Gas-Phase Reactions of Chromium and Chromium Fluoride Cations CrF_n^+ ($n = 0-4$) with Water and Nitrous Oxide

Ulf Mazurek,[a] Detlef Schröder,[a] and Helmut Schwarz*[a]

Dedicated, with admiration and in friendship, to Fulvio Cacace

Keywords: Chromium / Chromium fluorides / Hydrolysis / Gas-phase ion chemistry / Thermochemistry

The reactions of atomic chromium and chromium fluoride monocations CrF_n^+ (n = 0–4) with water and nitrous oxide were investigated by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. Besides slow condensation, Cr^+ is unreactive towards water, whereas all chromium fluoride cations undergo at least one Cr–F bond hydrolysis yielding the corresponding hydroxide concomitant with loss of neutral HF. While hydrolysis is complete for CrF^+ and CrF_2^+, proton transfer and HF losses compete with the hydrolysis of the second Cr–F bond in CrF_3^+ and CrF_4^+. Nevertheless, complete Cr–F bond hydrolysis is observed for the latter two cations as well. The results for the ion-molecule reactions with nitrous oxide are as follows: With the exception of CrF_3^+, which gives CrF_3O^+ in a good yield, all species investigated were found to be essentially unreactive towards N_2O. The ionisation energy of CrF_3O has been determined, $IE = 11.3 \pm 0.2$ eV. In addition, limits for the standard heats of formation of several chromium-containing cations have been derived.

Introduction

In previous studies, we investigated the formation of chromium and chromium fluoride monocations CrF_n^+ ($n = 0-4$) and their reactions with alkanes C_1 through C_4,[1] and phosphane.[2] The appearance of the species $Cr(OH)^+$, $CrF(OH)^+$, $Cr(OH)_2^+$, $CrF_2(OH)^+$, $CrF(OH)_2^+$, $Cr(OH)_3^+$ and CrF_3O^+ was detected, and attributed to the reactions of the chromium fluoride cations with water from the background of the mass spectrometer's high-vacuum system. As the presence of water is a widespread nuisance in mass spectrometry, we wanted to establish sound kinetic models for the reactions of chromium and chromium fluoride monocations with this neutral species. When investigating reactions of chromium and chromium fluoride cations with neutral species other than water, the kinetic models established here would allow for a more accurate description of the reaction systems as the contributions of background water could then be accounted for quantitatively.

In addition, we wanted to establish a firm basis for the formation of CrF_3O^+ hitherto attributed to a reaction of CrF_4^+ with water,[1] but not fitting into the general Cr−F bond hydrolysis scheme:

$$CrF_n^+ \xrightarrow[-HF]{+H_2O} CrF_{n-1}(OH)^+$$

Furthermore, we intended to expand our study to the generation of other chromium oxyfluoride cations and to investigate their gas-phase chemical properties.

Results and Discussion

Reactions with Water

The reactions of the CrF_n^+/H_2O systems are summarised in Figure 1. Species given in square brackets in this comprehensive reaction scheme were not observed experimentally but postulated, (i) as necessary intermediates in an observed reaction sequence [e.g., $CrF_2(OH)_2^+$] or, (ii) as products of reactions assumed to be reasonable by analogy to observed ones. A detailed discussion with regard to the parent ions CrF_n^+ ($n = 0-4$) follows below.

Cr^+

For argon-thermalised Cr^+ cations, only slow condensation yielding mono and di adducts was observed. However, for methane-thermalised Cr^+ cations, the di adduct $Cr(H_2O)_2^+$ was not detected. Consequently, this species is given in square brackets in Figure 1. Besides the water mono adduct $Cr(H_2O)^+$, a number of minor products that cannot be formed directly from Cr^+ and water [namely H_3O^+, CrO^+, $Cr(OH)^+$, CrO_2^+, and $Cr(OH)_2^+$] were observed. From these results, we draw the following conclusions: (i) Ground-state (^6S) bare chromium cations ($3d^5$) are essentially unreactive towards water. The only reaction ob-

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[a] Institut für Chemie, Technische Universität Berlin,
Straße des 17. Juni 135, 10623 Berlin, Germany
Fax: (internat.) + 49-30/314-21102
E-mail: Helmut.Schwarz@www.chem.tu-berlin.de

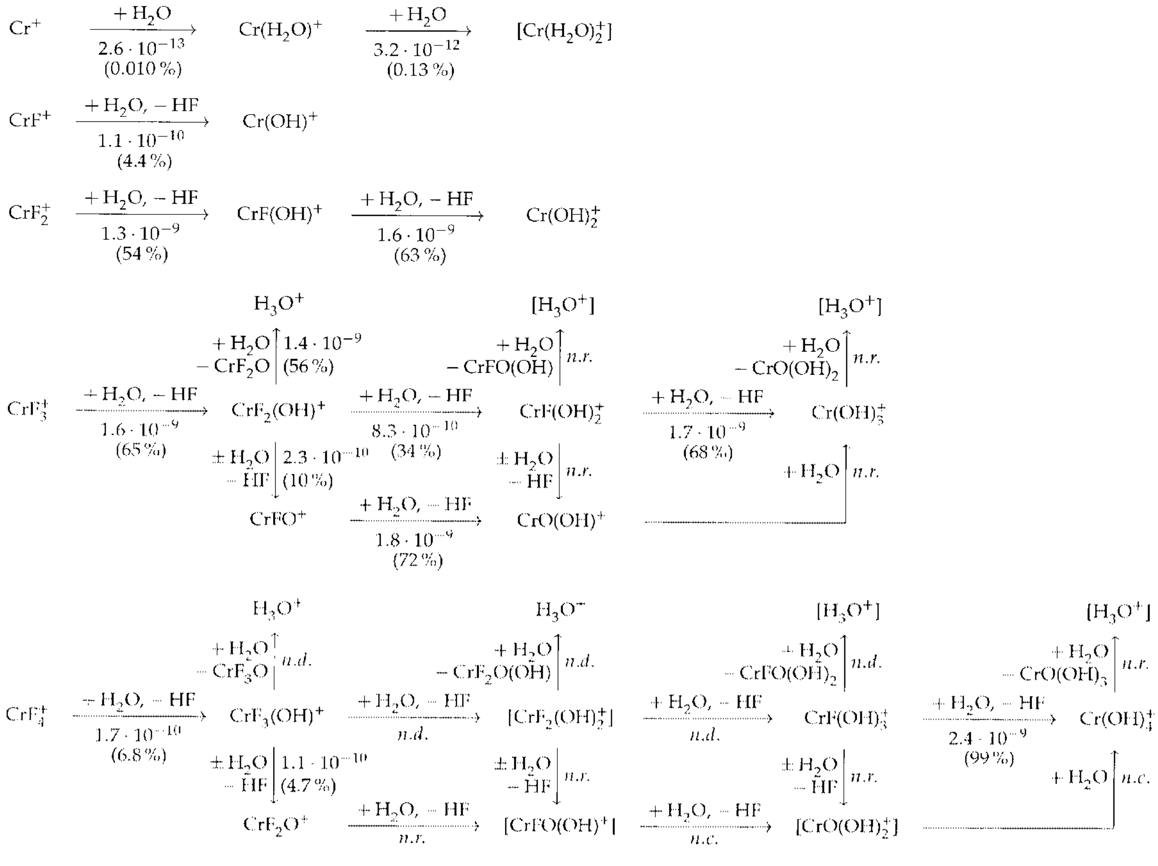

Figure 1. Reactions of CrF_n^+ (n = 0−4) with water; rate constants and reaction efficiencies φ (values in parentheses) are given as defined in the Exp. Sect.; for discussion, see text; abbreviations: *n.d.* = not determined (see text), *n.r.* = "no reactivity" indicating a reaction efficiency $\varphi < 0.05\%$, *n.c.* = not covered by this study because the reactant ion was not observed, see text

served is the slow mono adduct formation similar to that observed by Buckner et al. for the Cr^+/NH_3 system,[3] and by us for the CrF_n^+/PH_3 systems.[2] The failure of Cr^+ to activate O−H bonds parallels previous experimental findings for C−H[1,4] and N−H[3] bonds. (ii) Most probably, the condensation of ground-state Cr^+ by H_2O involves termolecular processes. In addition to water, prime candidates for third-body interactions are hydrocarbons and molecular oxygen present in the background of the mass spectrometer; the presence of the latter is supported by the formation of the cations CrO^+ and CrO_2^+. Interestingly, in a mass-spectrometric study of CrO_2^+ isomers, water was observed to catalyse the conversion of $Cr(O_2)^+$ to the chromyl cation.[5] Thus, the interplay between water and molecular oxygen is likely to exert a cooperative effect on the reactivity of Cr^+ cations. (iii) Based on this cooperative effect, we assume that the formation of $Cr(H_2O)_2^+$ from $Cr(H_2O)^+$ is outnumbered by reactions of the latter ion with O_2 rather than with H_2O. (v) The rate constants and reaction efficiencies, given in Figure 1, apply to argon-thermalised chromium cations. Due to the unknown influence of third-body interactions, they should be taken as upper limits of the effective bimolecular rate constants.

CrF^+

The only product of the reaction of CrF^+ with H_2O is $Cr(OH)^+$, corresponding to the loss of neutral HF, whose thermochemical stability may be considered as the driving force for the Cr−F bond hydrolysis. The reaction is rather inefficient compared with the corresponding reactions of CrF_2^+ and CrF_3^+ (see below).

CrF_2^+

In a reaction roughly twelve times as fast as that of CrF^+, CrF_2^+ reacts with water to form $CrF(OH)^+$ which, in turn, undergoes fast hydrolysis of the remaining Cr−F bond. Interestingly, the formal Cr^{III} species $CrF(OH)^+$ and $Cr(OH)_2^+$ do not undergo proton transfer to water, whereas several of their formal Cr^{IV} and Cr^{V} congeners (see below) do so.

CrF_3^+

CrF_3 reacts with water even faster than CrF_2^+, and undergoes facile hydrolysis of the first Cr−F bond. However, once $CrF_2(OH)^+$ has been formed, three different reaction channels exist as shown in Figure 1. First, $CrF_2(OH)^+$ may undergo further Cr−F bond hydrolysis, thus following the reaction scheme already observed for $CrF(OH)^+$. In addition, proton transfer from $CrF_2(OH)^+$ to water is facile, and the loss of HF yielding $CrFO^+$ is also observed. The latter reaction shall be discussed in more detail. At a first glance, HF loss from $CrF_2(OH)^+$ can proceed as a unimolecular reaction, thus apparently indicating that $CrF_2(OH)^+$ is a metastable ion. Otherwise, the activation energy needed to form a weakly binding HF ligand would have to be acquired by collision with another molecule. The actual observation of $CrF_2(OH)^+$ on the time scale of an FT-ICR experiment, however, implies that this cannot hold true. Limited to both a maximum of 10^3-10^4 ions for all species detected and a lower detection limit of 10^2 ions for *one* species,[6] the population of an ionic species is too small to be detected by an FT-ICR mass spectrum if that species undergoes unimolecular decay with rate constants of typically some 100 s^{-1}. Furthermore, the intramolecular formation of HF from two ligands pointing away from each other seems to be rather unlikely. For geometrically comparable cations, e.g. $HO-Fe^+-OH$[7−9] and $HO-V^+-OH$,[10] considerable energy barriers were determined for the 1,3-H shifts, and it is fair to assume comparable barriers to be associated with an unimolecular HF formation. By reference to the results for the iron and vanadium systems, we conclude that the loss of HF from $CrF_2(OH)^+$ proceeds as a water-mediated reaction as indicated in Figure 2.

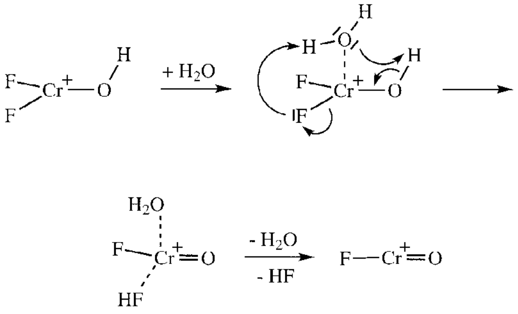

Figure 2. Conceptual illustration of water-mediated HF loss from $CrF_2(OH)^+$

It is suggested that water acts as a "proton shuttle" [11,12] in this reaction sequence, and that the intermediate is a metastable van-der-Waals complex of ionic $CrFO^+$, water, and HF, which looses both ligands easily. Notably, similar water-molecule participation has also been observed for the $Cr(O_2)^+$ cation,[5] the isomerisation of iron-coordinated cyclohexadienone to phenol,[13] and several metal-free systems.[14−16] While HF is known to be a weakly bound ligand and to "boil off" readily, the loss of H_2O from the intermediate complex can only be postulated from the observation of $CrFO^+$. The intermediate $CrFO^+\cdots H_2O$ cannot be distinguished from the long-lived cation $CrF(OH)_2^+$ by mass analysis only, because both cations have the same elemental composition.

At a first glance, the reaction mechanism depicted in Figure 2 may also explain the absence of the formal reaction $CrF(OH)^+ \rightarrow CrO^+ + HF$. If the O−Cr−F part of the $CrF(OH)^+$ cation was linear, the water molecule could no longer bridge the distance between the OH group and the fluoride ligand. However, based on its estimated endothermicity of at least 35 kcal mol^{-1}, this reaction can be ruled out a priori on thermochemical grounds.

In contrast to the variety of reactions observed for its predecessor $CrF_2(OH)^+$, ionic $CrF(OH)_2^+$ only undergoes hydrolysis of the remaining Cr−F bond. Both HF loss and proton transfer to water, as included in Figure 1, were ruled out on kinetic grounds. For an explanation of this different behaviour, we considered the electronic properties of $CrF(OH)_2^+$.

In a broader sense, the different effects of a fluorine atom and a hydroxy group on an adjacent atom shall be discussed with the help of Equation (1).

$$\begin{array}{lccccccccc} & CH_3OH & - & CH_2F^{\bullet} & \rightarrow & CH_2OH^{\bullet} & + & CH_3F \\ \Delta_f H^{\circ}_{298}\ (\text{kcal mol}^{-1})\text{:}^{[17]} & -48.2 \pm 0.1 & & -8 \pm 2 & & -6.2 \pm 1.5 & & -59 \end{array} \quad (1)$$

The overall reaction enthalpy of $\Delta_r H^{\circ}_{298} = -9 \pm 2.5$ kcal mol^{-1} indicates a comparable influence of the substituent X (X = F, OH) on a C−H bond. However, as the two corresponding cations require an ionisation energy of 9.1 eV and 7.6 eV, respectively, they are clearly distinct as far as thermochemistry is concerned. Delocalisation of the positive charge in CH_2OH^+ is a prime explanation for the lower *IE* of the corresponding neutral species. As a consequence, the corresponding reaction of cations, rather than radicals, [Equation (2)] strongly favours the formation of CH_2OH^+ as indicated by $\Delta_r H^{\circ}_{298} = -41.8 \pm 0.1$ kcal mol^{-1}.

$$\begin{array}{lccccccccc} & CH_3OH & + & CH_2F^{+} & \rightarrow & CH_2OH^{+} & + & CH_3F \\ \Delta_f H^{\circ}_{298}\ (\text{kcal mol}^{-1})^{[17]} & -48.2 \pm 0.1 & & 199 & & 168 & & -59 \end{array} \quad (2)$$

With respect to the chromium systems, we can conclude that the hydroxochromium cation can also be described as protonated chromium oxide, thus allowing for a considerable reduction of the formal charge on the metal centre compared with the chromium fluoride cation. From this explanation, it is evident that the stabilising effects of an OH group on a metal cation is much larger than the mere difference between the electronegativities of OH and F. Consequently, it is reasonable to assume that the metal centre in $CrF(OH)_2^+$ is less electron-deficient than in $CrF_2(OH)^+$. Thus, the tendency to increase the electron density at the metal centre in $CrF(OH)_2^+$ by the formation of a Cr−O double bond is less pronounced.

The oxyfluoride $CrFO^+$ undergoes facile hydrolysis of the remaining Cr−F bond, thus yielding $CrO(OH)^+$. This ion, in turn, could undergo addition of water similar to that investigated both experimentally and theoretically for various vanadium[10] and iron[9,18,19] oxides and oxohydroxide monocations. However, the kinetic data suggest that addition of water to $CrO(OH)^+$ is slow, if it occurs at all, in the pressure region examined. Thus, for the reactions of CrF_3^+ with water, three terminal product ions are observed with decreasing abundances; H_3O^+, $Cr(OH)_3^+$, and $CrO(OH)^+$. Regardless of their actual way of formation, the cationic chromium fragments eventually underwent hydrolysis of all Cr−F bonds originally present in CrF_3^+.

CrF_4^+

On reaction with water, $CrF_3(OH)^+$ is formed as the initial product. One might expect a further increase in the reaction rate relative to CrF_3^+; however, this hydrolysis reaction is remarkably slow. This "passive" behaviour of *thermalised* CrF_4^+ has already been observed in the reactions of this ion with methane and NF_3;[1] any excited CrF_4^+ cations can safely be assumed to have been hydrolysed during the period necessary to isolate CrF_4^+ due to the fact that they are much more reactive. However, the overall behaviour of the CrF_4^+/H_2O system resembles that of its CrF_3^+/H_2O congener: (i) The terminal reaction product, H_3O^+ (obtained by proton transfer from hydrolysed CrF_4^+ to H_2O) dominates over $Cr(OH)_4^+$ (complete Cr−F bond hydrolysis) and CrF_2O^+ where the latter is, by analogy, assumed to be formed by water-mediated HF loss from $CrF_3(OH)^+$. While CrF_2O^+ might be expected to undergo at least one further Cr−F bond hydrolysis, the product $CrFO(OH)^+$ could not be detected in our study, and the kinetic data suggest that CrF_2O^+ is indeed a terminal reaction product. (ii) Three different reaction pathways can be accessed from the first intermediate, $CrF_3(OH)^+$: proton transfer to water, further Cr−F bond hydrolysis, and water-mediated HF loss. While the latter reaction has already been addressed, the other two reaction channels shall be discussed in more detail here. The generation of H_3O^+ from CrF_4^+ and H_2O may occur, in principle, by two different reaction pathways [Equations (3) and (4)].

$$CrF_4^+ \xrightarrow[-\,HF]{+\,H_2O} CrF_3(OH)^+ \xrightarrow[-\,CrF_3O]{+\,H_2O} H_3O^+ \tag{3}$$

$$CrF_4^+ \xrightarrow[-\,CrF_4]{+\,H_2O} H_2O^+ \xrightarrow[-\,OH]{+\,H_2O} H_3O^+ \tag{4}$$

However, both the ionisation energies of CrF_4 and water (see Table 1), the failure to observe cationic H_2O^+ during the decay of CrF_4^+ and the concurrent increase in H_3O^+ disfavour the second reaction channel [Equation (4)]. Furthermore, in a double-resonance experiment, ejection of $CrF_3(OH)^+$ from the reaction cell caused the signal of H_3O^+ to vanish completely. Thus, the generation of H_3O^+ is attributed to the first reaction channel [Equation (3)]. However, additional formation of H_3O^+ from further-hydrolysed ions $CrF_2(OH)_2^+$ and $CrF(OH)_3^+$, cannot be ruled out so far and will be discussed in more detail below.

Remarkably, the signal for putative intermediate $CrF_2(OH)_2^+$ did not surpass the noise level in the kinetic investigation, while the signals for its supposed Cr−F bond hydrolysis products $CrF(OH)_3^+$ and $Cr(OH)_4^+$ did so; the latter species is a terminal product of the reaction sequence. The failure to observe $CrF_2(OH)_2^+$ turns the kinetic analysis into a nontrivial problem as is discussed as follows: (i) There is no single source for the protons transferred to water. If proton transfer from both $CrF_3(OH)^+$ and the formal Cr^{IV} species $CrF_2(OH)^+$ (see the CrF_3^+ section above) to water was allowed, it would be rather arbitrary to rule out a similar reaction for the formal Cr^V species $CrF_2(OH)_2^+$ and $CrF(OH)_3^+$. Whilst an F/OH ligand exchange reduces the electron deficiency at the chromium centre, the influence of this exchange on the OH proton acidity is not necessarily large. In contrast, the mere existence of two or even three OH groups in $CrF_2(OH)_2^+$ or $CrF(OH)_3^+$, respectively, compared with one in $CrF_3(OH)^+$ may, on statistical grounds, even increase the rate of proton transfer to water. On the other hand, proton abstraction from $Cr(OH)_4^+$ could be ruled out because the latter ion was found to be a terminal product of the reaction sequences. Thus, a gradual decrease in proton transfer relative to further Cr−F bond hydrolysis is likely. The overall picture is that for $CrF_n(OH)_m^+$, the acidity of the OH protons increases with n but decreases with m. However, it is impossible to establish the particular step sizes of that decrease a priori. (ii) If $CrF_2(OH)_2^+$ could have been observed in the kinetic study, the distribution between proton abstraction and further Cr−F bond hydrolysis could be determined on the basis of the evolution of the ion concentrations over time. However, as $CrF_2(OH)_2^+$ had to be regarded as a reactive intermediate formed in very low steady-state concentrations, any distribution ratio could occur between the two reaction pathways. If proton abstraction from $CrF_3(OH)^+$ is favoured, then proton abstraction for $CrF_2(OH)_2^+$ is not favoured, and vice versa. Similarly, if proton abstraction from $CrF_2(OH)_2^+$ is favoured, then proton abstraction for $CrF(OH)_3^+$ is not favoured, and again, vice versa.

The kinetic analysis was made easier by the following: (i) CrF_2O^+ was found to be a terminal product of the reaction system. In addition, the cations $CrFO(OH)^+$ and $CrO(OH)_2^+$ were not observed. Consequently, the reaction sequence $CrF_4^+ \rightarrow CrF_2O^+ \rightarrow Cr(OH)_4^+$ can be ruled out. (ii) While the $CrF_2(OH)_2^+$ ion, which is not observed, is to be considered as a reactive intermediate, its consumption by one or more reactions with water cannot be faster than the collision rate. (iii) The very same argument applies to $CrF(OH)_3^+$; regardless of its actual rate of formation, the cation cannot be consumed at a reaction rate exceeding the collision limit. (iv) In turn, the temporal evolutions of $CrF(OH)_3^+$, and especially $Cr(OH)_4^+$, set upper limits to the reaction rates in question.

However, one cannot determine without additional experiments (namely exposing isolated intermediates to water or double-resonance experiments) the extent to which H_3O^+ is formed from $CrF_3(OH)^+$, $CrF_2(OH)_2^+$, and perhaps $CrF(OH)_3^+$. In parallel, the fraction of $CrF_3(OH)^+$ which yields $CrF_2(OH)_2^+$ remains unknown as do the fractions of $CrF_2(OH)_2^+$ and $CrF(OH)_3^+$, which yield

$CrF(OH)_3^+$ and $Cr(OH)_4^+$, respectively. However, these additional experiments would be adversely affected by the unfavourable signal-to-noise ratios already hampering the present investigations. As a consequence, isolation of intermediates was not attempted, and we ceased the investigation and determined only the rate constants reported in Figure 1.

Relative Reaction Rates of Hydrolysis

Remarkably, the reaction rate of the first Cr−F bond hydrolysis (see Figure 1) increases by about one order of magnitude from CrF^+ to CrF_2^+. While the rates of the first hydrolysis reactions are similar for CrF_2^+ and CrF_3^+, a subsequent decrease by about one order of magnitude is observed when going from CrF_3^+ to CrF_4^+. We think that the interplay of the effective charge on the chromium centre, the steric hindrance exerted by the increasing number of fluorine atoms attached to the metal centre, and the "surface charge" (originating from the high electron density on the fluorine atoms constituting the ligand sphere of the chromium cation) of the different CrF_n^+ cations provides an appropriate explanation for the observed differences in the rate constants.We will discuss this interplay in more detail: (i) The increased rate of hydrolysis of CrF_2^+ compared with CrF^+ can be explained by the threefold influence of the higher effective charge on the chromium centre on increasing fluorination. First, the formation of the collision complex between the ion and the polar water molecule should be much more facile. Secondly, the resulting collision complex should possess a longer life-time due to the larger ion-dipole interaction. Finally, assuming a four-centre transition state, the increased effective charge at the chromium centre can be assumed to favour the actual Cr−OH bond formation/HF abstraction from the collision complex. (ii) While all arguments mentioned above hold true for the change from CrF_2^+ to CrF_3^+ as well, the increase in the rate constant is much less pronounced. Steric hindrance exerted by the three fluorine atoms attached to the chromium cation can be assumed to slow down the formation of the initial collision complex, irrespective of whether CrF_3^+ keeps the trigonal-planar structure of neutral CrF_3 (Cr−F bond length 1.732 Å[20,21]) or not. (iii) We suppose that the formal Cr^V species CrF_4^+ more or less keeps the tetrahedral structure of neutral CrF_4 (Cr−F bond length 1.704 Å[21,22]), since the formal Cr^V species CrF_3O forms a trigonal-pyramidal structure, i.e. a slightly distorted tetrahedral structure.[21] Thus, the outer-sphere of the CrF_4^+ ion is assumed to be dominated by four electron-rich fluorine atoms, such that formation of the collision complex with water proceeds rather slowly while the actual hydrolysis reaction should proceed at a rate similar to that for CrF_2^+ and CrF_3^+. Accordingly, we conclude that the retardation of the hydrolysis of the "inert" CrF_4^+ cation is not due to the actual F/OH exchange but to the formation of the initial collision complex.

In the preceding discussion, the focus was placed on the structural properties of the chromium fluoride cations. However, spin restrictions[23] discussed in more detail in the Thermochemistry Section below may contribute to the hydrolysis rate differences as well. For example, hydrolysis of a Cr−F bond in CrF_n^+ allows for the above-mentioned delocalisation of the positive charge of the reaction product. This delocalisation, in turn, might allow for a spin inversion on the chromium centre, thus giving rise to a considerable reaction barrier. However, the results of quantum-chemical calculations would be needed to discuss this point in more detail.

Reactions with Nitrous Oxide

The observation of several oxochromium fluoride cations during the hydrolysis reactions reported above prompted our interest in looking for a more facile way of generating them. Our results are described below.

Initial Experiments

When a mixture of chromium and chromium fluoride monocations CrF_n^+ ($n = 0-4$) was subjected to an oxygen pressure of $1.0 \cdot 10^{-8}$ mbar for a period of 24 s, at least 95% of the total ion intensity was due to the cations CrF_n^+ ($n = 0-4$) and their hydrolysis and/or charge-transfer products. Oxochromium fluorides and ions originating from them included $CrFO^+$ (max. 1%), its supposed hydrolysis product $CrO(OH)^+$ (max. 2%), CrF_3O^+ (max. 1%), and the possible hydrolysis product of CrF_2O^+, $CrO(OH)_2^+$ (max. 1%). Therefore, O_2 deemed inappropriate and was replaced by N_2O as a putatively more suitable oxidant. From a thermochemical point of view, the latter should be a much better oxygen-atom donor, irrespective of the substrate present [see Equations (5) and (6)].

$$O_2 \rightarrow O + O \qquad \Delta_r H^\circ_{298} = 119.2\ \text{kcal mol}^{-1}\ ^{[17]} \tag{5}$$

$$N_2O \rightarrow N_2 + O \qquad \Delta_r H^\circ_{298} = 40.0\ \text{kcal mol}^{-1}\ ^{[17]} \tag{6}$$

In a second initial experiment, subjecting a mixture of chromium and chromium fluoride monocations to nitrous oxide pressures of $2.0 \cdot 10^{-8}$ mbar and $5.0 \cdot 10^{-7}$ mbar for 32 s allowed for the detection of substantial amounts of CrF_3O^+. In addition, both NO^+, NF_2O^+ [24] and small amounts of $CrO(OH)^+$ (probably from $CrFO^+$), $CrFN_2O_2^+$, and $CrF_2N_2O_2^+$ were detected.

Reactions of Mass-Selected Ions

(i) Based on the already observed inertness of ground-state (^6S) bare chromium cations towards nitrous oxide[25,26] and the outcome of the initial experiments, no further attempts were undertaken to generate CrO^+. (ii) In the reaction of isolated CrF^+ and N_2O, the desired species $CrFO^+$ could not be detected, whereas $Cr(OH)^+$ formed by hydrolysis with background water dominated the product ion spectrum. Traces of H_3O^+ and NO^+ (not surmounting 3% of the total ion concentration) were attributed to the presence of excited CrF^+ cations. (iii) When isolated CrF_2^+ was exposed to N_2O, CrF_2O^+ was formed with a reaction efficiency of $\varphi = 0.16\%$, and the abundance of the ion was not more than 2% of the total ion concentration. Besides hydrolysis products and NO^+ (not exceeding 1% of the total ion concentration), the intermediate N_2O^+ and the final product H_3O^+, accounting for 2% of the total ion concentration, were detected (see the Thermochemistry Section below for discussion). Due to the low abundance of CrF_2O^+, isolation of this cation was not attempted. (iv) When isolated CrF_3^+ was subjected to N_2O pressure of $1.0{\cdot}10^{-8}$ mbar for a period of 20 s, CrF_3O^+ was formed with a reaction rate of $(7 \pm 1)\ 10^{-11}$ cm^3 $molecules^{-1}$ s^{-1} ($\varphi = 9 \pm 1\%$), regardless of whether CrF_3^+ was generated from Cr^+ by NF_3/Ar or pure NF_3 pulses. Note that the small error bars reported here are based on good agreement between two experiments, whereas the systematic error introduced by the pressure measurement (see the Exp. Sect.) has not yet been considered. The only other oxofluoride species observed was $CrFN_2O_2^+$, which accounted for 3% of the total ion concentration. One might suppose $CrFN_2O_2^+$ to be generated by addition of N_2O to $CrFO^+$, which, in turn, is generated from CrF_3^+ by a single Cr−F bond hydrolysis and subsequent HF abstraction (see above). However, double-resonance experiments revealed that $CrFN_2O_2^+$ is formed from $CrF_2(OH)^+$ exclusively, and not at all from $CrFO^+$. Consequently, the generation of $CrFN_2O_2^+$ from $CrF_2(OH)^+$ is attributed to the water-assisted rearrangement of $CrF_2(OH)^+$ into $(HF)CrFO^+$, and subsequent HF/N_2O ligand exchange to yield $(N_2O)CrFO^+$. Note that ligand-mediated H−F bond formation and subsequent ligand loss have already been referred to in the above discussion of the formal reactions $CrF_2(OH)^+ \rightarrow CrFO^+ + HF$ and $CrF_3(OH)^+ \rightarrow CrF_2O^+ + HF$. As N_2O is a weakly bound ligand,[27] subsequent ligand exchange with background water yields $(H_2O)CrFO^+$. Supposedly, the latter rearranges, probably assisted by a neutral water molecule in a reaction sequence similar to that in Figure 2, to its isomer $CrF(OH)_2^+$, which finally undergoes hydrolysis of the remaining Cr−F bond to yield $Cr(OH)_3^+$. Rate constants for both the formation and consumption of $CrFN_2O_2^+$ could not be determined due to the low signal-to-noise ratio of the ion. With regard to Cr−F bond hydrolysis of the observed species, CrF_3O^+ was found to be remarkably inert towards water, but the reaction of its predecessor ion CrF_3^+ with background water was found to be fast and hence limited the yield of CrF_3O^+ to a maximum of about 15% of the total ion concentration. (v) In order to achieve a good signal-to-noise ratio, CrF_4^+ was not mass-selected. When a mixture of CrF_4^+ (23%) and the noninterfering CrF_3O^+ (77%) was subjected to N_2O pressure of $1.0{\cdot}10^{-6}$ mbar for 8 s, CrF_4O^+ could not be detected. This result is in agreement with chemical intuition which suggests that it is unlikely that oxidation of the formal Cr^V species CrF_4^+ would be observed since the reaction product CrF_4O^+ would constitute a formal Cr^{VII} cation, i.e. a hypervalent cation.

The reactions of mass-selected chromium and chromium fluoride monocations with nitrous oxide are summarised in Figure 3. As in Figure 1, possible but experimentally not observed oxidation products are given in square brackets, and both reaction rate constants and reaction efficiencies φ (values in parentheses) are given as defined in the Exp. Sect.

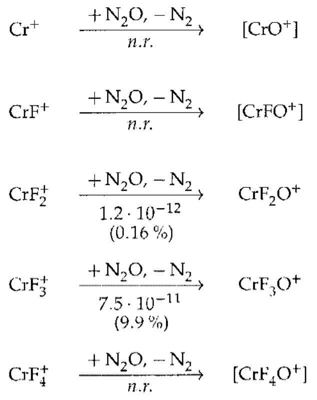

Figure 3. Reactions of CrF_n^+ ($n = 0-4$) with nitrous oxide; for discussion, see text; abbreviation: *n.r.* = "no reactivity" indicating a reaction efficiency $\varphi < 0.05\%$

Gas-Phase Generation of CrF_3O^+

While the absence of efficient oxygen transfer to chromium and chromium fluoride monocations CrF_n^+ ($n = 0-2, 4$) limited the present study to CrF_3^+, it simplified the experiments to a great extent. In contrast to requiring the use of two pulse valves, isolating a hydrolysis-sensitive intermediate, and optimising gas pressures and pulse lengths for two pulse valves,[2] good CrF_3O^+ intensities could be achieved by optimising the generation of CrF_3^+ from bare Cr^+ and pulsed-in NF_3, and then adding N_2O to the pulse valve already filled with NF_3. Subsequent optimisation of the length of the combined NF_3/N_2O pulse was not necessary; furthermore, isolation of CrF_3O^+ did not impose any problems.

Ionisation Energy

Chromium fluorides show a strong correlation between the number of electron-withdrawing fluorine atoms connected to the metal centre and the respective ionisation energies (see Table 1). However, the presence of doubly bonded oxygen does not necessarily affect the *IE*. On one hand, an oxygen ligand will withdraw electron density from the metal centre, and on the other hand, it may even donate electron density when the metal centre is already highly electron-deficient. Consequently, we wanted to establish a sound value for the yet unknown ionisation energy of CrF_3O. Exposures of CrF_3O^+ to ethylene [$IE = 10.5$ eV, charge-transfer (CT) reaction efficiency $\varphi = 170\%$] and to molecular oxygen ($IE = 12.1$ eV, CT reaction efficiency $\varphi < 0.05\%$) provide lower and upper limits, respectively, for the ionisation energy in question. The reaction with ethylene appears to proceed faster than the rate at which the reactants collide according to the capture theory.[28,29] While the agreement between rate constant determined by experiment and by this theory is very good for electron-transfer processes between species of similar *IE*s,[30] some pitfalls seem to exist when describing outer-sphere electron transfer between species with large *IE* differences. Most probably, the cross-section is underestimated in the latter case.

Unfortunately, a more precise determination of the ionisation energy of CrF_3O was adversely affected by the following facts: (i) For a large variety of readily available compounds, e.g. alkanes (C_2H_6, IE = 11.5 eV; C_3H_8, IE = 11.0 eV),[17] haloalkanes (CH_3Cl, IE = 11.2 eV; CH_2Cl_2, IE = 11.3 eV; CH_2ClF, IE = 11.7 eV),[17] and SiH_4 (IE = 11.6 eV),[17] dissociative ionisation is preferred and the yields of stable radical cations on removal of an electron are rather poor. (ii) The readily available cyano-substituted ethylenes, which yield stable radical cations (acrylonitrile, IE = 10.9 eV; both 1,2-dicyanoethylenes, IE = 11.2 eV; 1,1-dicyanoethylene, IE = 11.4 eV; tricyanoethylene, IE = 11.6 eV; tetracyanoethylene, IE = 11.7 eV),[31] are either difficult to handle or are insufficiently volatile to be employed in an FT-ICR experiment. (iii) Hexafluoroacetone (IE = 11.6 eV), which forms a stable radical cation and is sufficiently volatile undergoes α cleavage instead of charge-transfer when reacting with CrF_3O^+. Thus, for the determination of the *IE* of CrF_3O, the use of the "bracketing method", while relying largely on only one charge-transfer reaction [namely $CrF_3O^+ + COS$ (IE = 11.2 eV) $\rightarrow CrF_3O + COS^+$; reaction efficiency φ = 80%], deemed not indicated. Consequently, we correlated the efficiency of the presumably barrier-free reaction to the ionisation energy difference, [32] thus estimating the ionisation energy of CrF_3O to be 11.3 eV ± 0.2 eV (rounded up, and the error bar was based on the reaction rate uncertainty mentioned in the Exp. Sect.). Interestingly, this value is considerably lower than the ionisation energies of CrF_2O_2, as well as of CrF_4, and even slightly lower than the ionisation energy of the oxygen-free species CrF_3 (though within the experimental error margins, Table 1). Two reasons can account for the similarity of the ionisation energies of CrF_3 and CrF_3O. (i) In the formal Cr^{III} species CrF_3, the central chromium atom is already highly electron-deficient which disfavours additional electron withdrawal. (ii) Oxygen is not as electronegative as fluorine, thus it does not necessarily withdraw electron density from the chromium atom; in contrast, doubly bound oxygen may even donate electron density to the electron-deficient metal centre. However, in order to account for the influence of a Cr=O double bond on the ionisation energy quantitatively, the ionisation energies of CrF_nO (n = 1, 2) are needed as well.

Reactions

As CrF_3^+ is relatively easily oxidised to CrF_3O^+, we wondered if that property of the system could be employed in a catalytic oxidation cycle. First, we were interested in the oxidation of small alkanes. Kang and Beauchamp[33] found CrO^+ to selectively oxidise alkanes except methane. While the higher valency of the metal in CrF_3O^+ may help to fulfil this task, no reactions with methane were observed.

Table 1. Ionisation energies (*IE*) of CrF_3O and other species of interest[a]

Species	*IE* (eV)	Ref.
C_2H_4	10.5	[17]
COS	11.2	[17]
CF_3COCF_3	11.6 ± 0.1	[31]
O_2	12.1	[17]
H_2O	12.6	[17]
N_2O	12.9	[17]
Cr	6.8	[17]
CrF	8.4 ± 0.3	[17]
CrF_2	10.1 ± 0.3	[17]
CrF_3	11.5 ± 0.4	[1]
CrF_4	12.3 ± 0.3	[1]
CrO	7.9	[17]
CrO_2	10.3 ± 0.5	[17]
	9.7 ± 0.2	[66][b]
CrO_3	11.6 ± 0.5	[17]
CrF_2O_2	12.9	[31]
CrF_3O	11.3 ± 0.2	this work

[a] Values and error bars are rounded off to multiples of 0.1 eV; error bars are not given when they are less than 0.1 eV. [b] OCrO.

In contrast, replacing methane by ethane caused the formal transfer of a hydride anion from the hydrocarbon to CrF_3O^+; products indicative of the cleavage of the Cr−O bond were not observed. One might argue that unsaturated hydrocarbons like toluene or buta-1,3-diene could be suitable substrates for oxidation. While this might be perfectly true, it seems unlikely that CrF_3O^+ would transfer oxygen to them, rather than abstract hydride anions or capture electrons from the π-systems, simply because the *IE*s of these substrates are considerably lower than the *IE* of CrF_3O^+. The failure to transfer oxygen atoms to organic substrates has already been observed for other transition-metal complexes of higher oxidation states. For example, both MoO_3^+ and MoS_3^+ show exclusive electron capture and hydride abstraction from toluene,[34] and for the PtO_2^+/ethane system, electron and hydride anion transfer dominate the reactivity (40% and 15% of the reaction products, respectively).[35] Further, OsO_n^+ (n = 3, 4) exclusively abstracts one or two hydrogen atoms from methane, ethane, and propane.[36] From these previous and our present results, we inferred that CrF_3O^+ would also abstract hydride anions from higher alkanes, but is not suited for selectively oxidising them. Thus, we ceased this particular investigation and addressed the oxidation of carbon monoxide. Again, we were not successful: Carbon monoxide does not react with CrF_3O^+. A summary of the investigated reactions is given in Table 2.

Table 2. Reactions of CrF_3O^+ investigated in this study[a] [b] [c] [d]

IE determination							
CrF_3O^+	+	C_2H_4	($IE = 10.5$ eV)	$\xrightarrow{170\,\%}$	[Cr,F_3,O]	+	$C_2H_4^+$
	+	COS	($IE = 11.2$ eV)	$\xrightarrow{80\,\%}$	[Cr,F_3,O]	+	COS^+
	+	C_3F_6O[e]	($IE = 11.6$ eV)	$\xrightarrow{n.d.}$	[Cr,F_6,C,O]	+	$C_2F_3O^+$
	+	O_2	($IE = 12.1$ eV)	$\xrightarrow{n.r.}$			
Potential applications							
CrF_3O^+	+	CH_4		$\xrightarrow{n.r.}$			
	+	C_2H_6		$\xrightarrow{50\,\%}$	[Cr,F_3,O,H]	+	$C_2H_5^+$
				$\xrightarrow{3.4\,\%}$	[Cr,F_3,O,H_2]	+	$C_2H_4^+$
	+	CO		$\xrightarrow{n.r.}$			

[a] Reaction efficiencies φ are given as defined in the text. [b] For reaction efficiencies φ apparently greater than unity, see text. [c] *n.d.* = reaction efficiency φ not determined because the observed reaction is unsuited to determine the ionisation energy of CrF_3O. [d] *n.r.* = "no reactivity" indicating a reaction efficiency $φ < 0.05\%$. [e] Hexafluoroacetone.

Thermochemistry

Finally, we address the investigated reactions from a thermochemical point of view. Unless otherwise noted, two assumptions shall be made throughout this section: (i) The reactants are properly thermalised and (ii) severe kinetic barriers or spin restrictions[23] do not exist. Assumption (i) allows for the exclusion of endothermic reactions while assumption (ii) limits the reasons for a reaction's nonoccurrence to endothermicity (or the existence of at least one other, more exothermic reaction channel). As a consequence, the mere occurrence or absence of a reaction allows for establishing a $\Delta_fH°_T$ limit for one of the species involved, provided the standard heats of formation of all other species are known. To be more precise, the occurrence of a reaction at a temperature T allows for establishing a lower limit of a reactant's $\Delta_fH°_T$ value or an upper limit of a product's $\Delta_fH°_T$ value, whereas the absence of a reaction allows for establishing an upper limit of a reactant's $\Delta_fH°_T$ value or a lower limit of a product's $\Delta_fH°_T$ value. Maximum $\Delta_fH°_T$ values of reaction products can be utilised in follow-up reactions. Unfortunately, that does not hold true for minimum $\Delta_fH°_T$ values which makes an "inherited" bracketing impossible. However, the procedure is straightforward, and the limits are derived in Table 3 and presented together with those of their neutral counterparts in Table 4. From the heats of formation bond dissociation energies (*BDE*s) may be calculated in a straightforward manner. However, we do not report *BDE*s in this work because $\Delta_fH°_T$ *limits* allow for deriving bond-dissociation energy *limits* only, whereas other experimental techniques are available to determine the actual values.

Chromium Fluoride Hydrolysis Products

For $Cr(OH)^+$, a double upper limit of $\Delta_fH°_{298}$ can be derived (Table 3, Entries 1 and 2). While both results agree with each other and the literature value [(185.8 ± 3.0) kcal mol^{-1}[17,37]], their significance is low. Further, the smaller error bar of the higher value does not provide an advantage. A lower limit for $\Delta_fH°_{298}[Cr(OH)^+]$ cannot be derived on the basis of the reactions investigated here. Similar arguments apply to $\Delta_fH°_{298}[CrF(OH)^+]$ (Table 3, Entries 3 and 4) and to $\Delta_fH°_{298}[Cr(OH)_2{}^+]$ (Table 3, Entries 5 and 6). However, for $CrF(OH)^+$, the $\Delta_fH°_{298}$ limit obtained from the absence of proton transfer is more precise from the point of both its error bar and value, and for $Cr(OH)_2{}^+$, the difference between the two values is less pronounced and mostly due to the decrease in the size of the error bar.

For the hydrolysis of $CrF_3{}^+$ and its follow-up products, deriving the maximum $\Delta_fH°_{298}$ values for the hydrolysis products (Table 3, Entries 7, 9, and 10) is straightforward. Based on the *observed* proton transfer from $CrF_2(OH)^+$ to H_2O (Table 3, Entry 8), a *lower* limit for the heat of formation of the reactant ion can be determined for the first time in this study. In turn, the failure to observe proton transfer from both $CrF(OH)_2{}^+$ and $Cr(OH)_3{}^+$ (Table 3, Entry 11) to H_2O allows, in principle, for re-evaluating maximum $\Delta_fH°_{298}$ values for these cations but fails, in practice, for $CrF(OH)_2{}^+$ because the standard heat of formation of the

Table 3. Reactions investigated in this study and thermochemical data derived[a] [b]

Reaction[c]						Limit(s) Derived for **Boldface** Species	
(1)	CrF^+	$+ H_2O$	$\longrightarrow$	$\mathbf{Cr(OH)^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 205.6 \pm 7.3$[d]
(2)	$\mathbf{Cr(OH)^+}$	$+ H_2O$	$\not\longrightarrow$	CrO	$+ H_3O^+$		$\Delta_f H^{\ominus}_{298} < 242.4 \pm 1.6$
(3)	CrF_2^+	$+ H_2O$	$\longrightarrow$	$\mathbf{CrF(OH)^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 137.0 \pm 7.5$
(4)	$\mathbf{CrF(OH)^+}$	$+ H_2O$	$\not\longrightarrow$	$CrFO$	$+ H_3O^+$		$\Delta_f H^{\ominus}_{298} < 125.5 \pm 1.9$[d]
(5)	$CrF(OH)^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{Cr(OH)_2^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 144.3 \pm 7.5$
(6)	$\mathbf{Cr(OH)_2^+}$	$+ H_2O$	$\not\longrightarrow$	$CrO(OH)$	$+ H_3O^+$		$\Delta_f H^{\ominus}_{298} < 139.8 \pm 1.2$[d]
(7)	CrF_3^+	$+ H_2O$	$\longrightarrow$	$\mathbf{CrF_2(OH)^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 72.7 \pm 9.8$
(8)	$\mathbf{CrF_2(OH)^+}$	$+ H_2O$	$\longrightarrow$	CrF_2O	$+ H_3O^+$	$45.5 \pm 3.4 <$	$\Delta_f H^{\ominus}_{298}$
(9)	$CrF_2(OH)^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{CrF(OH)_2^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 80.0 \pm 9.8$
(10)	$CrF(OH)_2^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{Cr(OH)_3^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 87.3 \pm 9.8$
(11)	$\mathbf{Cr(OH)_3^+}$	$+ H_2O$	$\not\longrightarrow$	$CrO(OH)_2$	$+ H_3O^+$		$\Delta_f H^{\ominus}_{298} < 66.8 \pm 4.8$[d]
(12)	$CrF_2(OH)^+$		$\longrightarrow$	$\mathbf{CrFO^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 137.8 \pm 9.8$
(13)	$CrFO^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{CrO(OH)^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 145.1 \pm 9.8$[d]
(14)	$\mathbf{CrO(OH)^+}$	$+ H_2O$	$\not\longrightarrow$	CrO_2	$+ H_3O^+$		$\Delta_f H^{\ominus}_{298} < 175.1 \pm 1.2$
(15)	CrF_4^+	$+ H_2O$	$\longrightarrow$	$\mathbf{CrF_3(OH)^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 20.9 \pm 7.2$
(16)	$\mathbf{CrF_3(OH)^+}$	$+ H_2O$	$\longrightarrow$	CrF_3O	$+ H_3O^+$	$-18.2 \pm 12.4 <$	$\Delta_f H^{\ominus}_{298}$
(17)	$CrF_3(OH)^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{CrF_2(OH)_2^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 28.2 \pm 7.2$
(18)	$CrF_2(OH)_2^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{CrF(OH)_3^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 35.5 \pm 7.2$
(19)	$CrF(OH)_3^+$	$+ H_2O$	$\longrightarrow$	$\mathbf{Cr(OH)_4^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 42.8 \pm 7.2$
(20)	$\mathbf{Cr(OH)_4^+}$	$+ H_2O$	$\not\longrightarrow$	$CrO(OH)_3$	$+ H_3O^+$		$\Delta_f H^{\ominus}_{298} < 9.8 \pm 12$[d]
(21)	$CrF_3(OH)^+$		$\longrightarrow$	$\mathbf{CrF_2O^+}$	$+ HF$		$\Delta_f H^{\ominus}_{298} < 86.0 \pm 7.2$
(22)	CrF^+	$+ N_2O$	$\not\longrightarrow$	$\mathbf{CrFO^+}$	$+ N_2$	$217.9 \pm 7.3 <$	$\Delta_f H^{\ominus}_{298}$
(23)	CrF_2^+	$+ N_2O$	$\not\longrightarrow$	$\mathbf{CrF_2O^+}$	$+ N_2$	$149.3 \pm 7.5 <$	$\Delta_f H^{\ominus}_{298}$
(24)	CrF_3^+	$+ N_2O$	$\longrightarrow$	$\mathbf{CrF_3O^+}$	$+ N_2$		$\Delta_f H^{\ominus}_{298} < 85.0 \pm 9.8$

[a] Unless otherwise noted, data in kcal mol^{-1}. [b] For discussion, especially of multiple and/or seemingly contradicting entries, see text. [c] The table entries are numbered consecutively beginning with one. In order to avoid confusion with reactions given in the text, those given in this table will be referred to as, e.g., "Table 3, Entry 1". [d] Value considered to be more reliable. For discussion, see text.

corresponding neutral oxochromium hydroxide CrFO(OH) is unknown.

In addition, having established the upper limit for $\Delta_f H°_{298}[CrF_2(OH)^+]$, the maximum standard heats of formation for both $CrFO^+$ and its hydrolysis product $CrO(OH)^+$ can be derived (Table 3, Entries 12 and 13, respectively). However, these two limits should be used with care: all reactions discussed so far involved the same number of reactants and products thus allowing, by and large, for the neglecting of entropic terms. With the number of molecules changing in the course of the HF abstraction reaction (Table 3, Entry 12), this does not apply any longer, and uncertainties in the range of several kcal mol^{-1} may be introduced by neglecting entropic factors. The absence of proton transfer from $CrO(OH)^+$ to water (Table 3, Entry 14) does not allow for deriving a more precise $\Delta_f H°_{298}$ limit for that species.

The discussion of the CrF_4^+/H_2O system essentially parallels that of the CrF_3^+/H_2O system. The only remarkable difference is the occurrence of a second proton transfer reaction $CrF_2(OH)_2^+ + H_2O \rightarrow CrF_2O(OH) + H_3O^+$ which would have allowed for the determination of another minimum $\Delta_f H°_{298}[CrF_2(OH)_2^+]$ value provided $\Delta_f H°_{298}[CrF_2O(OH)]$ had been known.

Oxidation by Nitrous Oxide

As mentioned above, CrO^+ could not be generated from Cr^+ and N_2O, although the reaction is thermochemically favourable. We attribute this to a considerable twofold reaction (activation) barrier introduced by (i) the need to break the $3d^5$ configuration of the chromium cation and (ii) the missing electronic correlation between reactants and products of the reaction, $N_2O\ (^1\Sigma^+) + Cr^+\ (^6S) \rightarrow N_2\ (1\Sigma_g{}^+) + CrO^+\ (^4\Pi$[38]$)$, already pointed out by Armentrout et al.[39]

We would like to discuss this absence of a thermochemically favourable reaction in more detail. From the point of the experimentalist, assuring proper thermalisation of the reactants is a mere question of careful experimental set-up. Thus, a "false positive" (a reaction occurring despite its endothermicity) can be prevented. In contrast, activation barriers and spin restrictions are *intrinsic* properties of the sys-

Table 4. Heats of formation of chromium fluoride cations and other species of interest[a] [b] [c]

Species	$\Delta_f H^o_{298}$ (Neutral)		$\Delta_f H^o_{298}$ (Mono-cation)	
Cr	94.8	[17]	250.8	[17]
CrF	4.6 ± 2.4	[21]	198.3 ± 7.3	[1,17,21][d]
CrF_2	−103.2 ± 3.0	[21]	129.7 ± 7.5	[1,17,21][d]
CrF_3	−199.8 ± 3.4	[21]	65.4 ± 9.8	[1,21][e]
CrF_4	−270.0 ± 2.1	[21]	13.6 ± 7.2	[1,21][e]
CrO	43.6 ± 1.6	[67]	225.8 ± 1.6	[17,21][f]
CrO_2	−23.7 ± 1.2	[67]	213.8 ± 11.6	[17,21][f]
			209 ± 12	[66][g]
CrO_3	−77.3 ± 1.0	[67]	190.2 ± 11.6	[17,21] [f]
CrFO	−73.3 ± 1.9	[21]	< 137.8 ± 9.8	
CrF_2O	−153.3 ± 3.4	[21]	< 86.0 ± 7.2	
CrF_3O	−217.0 ± 12.4	[21]	43.6 ± 13.2	
CrF_4O	−262.5 ± 8.9	[21]		
Cr(OH)	18.9 ± 1.8	[67]	185.8 ± 3.0	[17,37][h]
			< 205.6 ± 7.3	
$Cr(OH)_2$	−76.9 ± 1.2	[67]	< 139.8 ± 1.2	
$Cr(OH)_3$	−150.9 ± 2.4	[67]	< 66.8 ± 4.8	
$Cr(OH)_4$	−207.6 ± 2.4	[67]	< 9.8 ± 12	
$Cr(OH)_5$	−259.9 ± 4.8	[67]		
$Cr(OH)_6$	−305 ± 12	[67]		
CrO(OH)	−59.0 ± 1.2	[67]	< 145.1 ± 9.8	
$CrO(OH)_2$	−132.0 ± 4.8	[67]		
$CrO(OH)_3$	−189 ± 12	[67]		
$CrO(OH)_4$	−242 ± 12	[67]		
CrF(OH)			< 125.5 ± 1.9	
$CrF(OH)_2$			< 80.0 ± 9.8	
$CrF(OH)_3$			< 35.5 ± 7.2	
$CrF_2(OH)$			see Table 3	
$CrF_2(OH)_2$			< 28.2 ± 7.2	
$CrF_3(OH)$			see Table 3	
N_2O	19.6	[17]		
O	59.6	[17]	373.6	[17]
OH	9.3 ± 0.3	[17]	309.1	[17]
H_2O	−57.8	[17,21]	233.0	[17]
H_3O			141	[17]
HF	−65.1 ± 0.2	[17,21]		

[a] All data in kcal mol^{-1}. [b] This work unless otherwise noted. [c] We report only "best values" here. For data evaluation, see the limits reported in Table 3 and the discussion in the text. [d] Calculated from the heat of formation[21] and the ionisation energy.[1,17] [e] Calculated from the heat of formation[21] and the ionisation energy.[1] [f] Calculated from the heat of formation[21] and the ionisation energy.[17] [g] OCrO. [h] Calculated from the heats of formation of Cr^+ and OH[17] and the bond dissociation energy (*BDE*) of Cr^+-OH.[37]

tem and cannot be circumvented by any experimental condition. Thus, a "false negative" (a reaction not occurring despite its exothermicity) cannot be detected without an independent determination of the thermochemical data.

Finally, one more point regarding oxidation by nitrous oxide shall be discussed here. Due to an orbital reorganisation,[40] linear N_2O needs to get bent in order to facilitate oxygen-atom transfer onto its reaction partner.[41,42]

The failure to generate $CrFO^+$ from CrF^+ and N_2O can be explained by the following. (i) The oxidation reaction is endothermic corresponding to $\Delta_f H°_{298}(CrFO^+) > 217.9 \pm 7.3$ kcal mol^{-1} (Table 3, Entry 22). However, this limit contradicts that derived from the decomposition of $CrF_2(OH)^+$, $\Delta_f H°_{298}(CrFO^+) < 137.8 \pm 9.8$ kcal mol^{-1} (Table 3, Entry 12), and this explanation cannot hold true. (ii) $CrFO^+$, once formed, is readily oxidised to yield $CrFO_2{}^+$. However, as the formal Cr^{VI} species $CrFO_2{}^+$ was not observed, it would have to be a fast-reacting intermediate, thus posing the question of its reaction partners and the resulting products. While traces of H_3O^+ and NO^+ were detected, the direct formation of H_3O^+ from $CrFO^+$ and background water is impossible, and the transfer of the nitride anion from N_2O appears rather unlikely. In parallel, hydride anion abstraction from H_2O would yield HO^+, which cannot be observed by our mass spectrometer (thus allowing for both facile formation and consumption of $CrFO_2{}^+$). However, the formation of HO^+ is highly unlikely on thermochemical grounds. Hence, this second explanation is excluded as well. (iii) The above-mentioned spin-inversion phenomena prevent the reaction from proceeding, i.e. assumption (ii) introduced in the first paragraph of this section does not apply. In this particular case, however, an upper limit for $\Delta_f H°_{298}(CrFO^+)$ could be derived independently from a reaction that does take place (Table 3, Entry 12), thus allowing for the ruling out of an erroneous $\Delta_f H°_{298}(CrFO^+)$ limit derivation (Table 3, Entry 22).

While CrF_2O^+ could be obtained in traces, it was impossible to isolate it from the mixture of hydrolysis products, which included traces of NO^+, the intermediate N_2O^+ and the final product H_3O^+. For a discussion, we apply the three-item scheme already utilised for $CrFO^+$: (i) Endothermicity of the reaction (Table 3, Entry 23) can be ruled out (Table 3, Entry 21). (ii) Facile oxidation of CrF_2O^+ by N_2O would yield $CrF_2O_2{}^+$, i.e., a formal Cr^{VII} species, which could explain the observation of N_2O^+ and H_3O^+ when CrF^{+}_{2} is exposed to N_2O according to Equations (7)−(11). Furthermore, it should be noted that $CrF_2O_2{}^+$ has been generated and its *IE* value determined.[43]

$$CrF_2 + N_2O \rightarrow CrF_2O^+ + N_2 \tag{7}$$

$$CrF_2O^+ + N_2O \rightarrow CrF_2O_2{}^+ + N_2 \tag{8}$$

$$CrF_2O_2{}^+ + N_2O \rightarrow CrF_2O_2{}^+ + N_2O^+ \tag{9}$$

$$N_2O^+ + H_2O \rightarrow N_2O + H_2O^+ \tag{10}$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \tag{11}$$

While the generation of H_3O^+ from N_2O^+ via H_2O^+ is consistent with established thermochemical data (Table 4), and its temporal evolution appeared to be properly modelled, the temporal evolution of N_2O^+ could not be reproduced on the basis of Equations (7)−(11). Furthermore, the value of k_{11} obtained by modelling was about two orders of magnitude smaller than the literature value.[44] Consequently, the generation of N_2O^+ was attributed to a parent ion or ions activated during the mass selection of CrF_2^+, and the formation of the formal Cr^{VII} species $CrF_2O_2^+$ from properly thermalised precursors was ruled out. (iii) As in CrF^+, the spin-inversion problem is a prime candidate for preventing the oxidation reaction of CrF_2^+.

In contrast to the CrF_n^+ cations discussed so far, CrF_3^+ reacts with N_2O to give CrF_3O^+ in good yields. Hence, an upper limit of $\Delta_fH_{298}(CrF_3O^+)$ can be derived (Table 3, Entry 24). On combination with the ionisation energy of the corresponding neutral species (see Table 1), an upper limit of $\Delta_fH°_{298}(CrF_3O) < -177.9$ kcal mol^{-1} is obtained. Basically, our value is in agreement with literature data;[21] however, it is about 40 kcal mol^{-1} too large. Thus, the inverted procedure, i.e. combining the literature value of $\Delta_fH°_{298}(CrF_3O)$ with the *IE* determined in this study, provides a reasonable value for $\Delta_fH°_{298}(CrF_3O^+)$ as given in Table 4.

Another conclusion is that the spin conservation requirement no longer hampers the transfer of the oxygen atom to the chromium fluoride cation. This could be explained by the fact that as the oxidation state of the chromium centre increases, the spin-orbit coupling increases, thus enabling a more facile intersystem crossing (spin inversion) and, consequently, a lower reaction barrier. This explanation may also account for the trend in the oxidation efficiencies from Cr^+ and CrF^+ (no reactivity observed) via CrF_2^+ (traces of CrF_2O^+ generated) to CrF_3^+ (facile reaction), which parallels, at least qualitatively, the increasing formal oxidation state of the chromium centre.

Conclusion

In this study, we have investigated the reactions of chromium and chromium fluoride monocations CrF_n^+ ($n = 0-4$) with water. Besides slow condensation, Cr^+ is unreactive, whereas progressive hydrolysis of the Cr−F bonds proceeds for CrF^+, CrF_2^+, CrF_3^+, and CrF_4^+. However, for the species $CrF_2(OH)^+$, efficient proton abstraction parallels the hydrolysis of the next Cr−F bond, and in the case of $CrF_3(OH)^+$, that proton transfer is even preferred over further Cr−F bond hydrolysis.

Furthermore, we have investigated the reactions of chromium and chromium fluoride monocations with the established oxygen-transferring agent nitrous oxide. Significant transfer of oxygen was observed for CrF_3^+ only. The ionisation energy of CrF_3O is 11.3 ± 0.2 eV. Attempts to transfer the oxygen atom from CrF_3O^+ to small alkanes or to carbon monoxide failed.

Experimental Section

Reactants: Nitrogen trifluoride (Praxair, 99.99%), nitrous oxide (Linde, 99.5%), argon (AGA Gas, 99.996%), and solid chromium (Balzers, > 99.9%) were used as purchased. Tap water was used without further purification. The water was put into a half-micro test tube directly connected to the gas-inlet system of the mass spectrometer and degassed by two freeze-evacuate-thaw cycles. Hexafluoroacetone, C_3F_6O, was liberated from its sesquihydrate (Merck-Schuchardt, > 97%) by reaction with phosphoric anhydride, P_4O_{10}, in analogy to literature procedures.[45−47] The dehydration reaction was carried out in a half-micro test tube directly connected to a leak valve of the mass spectrometer. Due to the differences between the boiling points of hexafluoroacetone (−28 °C/p_0)[46] and its water-containing hydrate (55−56 °C/107 mbar),[48] we assumed the dehydration process to be complete in the sense that no hexafluoroacetone hydrate was admitted into the reaction cell from the leak valve. However, the admission of water itself to the reaction cell could not be prevented in this "on-line" preparation of hexafluoroacetone. All reactant gases not mentioned so far were purchased from Linde and used without further purification.

Mass Spectrometer: All experiments were performed with a Bruker Spectrospin CMS-47X Fourier transform ion-cyclotron resonance (FT-ICR) mass spectrometer. The setup and operation have been described previously.[49,50] In brief, chromium monocations were generated from targets of pure chromium by laser desorption/laser ionisation[51,52] in the external ion source of the spectrometer using an Nd:YAG laser (Spectron Systems, $\lambda_{max} = 1064$ nm). The chromium ions were extracted from the source and transferred into the analyser cell via a system of electrostatic potentials. Next, the most abundant isotope ^{52}Cr (relative abundance 83.8%[53]) was mass-selected using FERETS,[54] a computer-controlled ion-ejection protocol that combines frequency sweeps and single-frequency pulses to optimise resonant excitation and ejection of all unwanted ions. After mass-selection, $^{52}Cr^+$ cations were allowed to react with pulsed-in reactant gas mixtures as described below.

Reactions with Water: After mass-selection, $^{52}Cr^+$ ions were exposed to pulsed-in nitrogen trifluoride/argon mixtures. Both the composition of the gas mixture and the length of the gas pulse were adjusted to maximise the yield of the desired chromium fluoride cation, CrF_n^+ ($n = 1-4$). Subsequently, the ion of interest was mass-selected using FERETS. Electronically excited Cr^+ ions, which are known to be efficiently thermalised by collision with methane[55] rather than argon,[1] were allowed to multiply collide with pulsed-in methane. In an additional series of experiments, however, Cr^+ cations were allowed to react with water after multiple collisions with argon rather than with methane. CrF^+ ions which are known to require thermalisation as well[1] were allowed to undergo multiple collisions with water and re-isolated using FERETS. Thermalisation deemed unnecessary for CrF_n^+ ($n = 2-4$) due to the purely exponential decays of their intensities during the reactions investigated. Water was admitted to the cell via a leak valve at a constant pressure measured by a calibrated[56] BALZERS IMG 070 ion gauge. The effective water pressures were $7.7\cdot10^{-9}$ mbar, $4.7\cdot10^{-9}$ mbar, $2.5\cdot10^{-9}$ mbar, and $7.7\cdot10^{-9}$ mbar for CrF^+, CrF_2^+, CrF_3^+, and CrF_4^+, respectively. For Cr^+, the pressure was in the range of $6.5\cdot10^{-9}$ to $1.0\cdot10^{-5}$ mbar.

Reactions with Nitrous Oxide: After mass selection, $^{52}Cr^+$ ions were exposed to pulsed-in nitrogen trifluoride/argon or nitrogen trifluoride/nitrous oxide mixtures, respectively. Both the composition of the gas mixtures and the length of the gas pulse were adjusted to maximise the yield of the desired chromium fluoride cation, CrF_n^+ ($n = 1-4$), or oxochromium fluoride cation, CrF_nO^+ ($n = 1-4$). The ion of interest was isolated using FERETS. Reactant gases were admitted to the cell via a leak valve at a constant pressure in the order of 10^{-8} to 10^{-7} mbar while the background pressure in the analyser cell of the spectrometer was in the range of $(2-4)\cdot10^{-9}$ mbar. To generate the ions of interest, we employed, in that order, (i) the established methodology of generating chromium fluoride monocations using nitrogen trifluoride, NF_3, as the fluorinating agent[1,2] and (ii) the time-honoured use of nitrous oxide, N_2O, for the transfer of the oxygen atoms. The latter has been proven to transfer oxygen to a wide variety of metal cations like Ti^+,[25] V^+,[25] Fe^+,[18,25] Zr^+,[25] Nb^+,[25] Mo^+ [57] and U_2^+.[58] It was not indicated to use the alternative approach of first generating chromium oxide monocations, CrO^+, and subsequently transferring fluorine atoms to them, due to the inefficient oxygen transfer to bare chromium ions, Cr^+,[25] which requires CrO^+ to be generated from CrO_2Cl_2.[33] CrF^+ ions, which are known to need thermalisation,[1] were allowed to multiply collide with nitrous oxide and re-isolated using FERETS. All other ions CrF_n^+ (n = 2−4) did not require thermalisation as mentioned above.

Analysis of Experimental Results: Elemental compositions of ions were determined by high-resolution mass spectrometry. Reaction sequences were derived from the temporal evolution of ion intensities and complementary double-resonance experiments.[59] In a double-resonance experiment, a supposed intermediate [e.g., $^{52}CrF(OH)^+$, m/z = 87.94165] is continuously ejected from the reaction cell by employing a constant radio-frequency pulse for a certain period of time. The resulting spectrum is compared with a reference spectrum originating from the very same experimental conditions, except that ejecting the supposed intermediate is replaced by "ejecting" a nonexisting hypothetical ion (e.g., m/z = 500). The disappearance of the signal of a product ion indicates that this ion originates, directly or indirectly, from the ejected one. Reaction kinetics were analysed using a computer program that determines rate constants and distribution ratios based on the experimentally observed evolution of ion intensities over time, and a flexible kinetic model.[60] The reported rate constants are measured bimolecular rate constants given in units of cm^3 $molecules^{-1}$ s^{-1}, whereas reaction efficiencies φ are given as fractions of the measured bimolecular rate constants and the gas-kinetic collision rates according to the capture theory.[28,29] The parameters used for H_2O were: dipole moment 1.854 D,[61] polarisability $1.45{\cdot}10^{-24}$ cm^3,[61] relative ion gauge sensitivity 0.97.[62] The parameters used for N_2O were: dipole moment 0.161 D,[61] polarisability $3.03{\cdot}10^{-24}$ cm^3,[61] relative ion gauge sensitivity 1.20.[62] The absolute error of the experimentally determined rate constants is in the range of ± 30%, while the relative rates are more precise (± 10%).[56] However, for reactions of CrF_n^+ (n = 2−4) ions with H_2O, the error is estimated to be in the range of ± 40% for the rate constants and ± 15% for their ratios due to the lower signal intensities. Ionisation energies can be determined by the "charge-transfer bracketing" method described in the following: In a series of experiments, the ion of interest is allowed to react with neutral species of known ionisation energies. Then, a *synopsis* of the ionisation energies of the reaction partners and the experimentally observed presence or absence of charge-transfer (CT) between the ion and the reaction partners allows for an estimation of the ionisation energy. Alternatively, the reaction efficiency φ of a charge-transfer reaction is correlated to the ionisation energy difference between the ion and its reaction partner: $\Delta_rG = \Delta_rG^\circ - RT\ln K$ with $K = k_{CT}/k_{\text{reverse CT}}$, $k_{CT} = \ln(\varphi/\varphi_{max})$, and $k_{\text{reverse CT}} = 1 - \ln(\varphi/\varphi_{max})$.[32] Both methods rely on the reasonable assumption that the activation barriers associated with the charge-transfer reactions are negligible. Heats of formation Δ_fH° given in this publication, are in thermochemical kilocalories ($kcal_{th}$) unless otherwise stated. When converting published values given in kilojoules, a conversion factor of 1 cal_{th} = 4.184 J[63] was applied. Ionisation energies (IE) are given in electron volts (eV), the conversion factors are 1 eV = 96.48534 kJ mol^{-1} = 23.06055 kcal mol^{-1}.[64] On calculating ion heats of formation from heats of formation and ionisation energies of the corresponding neutral species, the "stationary electron" or "ion" convention[65] was applied. To convert the data obtained at 298 K so that they are consistent with the "thermal electron" or "electron" convention, the amount of 1.481 kcal mol^{-1} needs to be added.[65]

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