). In brief, we found $CrC_3F_6O^+$, the monoadduct of Cr$^+$ and hexafluoroacetone, to undergo three (in some cases even four) hydrolytic C−F bond cleavages.[1] Consequently, we wanted to probe how far one could expand this new concept of Cr$^+$-assisted C−F bond activation. Previous experimental studies of C−F bond activation comprise the use of other metals in the condensed phase,[9−14] cation surface collisions,[15−17] and endothermic[18,19] and exothermic[20,21] gas-phase reactions; in addition, there exist a few quantum-chemical calculations addressing mechanistic aspects of metal cation mediated C−F bond activation.[22,23]

Table 1. Carbonyl Compounds R^1COR^2 Investigated

	R^1	R^2		R^1	R^2
1a	CF_3	CF_3	**1e**	CF_3	$COOC_2H_5$
1b	CF_3	CH_3	**1f**	C_6F_5	H
1c	CH_2F	CH_3	**1g**	C_6F_5	CH_3
1d	CH_3	CH_3			

In the study presented here, we kept the carbonyl group of hexafluoroacetone (R^1COR^2, $R^1 = R^2 = CF_3$) but replaced its substituents R^1 and R^2, as shown in Table 1. In brief, we focused on both the influence of decreasing acetone fluorination and the introduction of the pentafluorophenyl group into the system and investigated the reactions of the substrates shown in Table 1 with Cr$^+$ and the susceptibility of the respective adduct complexes toward hydrolysis. When appropriate, the results previously reported for hexafluoroacetone are quoted in this publication for the purpose of comparison.

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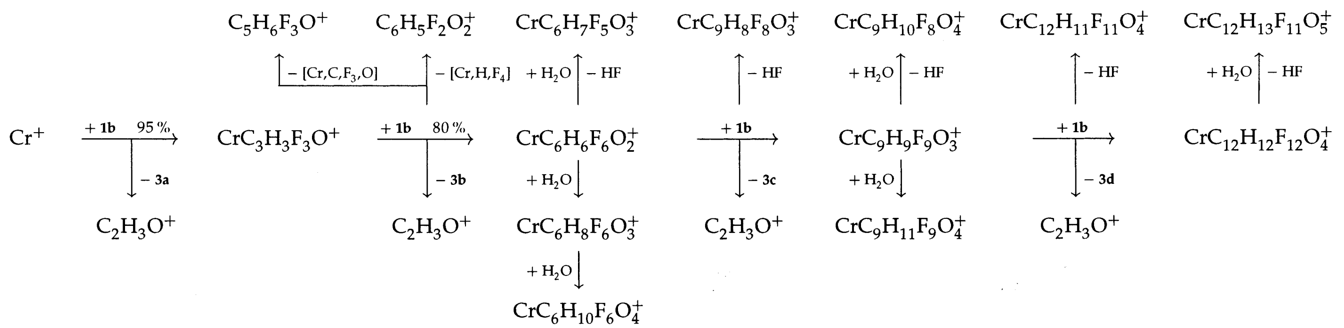


Figure 1. Major products generated from Cr^+, 1,1,1-trifluoroacetone ($C_3H_3F_3O$, **1b**), and background water. Only major reaction pathways are shown. For the chemical formulas of compounds **3a**−**d**, see text. For the first two association reactions, the respective branching ratios are given.

Results and Discussion

All experiments were carried out under high-vacuum conditions in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. While complexation of the chromium cation by up to four ligands is common among the investigated species, the dichotomy between complexation and follow-up reactions (hydrolysis and HF loss) observed for hexafluoroacetone no longer applies. In contrast, C−H, C−C, and C−F bond activations are observed as soon as associations of chromium cations and their neutral reaction partners take place.

Consequently, we present our results according to the respective substrate, pointing out features and trends when appropriate. In addition to investigating the chromium cations' reactions with **1a**−**g**, certain organochromium cations were mass-selected and exposed to well-defined pressures of water; the results are given in the text and incorporated into Table 3. However, major reactions with background water and products arising from them are included in the reaction schemes for the purpose of completeness, without being quantitatively analyzed. Prior to presenting the results, we briefly introduce the compounds' ID numbering. Following eq 1, reactants are abbreviated as **1** and monoadduct complexes as **2**. Neutral organochromium compounds formed concomitantly with acetyl cation generation in reactions with 1,1,1-trifluoroacetone (**1b**) are denoted as **3**. Intermediates generated from monofluoroacetone (**1c**) whose structures are discussed in some more detail (**4**) complete the list of abbreviations. In all cases, lower case letters indicate particular compounds.

$$Cr^+ + \underset{\mathbf{1}}{R^1COR^2} \rightarrow \underset{\mathbf{2}}{R^1COR^2Cr^+} \qquad (1)$$

1,1,1-Trifluoroacetone (1b). With branching ratios of 95% and 80% for the first and second association reactions, respectively, association dominates. For ternary and quaternary products, association keeps dominating, but branching ratios could not be determined due to the numerous reactions involving an unknown amount of background water present. Thus, a quantitative discussion of the complex reaction scheme (Figure 1, showing only major reaction pathways) is not indicated. However, three features should be pointed out. (i) For the monoadduct, $CrC_3H_3F_3O^+$ (**2b**), no hydrolysis products were observed. (ii) With a total branching ratio of 18% among the secondary reactions, the generation of $C_5H_6F_3O^+$ and $C_6H_5F_2O^+$ from the monoadduct **2b** and neutral **1b** is observed, indicating the loss of neutral [Cr,C,F$_3$,O] and [Cr,H,F$_4$], respectively. (iii) As shown for mass-selected adduct complexes, α cleavage at the carbonyl group parallels each association step, thus yielding $C_2H_3O^+$ concomitant with loss of neutral [Cr,C,F$_3$] (**3a**), [Cr,C$_4$,H$_3$,F$_6$,O] (**3b**), [Cr,C$_7$,H$_6$,F$_9$,O$_2$] (**3c**), and [Cr,C$_{10}$,H$_9$,F$_{12}$,O$_3$] (**3d**), respectively. The importance of α cleavage decreases with increasing ligation of the chromium center.

With respect to the generation of hydrogen fluoride and its evaporation from the organochromium complexes, two different ways exist, as shown in Figure 1. (i) HF may be generated by F/OH exchange with water, as in e.g.

$$CrC_6H_6F_6O_2^+ \xrightarrow[-HF]{+H_2O} CrC_6H_7F_5O_3^+$$

This exchange reaction is known for C−F−HF bonds[1] as well as for their Cr−F counterparts[6] and shall be referred to later. (ii) HF may also be generated upon complexation of another molecule of **1b**. As HF generation was observed for additions to di- and triadducts only, as in, e.g.

$$CrC_6H_6F_6O_2^+ \xrightarrow[-HF]{+\mathbf{1b}} CrC_9H_8F_8O_3^+$$

we assume HF to be formed from different ligand molecules which are in close proximity to each other. Similar observations were made for pentafluorobenzaldehyde (see below).

To elucidate the atomic connectivity, we subjected certain product ions to collision-induced dissociation (CID) experiments (see the Experimental Section for details). CID of the triadduct $CrC_9H_9F_9O_3^+$ yielded two ionic products, the diadduct and the acetyl cation. The diadduct $CrC_6H_6F_6O_2^+$, in turn, gave rise to two ionic products, the monoadduct and the bare chromium cation; furthermore, traces of CrF^+ and the acetyl cation were observed. Finally, the monoadduct $CrC_3H_3F_3O^+$ (**2b**) yielded two ionic products, Cr^+ and small amounts of CrF^+. Thus, one can safely assume the higher adducts to possess one or more molecules of **1b**, which are intact as far as the carbon skeleton is concerned. Nonetheless, the question of Cr^+ insertion into a C−F bond during the first association reaction remains. However, the small amount of CrF^+ generated in a CID experiment of $CrC_3H_3F_3O^+$ indicates that this insertion possesses only minor, if any, significance. Otherwise, one would expect a significantly larger yield of CrF^+ based on BDE(Cr^+−F) = 71.5 ± 7.3 kcal mol^{-1} [4] and the much

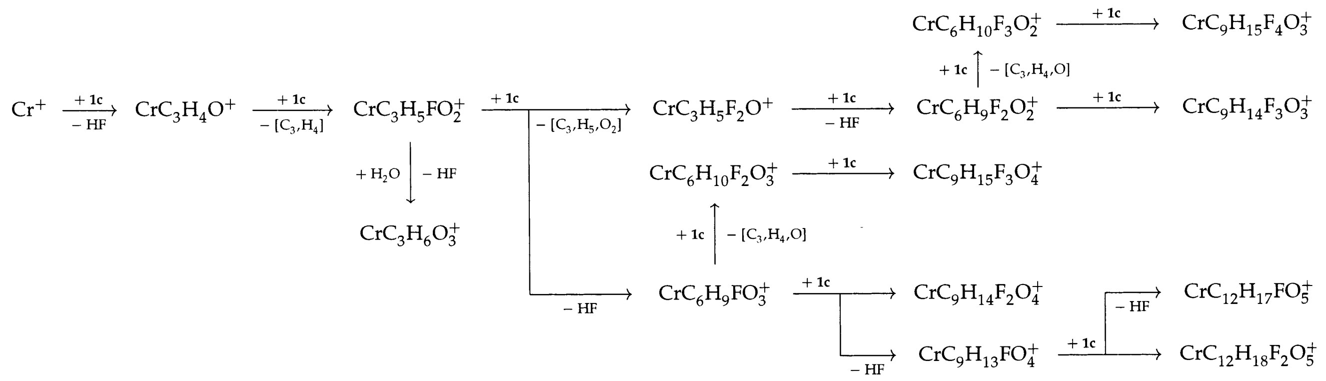
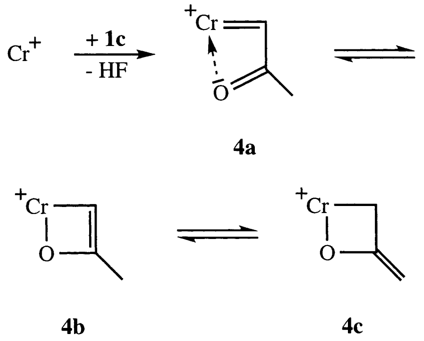


Figure 2. Major products generated from Cr^+, monofluoroacetone (C_3H_5FO, **1c**), and background water. The acetyl cation, $C_2H_3O^+$, which was observed in traces only, is not shown in the scheme.

smaller BDE($Cr^+{-}CR_3$) = 30.6 ± 1.2 kcal mol^{-1} ($CR_3 = C_2H_5$[24]). Consequently, we attribute the F/OH exchange mentioned above to hydrolytic cleavage of a C−F bond and not to that of an intermediary Cr−F bond.

Exposing mass-selected adduct ions to water showed F/OH exchange to occur with reaction efficiencies ϕ (see the Experimental Section for definition) of <0.3%, 7%, and 6% for the mono-, di-, and triadducts, respectively, whereas for these substrates organic ligand/water exchanges were found to proceed with efficiencies of 3%, 5%, and 16%, respectively. Thus, with the exception of $CrC_6H_6F_6O_2^+$, ligand exchange is more efficient than C−F bond hydrolysis. This ligand exchange, again, favors the complexation hypothesis discussed for the decomposition experiments over its possible bond-insertion counterpart. In addition to exchange reactions, simple water addition to mono-, di-, and triadducts was observed, as shown in Figure 1. Under the pressure regime investigated, the chromium cation appears to be limited to 4-fold complexation: addition of two water molecules was observed for the diadduct, whereas only one water molecule was complexed by the triaadduct and none by the tetraadduct.

Monofluoroacetone (1c). The monoadduct $CrC_3H_5FO^+$ (**2c**) could not be detected during the kinetic investigation. Instead, $CrC_3H_4O^+$ was the first product ion to be observed, thus indicating loss of neutral HF from the collision complex of Cr^+ and C_3H_5FO (**1c**). $CrC_3H_4O^+$, in turn, reacts with **1c** to yield $CrC_3H_5FO_2^+$ as the exclusive ionic product. This latter reaction needs to be commented upon, because the formal transfer of [H,F,O] from **1c** onto $CrC_3H_4O^+$ is rather unexpected. Our interpretation relies on a 1,1-elimination of HF during the formation of $CrC_3H_4O^+$ (**4a**), as sketched in Figure 3. At this point, however, we wish to address the reaction sequence summarized in Figure 2. While simple substrate addition to $CrC_3H_5FO_2^+$ was, again, not observed in this ion−molecule reaction, 90% of the reactant cations follow the HF-abstraction channel. The other channel corresponds to a formal O/F exchange, interpreted as concurrent addition of C_3H_5FO (**1c**) and loss of [C_3,H_5,O_2]. Later in the reaction sequence, substrate addition concomitant with HF loss accounts for numerous reactions, whereas F/OH exchange upon reaction with background water was observed for $CrC_3H_5FO_2^+$ only. Accordingly, exposure of mass-selected organochromium complexes toward water revealed that only $CrC_3H_5FO_2^+$ undergoes significant F/OH exchange (ϕ = 17%), whereas $CrC_6H_9FO_3^+$, $CrC_6H_{10}F_2O_3^+$, $CrC_9H_{13}FO_4^+$, and $CrC_{12}H_{17}FO_4^+$ are essentially unreactive (ϕ < 0.2%).



4a

4b **4c**

Figure 3. Possible generation and interconversion of species $CrC_3H_4O^+$.

A CID experiment of $CrC_3H_4O^+$ yielded comparable amounts of Cr^+ and CrO^+. As for the formal [H,F,O] transfer mentioned above, Figure 3 provides a reasonable explanation. In a 1,1-elimination reaction of HF that is unique for the substrates investigated in this study (see also the discussion of the aliphatic ketones' primary reaction rates below), we postulate the carbene **4a** to be formed. The dative O→Cr^+ bond might initiate the formation of the chromaoxacyclobutene **4b** and the chromaoxacyclobutane **4c**. From these three structures, the above-mentioned generation of both Cr^+ and CrO^+ in a CID experiment is plausible. Furthermore, the generation of $CrC_3H_5FO_2^+$ from $CrC_3H_4O^+$ and C_3H_5FO (**1c**) may be explained by concurrent loss of [C_3,H_4] from **4b** or **4c** and coordination of **1c**.

A CID experiment of the formally monooxygenated monoadduct $CrC_3H_5FO_2^+$ gave rise to $C_2H_3O^+$, Cr^+, CrF^+, $CrCH_2FO^+$, and $CrC_2H_2FO^+$. Consequently, it appears that the Cr−O unit may act as an oxidizing agent to the organic ligand as indicated by (i) the missing generation of CrO^+ upon decomposition of $CrC_3H_5FO^+$ and (ii) the loss of [C_3,H_5,O_2] from the collision complex of $CrC_3H_5FO_2^+$ and $CrC_3H_5FO^+$ (**1c**), as shown in Figure 2. On the other hand, CID fragment ions such as $C_2H_3O^+$ and $CrC_2H_2FO^+$ (loss of [C,H_3,O] from $CrC_3H_5FO_2^+$) indicate a collision-induced cleavage of the organic ligand, whose intraligand bonds have been weakened by coordination to the cation. The

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Table 2. Primary Reactions of Cr^+ with Acetones 1a−d[a]

	k_{exp}	θ	μ_D	α	R	PA[25]
1a[b]	0.39	3.6	0.395[45]	7.51	2.59[43]	159.3
1b	0.40	2.4	1.63	6.9	2.55	177.1
1c	7.3	30	2.47	6.5	2.52	190.0
1d	0.16	0.54	2.88[42]	6.39[42]	2.50[43]	193.9

[a] Rate constants k are given in 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. For the definition of reaction efficiencies ϕ (given in percent), see the Experimental Section. The parameters μ_D, α, and R are estimates of this work unless otherwise noted. Dipole moments (μ_D) are given in D and polarizabilities (α) in 10^{-24} cm^3. Relative ion gauge sensitivities (R) are dimensionless, and proton affinities (PA) are given in kcal mol^{-1}. [b] Taken from ref 1.

formally monofluorinated monoadduct $CrC_3H_5F_2O^+$ could not be isolated in concentrations sufficient for a CID experiment. For the formally monooxygenated diadduct $CrC_6H_{10}F_2O_3^+$, the cations $C_2H_3O^+$, CrF^+, and $CrCH_2FO^+$ and the monooxygenated monoadduct $CrC_3H_5FO_2^+$ dominate the CID product spectrum, with small amounts of Cr^+, $CrC_2H_3FO^+$, $CrC_2H_5FO^+$, and the HF-deprived monooxygenated diadduct $CrC_6H_9FO_3^+$ being observed as well. Again, one is safe to assume the α bonds of the ligand molecule to be weakened significantly by coordination to the chromium cation.

A unique feature in the reaction sequence is the formal HF addition as in, e.g., $CrC_6H_9FO_3^+ \rightarrow CrC_6H_{10}F_2O_3^+$. We wish to stress the point of *formal* addition, because hydrogen fluoride seems unlikely to coordinate the chromium cation after its elimination from C_3H_5FO in the encounter complex with the ligated chromium cation. HF is, by far, a too weakly coordinating ligand to act in such a way. Rather, a substitution of $[C_3,H_4,O]$ by C_3H_5FO is likely. The generation and loss of $[C_3,H_4]$ has already been addressed, and the generation of $[C_3,H_4,O]$ may be explained by the abovementioned oxidation capability of the Cr−O unit.

Primary Reactions of the Aliphatic Ketones. Systematic investigations revealed an inverse linear relationship between the number of fluorine substituents in acetones and their proton affinities.[25] Thus, we felt prompted to search for analogous regularities in the reaction efficiencies of eq 1 and exposed Cr^+ also to acetone (**1d**). At the pressure regime investigated, straightforward formation of mono- and diadducts was observed to proceed with reaction efficiencies of 0.54% and 6.3%, respectively, while only traces of tri- and tetraadducts could be detected. The rates and reaction efficiencies are summarized in Table 2.

Even considering the uncertainties in the calculation of the reaction efficiency ϕ originating from the estimation of the gas-phase kinetic parameters μ_D, α, and R, one is safe to say that monofluoroacetone (**1c**) cannot follow the other substrates' reaction mechanism. For these other compounds, one may postulate a roughly linear increase of ϕ with the number of fluorine atoms present in them. To be more cautious about the estimated parameters, the reaction efficiencies are of the same order of magnitude. Additionally hampering an interpretation is the fact that no information about the sites of initial complexation (carbonyl group vs fluorine atom or atoms) and their dependence on the degree of fluorination was available. Consequently, we address the differing behavior of **1c** only.

As already evident from a comparison of the primary reactions' stoichiometry, monofluoroacetone is the only substrate generating neutral HF. At this point, the generally missing reactivity of thermalized chromium cations[2−6] caused by their d^5 electronic configuration comes into play: evaporating a neutral species from the collision complex allows for an efficient release of the complexation energy. All other chromium cation−aliphatic substrate complexes have to dispose or dissipate that complexation energy by less efficient ways, e.g., IR photon emission. Consequently, the higher efficiency of the chromium cations' reaction with monofluoroacetone compared to reactions with the other aliphatic substrates is rationalized straightforwardly by a different reaction mechanism, and less feasible explanations shall not be discussed here.

$CrC_3HF_3O_3^+$. In our initial study,[1] we found the chromium cation−hexafluoroacetone monoadduct $CrC_3F_6O^+$ to undergo hydrolysis of at least three C−F bonds, yielding, inter alia, $CrC_3HF_3O_3^+$ as a key intermediate. On the basis of CID experiments, we assumed the latter to possess the structure of a trifluoropyruvic acid−chromium cation chelate (trifluoropyruvic acid = $CF_3COCOOH$). In this study, we wanted to probe this assumption by investigating an independently generated chromium cation−trifluoropyruvic acid complex. In our mass spectrometer, using the acid itself is impractical due to its unfavorable volatility (mp 119.5−122.5 °C[26]). Instead, we employed its ethyl ester, $CF_3COCOOC_2H_5$ (**1e**; bp 89 °C/p° [27]). Besides the intended McLafferty-type rearrangement concomitant with formation of $CrC_3HF_3O_3^+$, a variety of products was observed (see the Supporting Information for details). $CrC_3HF_3O_3^+$, however, was generated in good yields, thus allowing for comparison with the hydrolysis product obtained previously[1] from Cr^+, **1a**, and H_2O.

CID experiments of $CrC_3HF_3O_3^+$ generated in this study showed (i) the rise of Cr^+, CrF^+, CrF_2^+, and the hydrolysis products of the last two cations (attributed to collisions with background water in contrast to those with argon[1] and/or the hydrolysis of the corresponding chromium fluorides with background water[6]) but not of any organochromium cations and (ii) a sharp decrease of the $CrC_3HF_3O_3^+$ signal intensity compared to little increase of its fragment ions' signals. Thus, the experimental results for the hexafluoroacetone hydrolysis intermediate[1] $CrC_3HF_3O_3^+$ and those for the McLafferty-type product $CrC_3HF_3O_3^+$ are in both qualitative and quantitative agreement, corroborating our assumption about that ion's structure. Consequently, $CrC_3HF_3O_3^+$ is taken as a chelate of trifluoropyruvic acid and Cr^+ in which both the trifluoromethyl and the carboxyl groups bind to the chromium cation, whereas the central carbonyl group does not interact due to geometric constraint.

Pentafluorobenzaldehyde (1f). The primary reactions of pentafluorobenzaldehyde with Cr^+ are much more diverse than those of the aliphatic compounds. As shown in Figure 4, association (branching ratio 80%)

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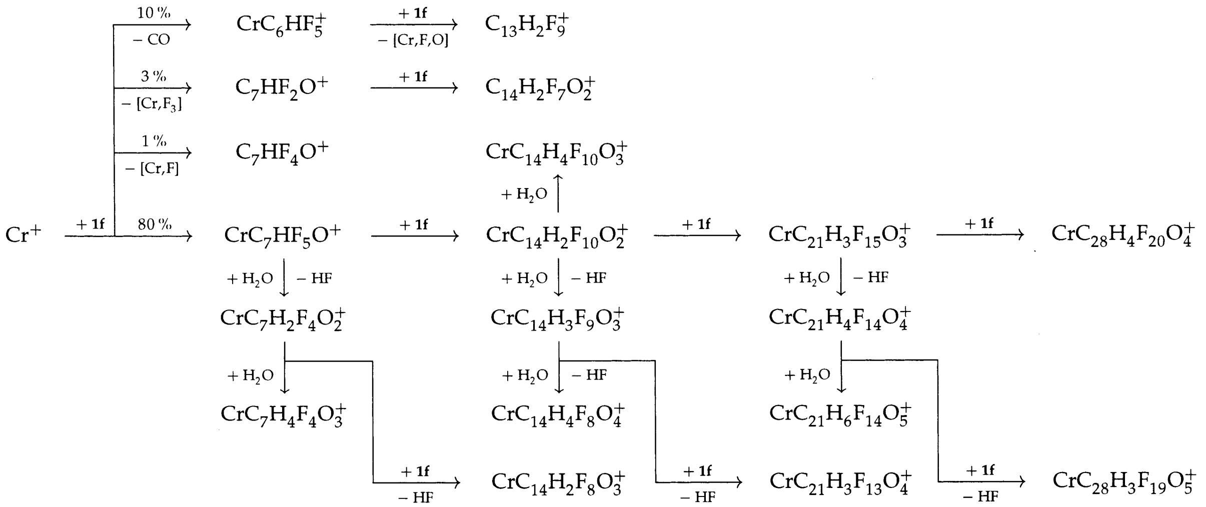

Figure 4. Major products generated from Cr^+, pentafluorobenzaldehyde (C_7HF_5O, **1f**), and background water.

dominates the reaction sequence. Decarbonylation accounts for about 10% of the chromium cations' consumption. Interestingly, the decarbonylation product $CrC_6HF_5^+$ loses [Cr,F,O] when reacting with another molecule of the aldehyde, thus indicating the operation of a carbon–carbon coupling process. Another feature to be pointed out is the abstraction of one or three fluorine atoms (1% and 3%, respectively) from the aromatic core accompanied by electron transfer from the aromatic onto the chromium cation. Comparable defluorination has also been observed for lanthanoid cations[21] and Nb^+ [28] but does not include electron transfer in these systems.

Other features of the system shall be commented upon briefly. (i) Hydrolysis (F/OH exchange) with background water was observed for the mono-, di-, and triadducts but not for the tetraadduct. (ii) Additions of **1f** to all of $CrC_7H_2F_4O_2^+$, $CrC_{14}H_3F_9O_3^+$, and $CrC_{21}H_4F_{14}O_4^+$ proceed with loss of neutral HF, thus indicating an intraligand HF abstraction already noticed for monofluoroacetone. (iii) Addition of background water was observed for $CrC_7H_2F_4O_2^+$, $CrC_{14}H_3F_9O_3^+$, and $CrC_{21}H_4F_{14}O_4^+$ but not analyzed in detail.

Collision-induced dissociation of the diadduct cation $CrC_{14}H_2F_{10}O_2^+$ gave rise to the monoadduct cation $CrC_7HF_5O^+$ and bare Cr^+. The monoadduct cation, in turn, decomposed upon CID predominantly into Cr^+, CrF^+, and $C_6HF_2^+$ (concomitant with formation of $[Cr,C,F_3,O]$, which is thought, on entropic grounds, to consist of CrF_3 and CO). Less abundant ions were $C_6HF_3^+$, $C_7HF_2O^+$, $C_7HF_3O^+$, and $C_7HF_4O^+$. On the basis of this general absence of fragments containing both chromium and ligand fragments other than fluorine atoms, we rule out insertion of the chromium cation into one of the ligand's C–F, C–C, or C–H bonds during association. In contrast, we assume the above-mentioned CrF_3 to be generated upon energy take-in of the monoadduct by sequential unzipping of three fluorine atoms from the benzene ring similar to the behavior of lanthanoid cations[21] and Nb^+.[28] Similar arguments apply to the observation of CrF^+.

Quantitative determination of the monoadduct hydrolysis revealed a reaction efficiency of 16%. The other adducts appear to undergo similar exchange reactions as well (see Figure 4) but were not mass-selected and exposed to water, due to their comparatively low concentrations. Apparently, the hydrolysis rate is highest for the monoadduct and decreases with increasing complexation.

2,3,4,5,6-Pentafluoroacetophenone (1g). In comparison to pentafluorobenzaldehyde (**1f**), the corresponding methyl ketone **1g** shows an even greater variety for the primary reactions with Cr^+, as shown in Figure 5. The decarbonylation already observed for pentafluorobenzaldehyde is found for the corresponding methyl ketone as well. Another similarity is the abstraction of up to three fluorine atoms from the aromatic core accompanied by electron transfer from the aromatic onto the chromium cation. In more detail, four processes yield more than 90% of the primary products. (i) Similar to **1f**, association constitutes the largest fraction of primary reactions with **1g** (branching ratio 32%). (ii) With a branching ratio of 26%, formation and loss of neutral HF upon complexation is second in importance among the reaction channels. (iii) Formation of $C_8H_3F_3O^+$ concomitant with loss of neutral CrF_2 accounts for 25% of the primary reactions and yields, most likely by some rearrangment, a stable and unreactive product ion. (iv) With a branching ratio of 9%, $C_8H_3F_4^+$ is formed, indicating the loss of neutral [Cr,F,O]. In addition, $C_7H_3F_2^+$ and $C_7H_3F_3^+$ were detected as primary products. Summing up these reactions and those just numbered as (iii) and (iv), a total branching ratio of 37% for fluoride anion transfer onto the chromium cation was observed.

Secondary and tertiary reactions are as follows. (i) $CrC_8H_2F_4O^+$, formed from Cr^+ and the ketone losing neutral HF, adds one molecule of the neutral, thus yielding $CrC_{16}H_5F_9O_2^+$, or undergoes hydrolysis of one C–F bond. (ii) The association product ion, $CrC_8H_3F_5O^+$, undergoes both further substrate addition and hydrolysis of one C–F bond. In a side reaction (branching ratio <6%), neutral chromium fluorides are generated. (iii) Notably, no tetraadduct, $CrC_{32}H_{12}F_{20}O_4^+$, was observed. In contrast, the HF-deprived tetraadducct $CrC_{32}H_{11}F_{19}O_4^+$ was found to be formed from $CrC_{24}H_8F_{14}O_3^+$.

A CID experiment of the monoadduct $CrC_8H_3F_5O^+$ did not yield a major product but a mixture of $C_2H_3O^+$, Cr^+,

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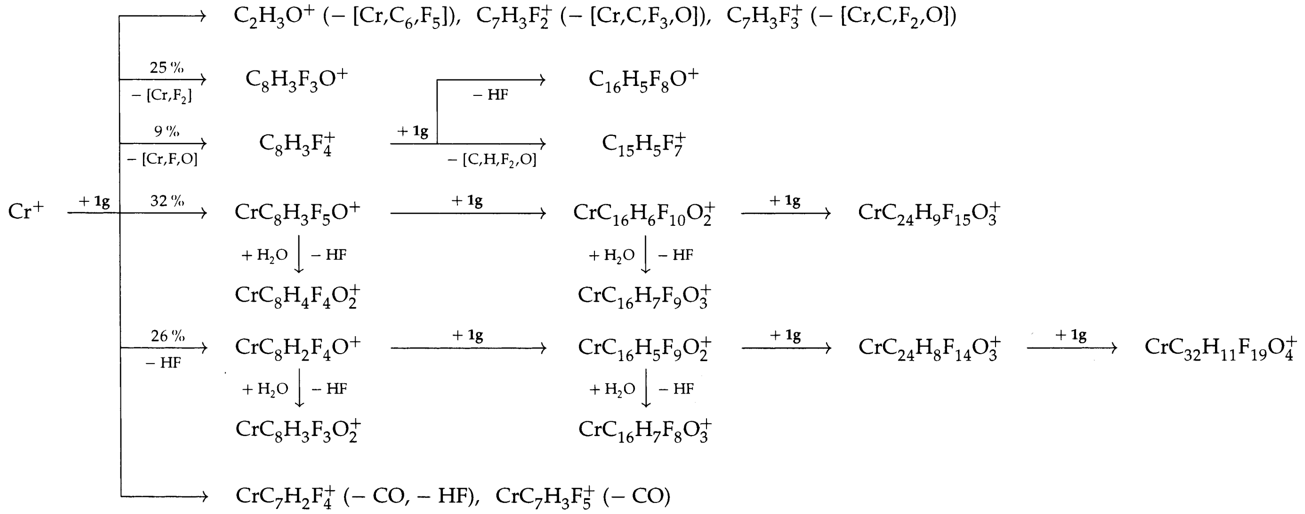

Figure 5. Major products generated from Cr^+, 2,3,4,5,6-pentafluoroacetophenone ($C_8H_3F_5O$, **1g**), and background water. Primary products accounting for less than 5% of the total ion concentration are summarized; reactions consuming them are not specified.

CrF^+, $C_7H_2F^+$, $C_7H_3F_2^+$, $C_7H_2F_2^+$, $C_7H_3F_3^+$, $C_8H_3F_3O^+$, and $C_8H_3F_4^+$. Notably, the last three ions as well as the acetyl cation were observed also in the kinetic investigation. Thus, the weakening of the same intraligand bonds appears to occur during both reaction with the chromium cation and the CID experiment.

Hydrolysis of mass-selected mono- and diadducts revealed F/OH exchange efficiencies of 10% and 2%, respectively, thus again showing the inverse relation between the degree of complexation and the chromium cation's ability to promote hydrolytic C−F bond cleavage.

Reactions of the Aromatic Substrates. In comparison to the aliphatic compounds investigated in this study, the reactions of the aromatic substrates pentafluorobenzaldehyde and 2,3,4,5,6-pentafluoroacetophenone with Cr^+ are remarkably diverse as far as the first reaction step is concerned. For both of the aromatic substrates, association is the most important among the primary reactions. Decarbonylation is a common feature but is more important for the aldehyde. In contrast, abstraction of fluorine anions from the aromatic ring is much more pronounced for the ketone. Complexation concomitant with HF loss, observed for secondary and tertiary reactions of monofluoroacetone and pentafluorobenzaldehyde, occurs for primary reactions of 2,3,4,5,6-pentafluoroacetophenone only. Thus, this indicates the need for acidic protons in order to lose HF intramolecularly from one ligand molecule.

In contrast to the aliphatic compounds, reaction rates and efficiencies could not be determined for their aromatic counterparts due to the complete lack of reliable data concerning the gas-phase kinetic parameters: i.e., dipole moment μ_D, polarizability α, and relative ion gauge sensitivity R. These parameters are essential for the determination of reaction rates and efficiencies, and guessing them was deemed not useful.

Conclusion

In the study presented here, we expanded the concept of C−F bond activation by coordination of a chromium cation in the gas phase.[1] C−F bond hydrolysis originally found for hexafluoroacetone was observed for all fluorinated substrates investigated here, namely 1,1,1-trifluoroacetone, monofluoroacetone, pentafluorobenzaldehyde, and 2,3,4,5,6-pentafluoroacetophenone. With the exception of 1,1,1-trifluoroacetone, C−F bond hydrolysis becomes less efficient with increasing complexation. To explain this behavior, we refer to the electron density at the cationic chromium center which, obviously, increases with the number of coordinating ligands. This increasing electron density, in turn, corresponds to the decreasing electron withdrawal from a particular ligand or bond, respectively, thus activating the particular bond to a lesser extent. In this context, it shall also be noted that the aromatic substrates investigated here undergo only one F/OH exchange, despite the presence of five fluorine substituents at their aromatic cores.

In contrast to hexafluoroacetone, a variety of reactions accompanying the complexation is observed for the substrates investigated here and attributed to the structurally more diverse substrate molecules. One of the newly introduced reaction pathways is HF abstraction from ligand molecules, occurring both intramolecularly and intermolecularly. However, intramolecular HF abstraction was unambiguously observed for monofluoroacetone only where it occurs as a 1,1-elimination. When 1,1-HF elimination is impossible, interligand HF formation may occur intermolecularly, as observed for 1,1,1-trifluoroacetone and pentafluorobenzaldehyde. 2,3,4,5,6-Pentafluoroacetophenone, however, loses HF in the first association reaction without being capable of undergoing 1,1-elimination. Most likely, the interplay of the highly acidic methyl protons and the cation-mediated activation of the aromatic C−F bonds gives rise to this reaction channel.

Competing with HF loss, α cleavage is a versatile reaction pathway, leaving behind a fluorine-rich neutral organochromium fragment and—preferably—the acetyl cation. This charge distribution upon fragmentation of the encounter complex is in agreement with chemical intuition. For aromatic reaction partners, the α cleavage may cause loss of neutral CO, with the organic fragment remaining coordinated to the chromium cation. Finally,

Table 3. Diversity of C−F Bond Activation Reactions[a−c]

	br					ϕ	
	I-Add	I-HF	II-HF	I-CrF$_n$	II-CrF$_n$	I-F/OH	II-F/OH
1a[d]	100	n.a.	n.a.	−	n.o.	37	n.o.
1b	95	−	−	−	18	<0.3	7
1c[e]	−	100	90	−	−	17	<0.2
1f	80	−	−	4	−	16	n.d.
1g	32	26	−	37[f]	<6	10	2

[a] For a systematic description, the different reaction types were abbreviated as follows. (i) "I" and "II" denote the mono- and diadducts, respectively. (ii) "Add" stands for simple adduct formation, "F/OH" indicates hydrolytic cleavage of a C−F bond, and "HF" symbolizes loss of that neutral upon formation of the respective mono- or diadduct. Similarily, "CrFn" represents loss of [Cr,Fn] upon the respective adduct formation. [b] All numbers are given in percent. They are either branching ratios (br) or reaction efficiencies (ϕ). For definitions, see the Experimental Section. [c] Abbreviations: n.a., not applicable; n.d., not determined; n.o., reactant cation not observed, −, not observed. [d] Taken from ref 1. [e] Data for F/OH exchange apply to the monooxygenated mono- and diadducts. [f] Includes 9% formation of [Cr,F,O] (see Figure 5).

C−F bond activation concomitant with fluorine atom/fluoride anion transfer onto the chromium cation may accompany complexation, as observed for 1,1,1-trifluoroacetone and the aromatic substrates pentafluorobenzaldehyde and 2,3,4,5,6-pentafluoroacetophenone. At least for the last two substrates, we favor the "sequential zipping" of fluorine atoms from the aromatic ring already proposed for Nb^+/tetrafluorobenzene isomers[28] and earlier observed for lanthanoide cations reacting with hexafluorobenzene.[21] Table 3 summarizes the various C−F bond activating reactions investigated in this study.

To summarize, Cr^+-assisted hydrolytic C−F bond activation in the gas phase is not limited to hexafluoroacetone but is most efficient for this neutral: For hexafluoroacetone, up to four C−F bonds are hydrolyzed, whereas for each of the substrates investigated here only one C−F bond per ligand molecule is involved in this reaction. On the other hand, ways of bond activation not observed for monofluoroacetone occur only for the substrates investigated here. Thus, we wish to point out that the different ways of activating C−F bonds open a 3-fold perspective of bond activation, namely intramolecular HF abstraction, F/OH exchange upon reaction with water, and multiple fluorine atom abstraction from pentafluorophenyl groups. Consequently, further investigation in order to favor one or the other way of metal cation induced C−F bond activation is indicated.

Experimental Section

Note of Caution. Monofluoroacetone (**1c**) is highly toxic and should be handled with extreme care. In vivo, **1c** is oxidized to monofluoroacetate,[29] which is eventually converted into fluorocitrate.[30] The latter blocks aconitase, a key enzyme in the citric acid (Krebs) cycle.[30]

Chemicals. Metallic chromium and gaseous hexafluoroacetone (**1a**, Fluorochem, anhydrous, 97%) were used as purchased. 1,1,1-Trifluoroacetone (**1b**, Acros, 98+%), monofluoroacetone (**1c**, Aldrich, 99%), acetone (**1d**, Aldrich, HPLC grade, 99.9+%), ethyl trifluoropyruvate (**1e**, Aldrich, 97%), pentafluorobenzaldehyde (**1f**, Aldrich, 98%), 2,3,4,5,6-pentafluoroacetophenone (**1g**, Aldrich, 97%), and tap water are all liquids and were used without further purification with the exception of degassing by repeated freeze−evacuate−thaw cycles.

Mass Spectrometer. All experiments were performed with a Bruker Spectrospin CMS-47X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, whose setup and operation have been described previously.[31,32] In brief, chromium monocations were generated from targets of pure chromium by laser desorption/laser ionization[33,34] in the external ion source of the spectrometer using a Nd:YAG laser (Spectron Systems, λ_{max} 1064 nm). The chromium ions were extracted from the source and transferred into the analyzer cell via a system of electrostatic potentials. Next, the most abundant isotope ^{52}Cr (relative abundance 83.8%[35]) was mass-selected using FERETS,[36] a computer-controlled ion-ejection protocol that combines frequency sweeps and single-frequency pulses to optimize resonant excitation and ejection of all unwanted ions. Chromium cations were thermalized by multiple collisions with the leaked-in substrates themselves. Thermalization was assumed to be complete on the basis of a purely exponential decay of the chromium cations' concentrations during the kinetic measurements. Reactant gases were admitted to the cell via a leak valve at a constant pressure measured by a calibrated[37] BALZERS IMR 132/IMG 070 ion gauge. The background pressure in the reaction cell was 0.2×10^{-8} mbar. To investigate the adduct formations (eq 1), $^{52}Cr^+$ cations were exposed to the leaked-in reaction partners. For the hydrolysis reactions, the complexes of interest were generated by pulsing in the respective neutral after mass selection of the $^{52}Cr^+$ cations, mass-selected, and exposed to leaked-in water.

Analysis of Experimental Results. Elemental compositions of ions were established by high-resolution mass spectrometry. Reaction mechanisms were derived from kinetic arguments, isolation of intermediates, and observation of their respective product ions and complementary double-resonance experiments.[38] Rate constants are given in units of cm^3 molecule^{-1} s^{-1} and were determined using a computer program that determines rate constants of consecutive and parallel reactions based on a flexible kinetic model and experimentally observed ion intensities.[39] The reported reaction efficiencies ϕ are given as fractions of the measured bimolecular rate constants and the gas-kinetic collision rates according to the capture theory:[40,41] $\phi = k_{exp}/k_{cap}$. Parameters for aliphatic substrates (see Table 2) not available from the literature were estimated on the basis of known anchor values and trends for related compounds. The parameters used for water were dipole moment 1.854 D,[42] polarizability 1.45×10^{-24} cm^3,[42] and relative ion gauge sensitivity 0.97.[43] The absolute error of the rate constants is estimated to be in the range of ±30%, while the ratios of the rate constants are more precise (±10%).[37] For

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the aromatic substrates, no attempts were undertaken to estimate the completely unknown gas-kinetic parameters. Instead of reaction efficiencies, branching ratios (i.e., the fraction of products generated in a particular reaction) are given in Table 3.

To elucidate the connectivity of ionic species, collision-induced dissociation (CID) experiments[44] were undertaken. In a CID experiment, the ion of interest is subjected to a pressure of typically $(5-10) \times 10^{-8}$ mbar of a nonreacting gas (typically a noble gas; here argon) after having been kinetically activated by a low-energy radio frequency pulse. Observed fragmentation reveals information about the ion's connectivity.

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Supporting Information Available: Figure 6, giving major products generated from Cr^+ and ethyl trifluoropyruvate. This material is available free of charge via the Internet at http://pubs.acs.org.

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