GENERATION AND REACTIVITY OF CHROMIUM FLUORIDE CATIONS (CrF_n^+, *n* = 0–4) IN THE GAS PHASE

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Received May 18, 1998
Accepted June 1, 1998

Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

Gaseous chromium fluoride monocations CrF_n^+ (n = 1–4) can be prepared by sequential fluorine-atom transfer from nitrogen trifluoride, NF_3, to chromium cation. In addition, formal F^- anion transfer to CrF_n^+ (n = 2–4) to yield the corresponding neutral chromium fluorides CrF_{n+1} is observed. In conjunction with a re-evaluation of previous data, the present results provide a consistent picture of the thermochemistry of neutral and cationic chromium fluorides. The reactivity of the CrF_n^+ ions towards alkanes is investigated in a Fourier-transform ion cyclotron resonance mass spectrometer. While "bare" Cr^+ does not react with alkanes, the chromium fluoride cations CrF_n^+ do; CrF_3^+ and CrF_4^+ are even capable of activating methane. With both increasing oxidation state of chromium and increasing chain lengths of the alkane, the branching ratio of the possible reaction pathways shifts from homolytic C–H and C–C bond activation to hydride- and methanide-ion transfer to yield carbocations, and finally electron transfer generating hydrocarbon radical cations.

Key words: Chromium fluorides; Gas-phase ion chemistry; C–H bond activation; Electron transfer; Oxidation state.

The reactivity of transition metal ions in the gas phase has gained considerable attention in the past[1]. However, most of the previous investigations focused on the reactions of "bare" or monoligated transition metal monocations of lower oxidation states towards alkanes and selected model substrates for C–H and C–C bond activation. Detailed studies of the role of higher oxidation states in the gas phase are scarce, however, although higher oxidation states of chromium, *e.g.* chromium(VI) compounds, are of widespread use in oxidation reactions[2,3], and in a series of other processes such as the halogen–halogen exchange in chlorofluorocarbons and hydrofluorocarbons[4–6]. Thus, a

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direct comparison of the reactivity of the different oxidation states remains difficult and is mostly limited to certain specific cases, *e.g.* the series of OsO_n^+ cations[7].

We became interested in a systematic study of the reactivity of transition metals towards alkanes as a function of the formal oxidation state of the metal. For reasons of convenient preparation as well as an adequate description by the formalism of oxidation states, we have chosen to employ the most electronegative element, fluorine, as the covalent binding partner of the metal in this study. Due to the particularly rigid electronic properties of fluorine, *i.e.* both high electronegativity and low polarizability, it forms strong, significantly polarized bonds to most metals (M) with few back-donation from F to M almost irrespective of the actual charge[8]. Thus, increasing incorporation of fluorine shall represent a suitable mimic in terms of increasing oxidation state. The choice of chromium as a transition metal is due to its numerous synthetic applications in redox reactions as well as its particular behaviour in the gas phase. Thus, ground state Cr^+ (^6S) is among the least reactive species among all atomic transition metal monocations studied so far[9], while a reversed order of reactivity was found in the series of the monochloride cations MCl^+ (M = Cr, Mn, Fe) in which *only* $CrCl^+$ was found to be capable of activating simple alkanes[10]. Previous studies on the preparation and properties of chromium fluorides were undertaken for neutral CrF (refs[11,12]), CrF_2 (ref.[13]), CrF_3 (ref.[14]), CrF_4 (ref.[15]), CrF_5 (refs[16,17]), and CrF_6 (refs[18,19]). However, thermochemical information about cationic CrF_n^+ species is limited[20–22], and to the best of our knowledge, no ion/molecule reactions of gaseous CrF_n^+ have been described so far.

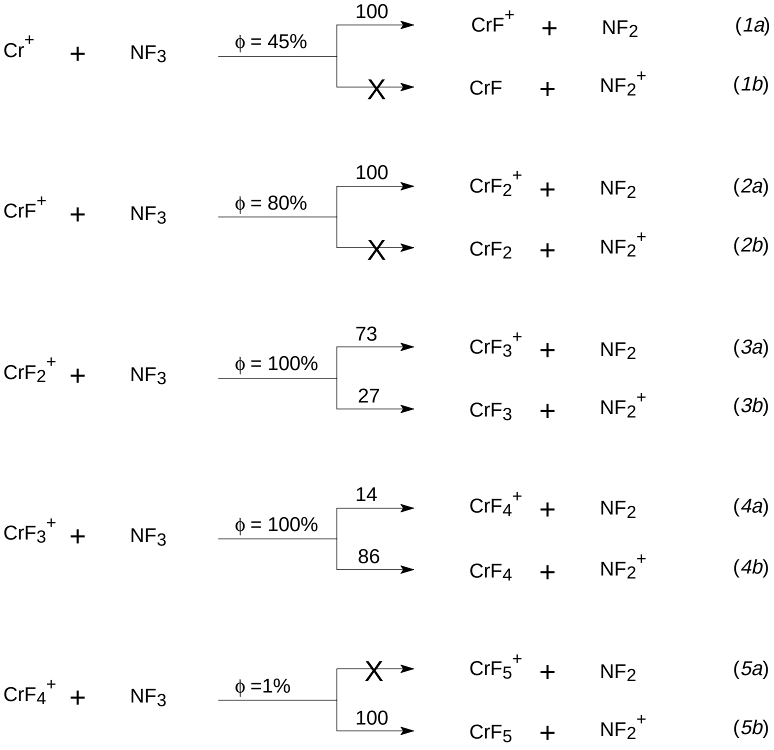
EXPERIMENTAL

The experiments were performed with a Bruker Spectrospin CMS 47 Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer whose setup and operation have been described previously[23,24]. In brief, chromium ions Cr^+ were generated from targets of pure chromium (Balzers, >99.9%) by laser desorption/laser ionization[25,26] in the external ion source using a Nd : YAG laser (Spectron Systems; λ_{max} = 1 064 nm). The chromium ions were extracted from the source and transferred *via* a system of electrostatic potentials into the analyzer cell. Then, the most abundant isotope ^{52}Cr (relative abundance 83.79%) was isolated using FERETS (ref.[27]), 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 isolation, the chromium ions were allowed to react with pulsed-in nitrogen trifluoride or nitrogen trifluoride–argon mixtures, respectively. Nitrogen trifluoride (99.99%) was purchased from Union Carbide and Praxair, the alkanes (>99.5%) were obtained from Linde, and Argon (99.996%) was purchased from AGA. [2,2-$^2H_2$]Propane was obtained from IG Chemikalien, Ismaning, Germany. The pulse lengths applied for gaseous NF_3 were adjusted in order to maximize the yields of the desired chromium fluoride cation, CrF_n^+ (n = 0–4). The ions of interest were mass-selected using FERETS again. Unless stated otherwise, the isolated ions were thermalized by allowing them to collide with either pulsed-in argon and/or the reactant gas by appropriate tuning of the pulse and delay sequences. Neutral reactants were admitted to the cell *via* a leak valve at a constant pressure in the order of (0.5–10) . 10^{-8} mbar (1 mbar = 10^2 Pa) measured by a calibrated ion gauge[28] (BALZERS IMG070). Rate constants were determined either from the pseudo first-order decay of the reactant ions or using a computer program that determines rate constants in consecutive reactions based on a flexible kinetic model and experimentally observed ion intensities[29]. The reported rate constants are given as percentages of the reaction efficiencies (ϕ); the latter representing the ratio of the measured bimolecular rate constants and the gas-kinetic collision rates calculated according to the capture theory[30–32]. The absolute error of the rate constants amounts to ±30%, while the relative rate constants are more precise (±10%, ref.[28]). Branching ratios were determined by the computer program mentioned above[29] or derived from an extrapolation of the individual product intensities to zero reaction time with explicit consideration of the background reactions (see below).

RESULTS AND DISCUSSION

Generation and Thermochemistry of the Chromium Fluoride Monocations CrF_n^+ (n = 1–4)

Chromium fluoride monocations CrF_n^+ (n = 1–4) were prepared by sequential fluorine-atom transfer from NF_3 to atomic chromium cation Cr^+. In competition with fluorine-atom transfer, also fluoride-ion transfer from NF_3 to CrF_n^+ to yield neutral CrF_{n+1} concomitant with NF_2^+ formation is observed for n = 2–4 (Scheme 1). Accordingly, the



SCHEME 1

sequence of reactions converges to yield mostly NF_2^+ cation as the terminal reaction product. Figure 1 displays the temporal evolution of the ion signals which is hardly dependent on the degree of ion thermalization *via* argon-buffer gas pulses except for CrF^+ (see below). Formation of formal Cr(VI) fluorides, either CrF_5^+ or CrF_6, is not observed experimentally. However, this result does not prove the non-existence of these species which have previously been postulated for CrF_6 (refs[16,18,33,34]), though it was claimed as well that CrF_6 does not exist, or at least, has not been properly characterized so far[17,35,36]. The only formal Cr(VI) species observed in our experiments is CrF_3O^+, probably formed in the reactions of CrF_4^+ with traces of water being present in the background of the high-vacuum system of the mass spectrometer. Further investigations of CrF_3O^+ were, however, not pursued because we do not consider CrF_3O^+ to serve as an appropriate model for a Cr(VI) compound due to the particular binding situation of the metal–oxo units[37,38]. Thus, the character of the Cr–O bond is suggested to be largely covalent as indicated by the constant decrease of the experimental Cr–O bond lengths when going from CrFO to CrF_4O (ref.[22]) as well as the results of quantum mechanical calculations[19].

In the comparison of the reactivity of nitrogen trifluoride towards (i) thermalized and (ii) non-thermalized chromium cations significant differences are found for CrF^+. The differences in the reactivities of the other ions investigated were small and could be easily attributed to the experimental uncertainties. Thus, we conclude that after the thermalization with methane neither translationally nor electronically excited Cr^+ is present in our experiments. When investigating the reactions of both thermalized and

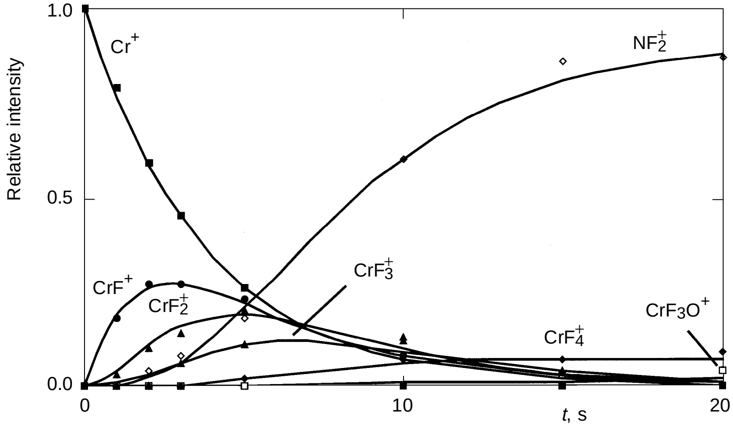


FIG. 1

Time dependence of the ion intensities in the sequential reactions of methane-thermalized Cr^+ with NF_3 ($p = 1.0 . 10^{-8}$ mbar). Experimental data are shown as points, modelled data are shown as curves. The observed species are indicated as follows: ■ Cr^+; ● CrF^+; ▲ CrF_2^+; ▲ CrF_3^+; ◆ CrF_4^+; ✧ CrF_3O^+; ❐ NF_2^+

non-thermalized CrF^+ with alkanes, we estimated the fraction of electronically excited-state ions to be about 10% of the total of this species formed by analyzing the reactivity of CrF^+ towards ethane which vanishes upon thermalization. Interestingly, these excited CrF^+ ions could not be thermalized by collision with argon or NF_3, but upon collision with the alkanes prior to smooth re-isolation of CrF^+. These results suggest that an electronically excited state of CrF^+ is formed from non-thermalized Cr^+ which is consistent with the prediction of low-lying excited states in quantum mechanical calculations by Harrison[39]. The only other species found to populate electronically excited states was CrF_4^+. Non-thermalized chromium tetrafluoride cation shows rapid reaction with methane while its ground-state reactivity towards CH_4 is small. In addition, the reactivity of non-thermalized CrF_4^+ towards NF_3 was found to be nine times as high as the ground-state reactivity towards the same reactant. Hence, the excited state can be depleted by reaction with NF_3.

From the mere occurrence of reactions (*1*)–(*5*) for the thermalized ions (Scheme 1), some valuable thermochemical information can be derived, because only thermoneutral or exothermic reactions can occur under the conditions prevailing in our experimental setup[40]. Thus, fluorine-atom transfer (labelled as reactions (*a*) in Scheme 1) from NF_3 can only occur if the respective bond dissociation energy $D(F_nCr^+–F)$ is equal to or larger than $D(F_2N–F)$ = 58 kcal/mol (1 kcal = 4.18 kJ). Similarly, reactions (*b*) require the heterolytic bond cleavage energy $D(F_nCr^+–F^–)$ to exceed 247 kcal/mol (or 10.7 eV)

TABLE I
Heats of formation, ΔH_f^0 (kcal/mol), of neutral chromium fluorides in the gas phase and of other species relevant in this work.

Species	ΔH_f^0, kcal/mol		
	ref.[41]	ref.[22]	ref.[42]
Cr	–	–	94.8
CrF	5	4.6 ± 2.4	–
CrF_2	–52	–103.2 ± 3.0	–
CrF_3	–158	–199.8 ± 3.4	–
CrF_4	–	–270.0 ± 2.1	–
CrF_5	–	–290.7 ± 5.3	–
F	–	–	19.0
NF_2	–	–	8
NF_3	–	–	–31.0
NF_2^+	–	–	275
Cr^+	–	–	250.8

which is the amount of energy required for the process $NF_3 \rightarrow NF_2^+ + F^-$. Unfortunately, two largely divergent sets of data exist for the neutral CrF_2 and CrF_3 (Table I) which differ by more than 40 kcal/mol in terms of heats of formation[22,41]. Thus, prior to a detailed analysis of the present data with respect to thermochemical quantities, a consistent set of data needs to be established for the neutral chromium fluorides. Such a selection is, fortunately, possible by combining the known data with our results in terms of a thermochemical cycle. Let us begin this evaluation with the heat of formation for neutral chromium(I) fluoride, *i.e.* $\Delta H_f^0(CrF) = 4.6 \pm 2.4$ kcal/mol, upon which both literature sources agree[22,41]. Taking the previously measured value[41,42] of 8.4 ± 0.3 eV for the ionization energy (I) of CrF (see below), we obtain $\Delta H_f^0(CrF^+) = 199 \pm 9$ kcal/mol. Thus, the experimentally observed occurrence of reaction (*2a*) implies the process to be either exothermic or at least approximately (±1 kcal/mol for $\phi = 80\%$) thermoneutral, and by such it requires $\Delta H_f^0(CrF_2^+) < 160 \pm 10$ kcal/mol. In conjunction with $I(CrF_2) = 10.1 \pm 0.3$ eV (refs[41,42]) (see below), we arrive at an upper bound of $\Delta H_f^0(CrF_2) < -73 \pm 12$ kcal/mol. While this value is certainly too large because it assumes reaction (*2a*) to be thermoneutral (see below), $\Delta H_f^0(CrF_2) = -52$ kcal/mol given in thermochemical tables[41,42] is beyond reasonable error limits, and is therefore incorrect. Accordingly, we neglect this value and adopt the complete set of data recently reported by Ebbinghaus[22] for the neutral chromium fluorides.

In their previous study on Cr, Mn, and Fe fluorides, Zmbov and Margrave[20] also reported ionization energies of gaseous chromium fluorides based on appearance energy measurements. Due to the obvious discrepancy of the neutral values, however, as well as possible sources of error in appearance energy measurements, we have cross-checked these values by reacting the mass-selected CrF_n^+ ions ($n = 1–4$) with appropriate substrates of known ionization energies in order to determine $I(CrF_n)$ by the bracketing method. Assuming a complete thermalization of the precursor ions, the occurrence or absence of electron transfer from the neutral substrate to the ion of interest can be used to determine the (adiabatic) ionization energy of the corresponding neutral counterparts. In the particular case of electron transfer, we neglect kinetic barriers such that the reaction efficiency can be regarded as a direct measure of the reaction thermochemistry. Thus, very exothermic electron transfer occurs with unit efficiency, highly endothermic electron transfer does not take place at all, and in the intermediate energy range from *ca* –5 to +5 kcal/mol the rate constant is a sigmoid function of the reaction enthalpy, because also slightly endothermic reactions (<0.2 eV) may occur under FT-ICR conditions to a certain extent due to thermal contributions[40]. Even though the assumption of barrierless electron transfer seems appropriate, there exists a serious restriction to this approach which needs to be pointed out. In any case in which besides electron transfer also other efficient reaction channels are accessible (*e.g.* bond activation), charge transfer may be suppressed and eventually disappear completely due to this competition. Accordingly, in reactions occurring with efficiencies close to unity, the absence of a particular process cannot be used in the bracketing approach.

In the corresponding bracketing experiments it is found that CrF^+ cation undergoes charge transfer with naphthalene (I = 8.1 eV), but not with quinoline (I = 8.6 eV), thus fully confirming the previous value[41,42] $I(CrF) = 8.4 \pm 0.3$ eV. Similarly, good agreement with $I(CrF_2) = 10.1 \pm 0.3$ eV (refs[41,42]) was found in that CrF_2^+ cation undergoes charge transfer with hexafluorobenzene (I = 9.9 eV) but not with ethylene (I = 10.5 eV). As expected, however, some deviation was found for the higher chromium fluorides. Thus, the absence of *any* reactivity of CrF_3^+ cation towards oxygen (I = 12.1 eV) conflicts with $I(CrF_3) = 12.2 \pm 0.3$ eV reported by Zmbov and Margrave[20]. In conjunction with the occurrence of rapid charge transfer of CrF_3^+ with carbonyl sulfide (I = 11.2 eV), we therefore establish a value of $I(CrF_3) = 11.5 \pm 0.4$ eV. Similarly, the bracketing method suggests $I(CrF_4) = 12.3 \pm 0.3$ eV due to the occurrence of rapid charge transfer in the reaction of CrF_4^+ with O_2 (I = 12.1 eV), negligible charge transfer with methane (I = 12.6 eV) and its complete absence with NF_3 (I = 13.0 eV). These ionization energies of the neutral chromium fluorides also nicely agree with the branching ratios between the paths (*a*) and (*b*) observed in reactions (*1*)–(*5*). Thus, in the reactions of Cr^+ and CrF^+ with NF_3, fluoride transfer to afford NF_2^+ cation is not observed at all because $I(CrF)$ and $I(CrF_2)$ are much lower than $I(NF_2^{\bullet}) = 11.6$ eV. Channel (*b*) begins to compete in the reaction of NF_3 with CrF_2^+, but yet the formation of cationic CrF_3^+ + $NF_2^{\bullet}$ predominates as compared to the route leading to the charged-permuted products NF_2^+ + CrF_3. In contrast, route (*b*) prevails in reaction (*4*) because $I(NF_2^{\bullet}) = 11.6$ eV is significantly lower than $I(CrF_4) = 12.3 \pm 0.3$ eV. Along this series of reactions, the exclusive observation of channel (*b*) in reaction (*5*) implies that $I(CrF_5)$ is at least of similar size as $I(CrF_4)$ and most likely even exceeds it; tentatively, we assign $I(CrF_5) >$ 12.5 eV.

Combination of this thermochemical information leads to the energetics of gaseous chromium fluorides as depicted in Table II. This background information shall provide a solid basis for the understanding of the ion/molecule reactions described further below. Furthermore, we would like to point out that this set of data is consistent with all reactions described here in that those processes which are observed to occur experimentally are also predicted to be exothermic. The trends among the CrF_n series are quite smooth and follow general expectation. Thus, the ionization energies increase with n, while the Cr–F bond energies decrease with increasing oxidation state of the metal. The only notable exception from this rule is the couple CrF/CrF_2 for which $D(Cr–F) < D(FCr–F)$ for the cations and the neutrals as well. This difference can be attributed to the particular electronic structure of chromium. For example, for formation of CrF^+ in its $^5\Sigma^+$ ground state[39] from the atoms, the half-filled $4s^03d^5$ configuration of bare Cr^+ needs to be broken. Accordingly, a considerable amount of exchange energy is lost upon Cr^+–F bond formation, thus lowering the bond energy. In contrast, the monofluoride can be viewed as the "prepared state" (for similar effects in sequential Mo–O bond stregths see refs[43,44]) to accept a second fluorine ligand upon formation of the difluoride which we assume to have a quartet ground state. This rationale also accounts for the finding that the reaction of bare Cr^+ with NF_3 has a moderate efficiency although it is predicted to be exothermic by about 13 kcal/mol.

Reactivity of the Chromium Fluoride Monocations Towards Alkanes

Before discussing the reactions of CrF_n^+ cations with alkanes, let us briefly address the reactions occurring with background water. Thus, sequential exchanges of the fluorine ligands by hydroxy groups are observed. Obviously, the strong H–F bond in hydrogen fluoride provides the driving force for this reaction; for example, reaction (*6*) is exothermic by about 17 kcal/mol based on $D(Cr^+–OH) = 71 \pm 3$ kcal/mol (ref.[45]).

$$CrF^+ + H_2O \rightarrow CrOH^+ + HF \tag{6}$$

Similar substitution reactions are observed for almost all ions under investigation, thus CrF_2^+ yields $FCr(OH)^+$ and then $Cr(OH)_2^+$, $(C_3H_6)CrF^+$ yields $(C_3H_6)CrOH^+$ *etc.*; the pseudo first-order rate constants of these processes showed typical day-to-day variations depending on the actual water content of the machine. Obviously, also the above mentioned CrF_3O^+ cation is formed by reaction with background water. However, due to the variety of $Cr(OH)_mF_n^+$ species present at longer reaction times, we could not

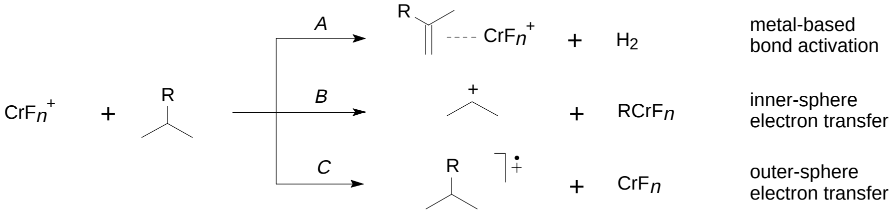
TABLE II
Bond dissociation energies $D(F_nCr–F)$ in kcal/mol of gaseous neutral and cationic chromium fluorides and ionization energies in eV of the neutral species.

Species	$D(F_nCr–F)$, kcal/mol		*I*, eV
	neutral[a]	cation[b]	
Cr–F	109 ± 2	71 ± 9	8.4 ± 0.3[c,d]
FCr–F	127 ± 5	88 ± 9	10.1 ± 0.3[c,d]
F_2Cr–F	116 ± 6	84 ± 11	11.5 ± 0.4[b,e]
F_3Cr–F	89 ± 5	70 ± 13	12.3 ± 0.3[b]
F_4Cr–F	40 ± 7	<58[f]	>12.5[g]

[a] ref.[22] [b] This work. [c] ref.[20] [d] Value confirmed in this work by means of charge-transfer bracketing. [e] Value given by ref.[20] was revised in this work by means of charge transfer bracketing. [f] Upper limit derived from the absence of CrF_5^+ in the reaction of CrF_4^+ with NF_3. [g] Estimated based on the branching of the reactions (*5a*) and (*5b*), see text.

unambiguously clarify the precursor for CrF_3O^+; a plausible sequence involves the reactions $CrF_4^+ + H_2O \rightarrow CrF_3(OH)^+ + HF$ and $CrF_3(OH)^+ + NF_3 \rightarrow CrF_3O^+ + HF + NF_2$. In the analysis of the reaction of CrF_n^+ ions with alkanes, these background reactions were fully deconvoluted, however, and unless noted otherwise these reactions with background water are not reported.

As a representative set of substrates in the study of the reactivities of CrF_n^+ cations as a function of the oxidation state, we have chosen some simple alkanes. Conceptually, three different types of reactions are conceivable which are depicted for an alkane C_3H_7R in Scheme 2. (*A*) Metal-mediated C–H and/or C–C bond activation *via* oxidative addition followed by reductive elimination to yield closed shell neutrals. For example, the first step of alkane dehydrogenation by CrF^+ is assumed to be a bond insertion of the metal fragment which is followed by β-hydrogen transfer and loss of dihydrogen. Note that the metal preserves its oxidation states in the reactants and products. The thermochemical driving force for dehydrogenation is provided by the formation of an alkene which serves as a ligand to the metal ion[1], *i.e.* $D(FCr^+–C_3H_6) > 29.8$ kcal/mol. In the insertion intermediates, however, higher oxidation states of the metal are involved such the propensity of this route is expected to decrease with increasing number of fluorine ligands. (*B*) As the oxidation state of the metal increases the fragment becomes more electron withdrawing such that bond activation involving formal anion transfer becomes accessible to afford carbocations together with neutral chromium fragments $RCrF_n$. As this process involves reduction of the metal, we assign this route as a formal *inner-sphere* electron transfer from the hydrocarbon residue to the metal. (*C*) If the oxidation state increases further, the recombination energy of CrF_n^+ may also permit *outer-sphere* electron transfer from the alkane to chromium to afford organic cation radicals and neutral CrF_n.



SCHEME 2

As expected, the reactivity of the CrF_n^+ cations increases with the number of fluorine ligands (Table III). Thus, thermalized bare Cr^+ cations do not react with any of the alkanes studied[9]; however, translationally as well as electronically excited chromium cations activate alkanes[46–48]. The monofluoride cation CrF^+ is found to dehydrogenate propane and higher alkanes, and CrF_2^+ already promotes C–H bond activation of ethane, and CrF_3^+ as well as CrF_4^+ are even capable of activating methane. Quite clearly, there exists an increase in reactivity for the higher-oxidized chromium species and parallel to this trend, we observe a significant switch from homolytic bond cleavage to hydride or electron transfer. For CrF_4^+, however, hydride transfer (for methane through propane) and methyl group transfer (for both n-butane and isobutane), respectively, outnumbers the electron transfer which had accounted for a substantial fraction of the reactivity of

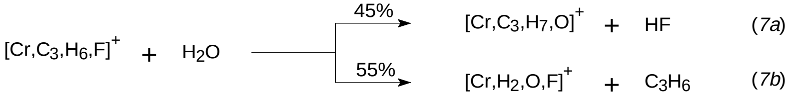
TABLE III
Efficiencies (bold figures, given as percentages of the collision rate constants) and ionic products of the reactions of chromium fluoride cations with alkanes in the gas phase. For the explanation of reaction channels *A*, *B*, *C*, see Scheme 2 and text[a].

Alkane	Cr^+	CrF^+	CrF_2^+	CrF_3^+	CrF_4^+
CH_4	**n.r.**	**n.r.**	**n.r.**	**40**	**0.7**
A				25% $CrF_2CH_3^+$	15% $CrF_3CH_3^+$
					85% CrF_2^+
B				75% CH_3^+	
C_2H_6	**n.r.**	**n.r.**	**8**	**100**	**100**
A			100% $CrFC_2H_5^+$	20% $CrFC_2H_4^+$	
B				80% $C_2H_5^+$	35% $C_2H_5^+$
C					20% $C_2H_4^+$
					45% $C_2H_6^+$
C_3H_8	**n.r.**	**2**	**40**	**100**	**100**
A		100% $CrFC_3H_6^+$	7% $CrFC_3H_5^+$		
B				10% $C_2H_5^+$	5% $C_2H_5^+$
			93% $C_3H_7^+$	50% $C_3H_7^+$	60% $C_3H_7^+$
C				5% $C_2H_4^+$	20% $C_2H_4^+$
					7% $C_3H_6^+$
				35% $C_3H_8^+$	8% $C_3H_8^+$
n-C_4H_{10}	**n.r.**	**20**	**60**	**100**	**100**
A		100% $CrFC_4H_8^+$	4% $CrFC_3H_5^+$		
B				55% $C_3H_7^+$	75% $C_3H_7^+$
			96% $C_4H_9^+$	10% $C_4H_9^+$	10% $C_4H_9^+$
C				10% $C_3H_6^+$	3% $C_3H_6^+$
				25% $C_4H_{10}^+$	12% $C_4H_{10}^+$
i-C_4H_{10}	**n.r.**	**20**	**80**	**100**	**100**
A		100% $CrFC_4H_8^+$			
B			30% $C_3H_7^+$	45% $C_3H_7^+$	72% $C_3H_7^+$
			70% $C_4H_9^+$	5% $C_4H_9^+$	5% $C_4H_9^+$
C				50% $C_3H_6^+$	23% $C_3H_6^+$

[a] n.r. stands for no reactivity indicating an upper limit ϕ = 0.01%.

propane and the butanes towards CrF_3^+. However, before analyzing these trends in the reactivity of CrF_n^+ cation with respect to the role of the oxidation state, some of the reactions should be addressed more specifically.

A) Significant enhancement of the reactivity of chromium by the fluorine ligand in CrF^+ becomes obvious by comparison to Cr^+ and $CrCl^+$ which both do *not* activate propane under thermal conditions[9,10], while CrF^+ dehydrogenates propane, though not very efficiently ($\phi \approx 0.02$). If [2,2-$^2H_2$]propane is reacted with CrF^+, losses of H_2 and HD are observed in a ratio of 40 : 60, which is not too different from that expected for a complete equilibration of H and D atoms (56 : 44). Loss of D_2 to yield $[Cr,C_3,H_6,F]^+$ could not be detected above the signal-to-noise level (4%), however, not more than 3% can be expected for complete equilibration. Accordingly, a reversible step in the reaction mechanism must allow for H/D scrambling. The structure of the ionic reaction product $[Cr,C_3,H_6,F]^+$ is elucidated by the subsequent reactions (*7a*) and (*7b*) with background water (Scheme 3).

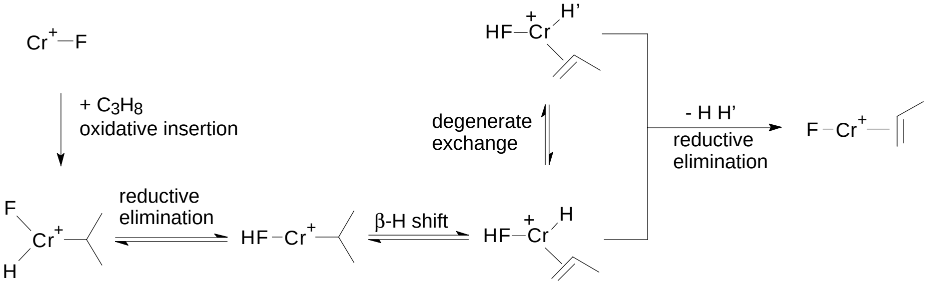


SCHEME 3

In the corresponding reactions of the [^{2}H]- and [$^2H_2$]-labelled ions formed from CrF^+ and [2,2-$^2H_2$]propane, only HF is lost in reactions (*7a*) and only labelled propenes are lost in reactions (*7b*). Thus, in analogy to reactions (*7a*) and (*7b*), $[Cr,C_3,H_4,D_2,F]^+$ yields $[Cr,C_3,H_5,D_2,O]^+$ and $[Cr,H_2,O,F]^+$, respectively, while $[Cr,C_3,H_5,D,F]^+$ yields $[Cr,C_3,H_6,D,O]^+$ and $[Cr,H_2,O,F]^+$, respectively. These results suggest formation of the propene complex $(C_3H_6)CrF^+$ as the reaction product, *i.e.* reaction (*7a*) corresponds to an exchange of the fluorine ligand by OH in analogy to reaction (*6*) and reaction (*7b*) is due to displacement of the propene ligand by water. Further information with respect to the initial attack of propane by CrF^+ can be gained from the observation that only $C_3H_6D^+$ cation concomitant with neutral [Cr,D,F] but not $C_3H_5D_2^+$ in the reaction of non-thermalized CrF^+ with [2,2-$^2H_2$]propane. Thus, the initial step in the reaction of propane with CrF^+ is assumed to exhibit a high preference for C–H bond activation of the secondary position.

With respect to the reaction mechanism, a plausible scenario suggests that C–H bond activation of the methylene group is followed by a series of reversible hydrogen-atom transfers that are terminated by loss of dihydrogen (Scheme 4). While this scheme would mechanistically also allow for loss of neutral hydrogen fluoride, this channel is not observed experimentally because formation of $Cr(iso\text{-}C_3H_7)^+$ + HF is predicted to be endothermic by about 6 kcal/mol (refs[42,47]).

B) In the reaction of CrF_2^+ with ethane, dehydrofluorination is observed exclusively. The product ion $[Cr,C_2,H_5,F]^+$ may either exhibit an inserted structure, *i.e.* ethylchromium fluoride, $C_2H_5CrF^+$, or correspond to a mere ion–dipole complex, *i.e.* either $(C_2H_4)Cr(HF)^+$ or $Cr(C_2H_5F)^+$. Unfortunately, the consecutive reactions with background water do not permit a distinction between these options, because the reaction products are compatible with all structures. For example, $[Cr,C_2,H_6,O]^+$ may be formed from either $C_2H_5CrF^+$ or $(C_2H_4)Cr(HF)^+$, $[Cr,F,H_2,O]^+$ may arise from $C_2H_5CrF^+$ or $(C_2H_4)Cr(HF)^+$, $[Cr,F,O,H]^+$ may be formed from both $C_2H_5CrF^+$ and CrF_2^+, and finally, $[Cr,H_2,O]^+$ can only be formed from $Cr(C_2H_5F)^+$. Nevertheless, this is the almost exclusive reaction product of CrF_2^+ with alkanes in which the chromium remains in a charged state, while carbocation formation prevails for propane and butane. As it is not reasonable to expect fundamental changes of the reaction mechanisms along this series, we conclude that formation of $C_2H_5^+$ from the CrF_2^+/C_2H_6 couple is simply endothermic. Together with the formation of $C_3H_7^+$ for the CrF_2^+/C_2H_6 couple, we arrive at $\Delta H_f^0(CrF_2H) = -96 \pm 9$ kcal/mol. This value implies the formation of the neutral hydrido chromium(III) difluoride $HCrF_2$ with $D(H\text{–}CrF_2) > 45$ kcal/mol, because generation of CrF + HF is not feasible ($\Sigma\Delta H_f^0 = -60 \pm 3$ kcal/mol) and formation of the neutral chromium(I) species (HF)CrF would require an interaction energy of at least 24 kcal/mol which appears unreasonably large for a mere van der Waals complex of two neutral species. Finally, similar to the results obtained for the diatomic CrF^+ cation, monolabelled $C_3H_6D^+$ is the only (>98%) carbocation formed in the reaction of CrF_2^+ with $[2,2\text{-}^2H_2]$propane, indicating a large degree of selectivity of the formal hydride transfer from propane to CrF_2^+.



SCHEME 4

C) The reactions of CrF_3^+ and CrF_4^+ with alkanes show low selectivities and rather complex product distributions. Moreover, except for a minor channel for the CrF_3^+/CH_4 couple, the chromium is part of the neutral fragments. In addition, the selectivity in hydride transfer is drastically diminished; for example, a 3 : 1 ratio of $C_3H_6D^+$ and $C_3H_5D_2^+$ is obtained in the reaction of CrF_3^+ with $[2,2\text{-}^2H_2]$propane. Thus, a more detailed product analysis for CrF_3^+ and CrF_4^+ seems not indicated. One interesting aspect concerns, however, the reaction efficiency with methane which decreases drastically from CrF_3^+ to CrF_4^+. Obviously, thermochemical effects cannot explain this trend, because $I(CrF_4) > I(CrF_3)$ and $D(F_3Cr–F) > D(F_2Cr–F)$. Rather, we propose that this behaviour is due to the structure of CrF_4^+ which supposedly has T_d symmetry with the positive charge being located on the central chromium and the electronic structure of the molecule's surface being characterized by the fluorine atoms' negative partial charges. Consequently, the reaction of two T_d symmetrical molecules with electronically "saturated" surfaces, *i.e.* CrF_4^+ and CH_4, is expected to be less efficient than the reaction of species having other geometric and electronic structures, *i.e.* CrF_3^+ and CH_4.

Finally, we would like to analyze in brief the reactivity as a function of oxidation state in order to evaluate possible trends (Fig. 2). For this purpose, we schematically treat the reaction products according to the classification defined above in Scheme 2. As defined above, category *A* describes metal-based bond activation in which the positive charge is more or less localized at the metal and organic closed-shell neutrals are lost. Category *B* refers to *inner-sphere* electron transfer and comprises all formal anion transfers from the alkanes to the chromium fluoride cations which lead to (closed-shell) carbocations. Finally, category *C* describes direct *outer-sphere* electron transfer to afford organic radical cations along with neutral species CrF_n. In addition to these categories, each channel in the reactions from methane through isobutane is weighted with respect to the reaction efficiency. By such a scheme, the relative reactivities of the CrF_n^+ cations can be obtained[49,50]. Thus, for low-valent metal complexes we expect primarily metal-based reactions which can show a significant degree of selectivity. With increasing oxidation state, Lewis acidity increases, and both hydride and alkanide anion abstraction begin to compete. Nevertheless, a significant degree of selectivity is

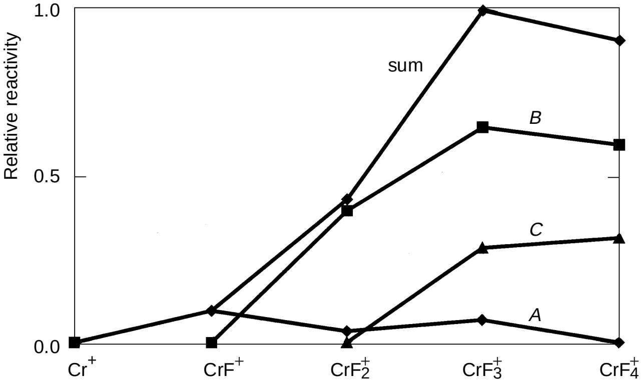


FIG. 2

Relative reactivities of CrF_n^+ cations towards alkanes from methane through isobutane. Processes *A*, *B*, and *C* are described in the text and in Scheme 2. The relative reactivities (ϕ_{rel}) are determined as the fraction of the sum of reactions leading to products of a particular category in conjunction with the overall efficiency of the respective reaction and divided by the number (*n*) of reactions considered, i.e. $\phi_{rel} = \Sigma(\phi_i \cdot k_i / \Sigma k_i)/n$. sum refers to the total of the processes *A*, *B*, and *C*. The processes are indicated as follows: ◆ *A*, ■ *B*, ▲ *C*, ◆ sum observed in anion transfer though carbocationic rearrangements of the products are likely to occur. Further increase of the formal oxidation state allows for outer-sphere electron transfer from the neutral substrate to the cationic metal fragment, and several reactions begin to compete while the selectivity decreases drastically. In conclusion, the concept of increasing reactivity by oxidation of the metal holds true, but it is likely to be associated with a significant loss of selectivity. Hence, "brute-force" enhancement of reactivity by means of high oxidation states is not the method of choice to selectively activate particular bonds in alkanes.

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung.

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