Which Electronic State Is Involved in the Activation of CH- and CC-Bonds of 4-Octyne by Bare Chromium Ions?**

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Abstract: In previous work we reported the unexpectedly rich gas-phase chemistry of complexes of $Cr^{\oplus}$ with 4-octyne. Results, based on high-resolution translational energy loss spectroscopy (HRTELS) and charge stripping mass spectrometry (CSMS), are now presented which prove that $Cr^{\oplus}$ generated by electron impact ionization of $[Cr(CH_3COCH_2COCH_3)_3]$ corresponds to the ground state of $Cr^{\oplus}$ ($3d^5$, a^6S). It is also demonstrated that $Cr^{\oplus}$-induced CH- and CC-bond activations, followed by reductive eliminations of H_2, CH_4 and C_2H_4, are truly unimolecular reactions with practically no collision-induced contributions.

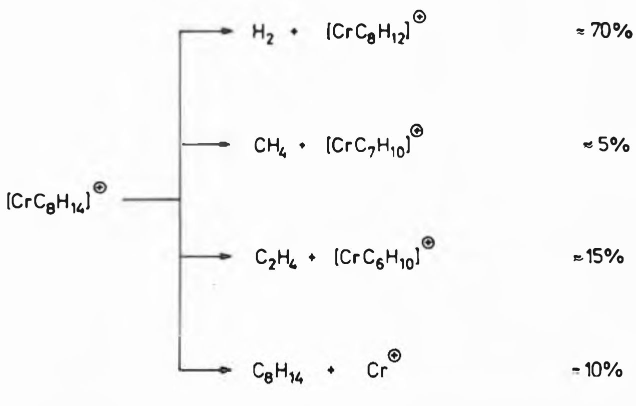
There are many reports on the low (if not absent) reactivity of ground-state bare chromium(I) ions with organic substrates[1]. In most cases in which oxidative addition of a bond R–X (X = C, H, N, O, halogen) to $Cr^{\oplus}$ has been observed the reaction was ascribed to the presence of long-lived (> ms)[1f] low-lying, excited electronic states of $Cr^{\oplus}$. There is indeed ample evidence [1a, b, e, f] that electron impact ionization of $[Cr(CO)_6]$ generates both ground state ($3d^5$, a^6S) and approximately 70% long-lived excited state metal ions. While the former are interpreted to be nonreactive, the latter with so far not unambiguously identified electronic states are suggested to be involved in the insertion of the bare metal ion into the R–X bonds.

In distinct contrast to most reports we recently noted[2] that the gas-phase reaction of bare $Cr^{\oplus}$ (generated by 100 eV electron impact ionization of $[Cr(CH_3COCH_2COCH_3)_3]$) with C_8H_{14} (4-octyne) is unexpectedly versatile in that both CH- and CC-activations take place. Without being subjected to further collisional activation the complex $[CrC_8H_{14}]^{\oplus}$ gives rise to the products shown in Scheme 1 (expressed in % fragment ions generated from mass-selected $[CrC_8H_{14}]^{\oplus}$ complexes). It should be mentioned, that the product distribution shown in Scheme 1 is not sensitive to the mode by which the $[CrC_8H_{14}]^{\oplus}$ complexes are made. For example, generation of $Cr^{\oplus}$ by 100 eV ionization of $[Cr(CO)_6]$ or by fast atom bombardment of aqueous solutions of either $CrCl_3$ or CrO_3 with 8 keV xenon atoms resulted in $[CrC_8H_{14}]^{\oplus}$ complexes whose unimolecular dissociations were practically the same as those shown in Scheme 1.

From the study of deuterated isotopomers of 4-octyne further details were revealed which are pertinent to the mechanism of fragment ion formations. For example, $Cr^{\oplus}$-induced dehydrogenation follows a clean 1,2-elimination involving 22% hydrogen from C-1/C-2 and 78% from positions C-2/C-3, respectively. From a study of the kinetic isotope effect it was further concluded that the rate-determining step is not associated with the oxidative addition of a carbon-hydrogen bond to the metal ion but rather to the reductive elimination of a hydrogen molecule. The positional loss of hydrogen atoms («scrambling») which is often observed in gas-phase chemistry of hydrocarbons is not observed in the $[CrC_8H_{14}]^{\oplus}$ system.

$Cr^{\oplus}$-induced demethanation is also a clean process in that methane is exclusively formed in a formal 1,2-elimination mode involving the terminal, intact CH_3 group and a H atom which originates from C-3. Highly remarkable isotope effects were reported[2] for this process, the origins of which are, however, not yet fully understood.

Scheme 1



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The $Cr^{\oplus}$-induced elimination of C_2H_4 from $[CrC_8H_{14}]^{\oplus}$ is also quite unique in that the reaction is, as is the case for the $Fe^{\oplus}$-induced loss of C_2H_4 from $Fe^{\oplus}$/4-octyne[3], highly site-specific; the neutral is formed without any hydrogen scrambling from C-1/C-2. In contrast to $Fe^{\oplus}$, however, the isotope effect is associated with the insertion of $Cr^{\oplus}$ into the CH-bond of the terminal methyl group; for the $[CrC_8H_{14}]^{\oplus}$ system the detachment of ethylene is not affected by an isotope effect. Quite interestingly, the opposite holds for $Fe^{\oplus}$/4-octyne[3].

No doubt that these unprecedented results raise several questions, as for example: (i) Can one rule out collision-induced contribution as a major source to the reactions described in Scheme 1? (ii) Which states of $Cr^{\oplus}$ are involved?

In the following, experiments are reported which address these questions and which shed further light on the truly remarkable gas-phase chemistry of $Cr^{\oplus}$ with organic substrates. In particular, it will be demonstrated that (i) the reactions described in Scheme 1 (except for the ligand detachment of C_8H_{14}) are not collision-induced and (ii) the $Cr^{\oplus}$ species generated by 100 eV electron impact ionization of $[Cr(CH_3COCH_2COCH_3)_3]$ under pressure conditions comparable to the one used in the formation of $[CrC_8H_{14}]^{\oplus}$ complexes correspond to the ground state of $Cr^{\oplus}$ ($3d^5$, a^6S).

Experimental Section

The experimental set-up has been described in detail in earlier papers[2, 3d, 4]. Briefly, bare $Cr^{\oplus}$ ions were generated by 100 eV electron impact ionization of $[Cr(CH_3COCH_2COCH_3)_3]$ which was introduced together with 4-octyne via the direct insertion probe and the septum inlet system, respectively, in the chemical ionization source of a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer of BEB configuration (B denotes magnetic and E electric sector)[5] at the following conditions: emission current 0.5 mA; repeller voltage 0 V; acceleration voltage 8 kV; mass resolution 3000 (10% valley definition); ion-source housing pressure $10^{-5.5}$ mbar (the actual pressure in the ion source is unknown but likely to be of the order of several tenths of a mbar); ion-source temperature 200 °C. Fast atom bombardment experiments were performed as described previously[6]. The ion-source generated metal ion/alkyne complex $[CrC_8H_{14}]^{\oplus}$ of 8 keV kinetic energy was mass-selected and focussed with B(1)E; unimolecular dissociations occurring in the field-free region between E and B(2) were monitored by scanning B(2). Collisional activation (CA)[7] of $[CrC_8H_{14}]^{\oplus}$ ions was brought about by introducing helium as a collision gas in the differentially pumped collision cell located in the field-free region between E and B(2). The pressure in the collision cell-housing was varied between 10^{-8} mbar (which corresponds to practically *no* collision events) and 10^{-5} mbar.

In order to probe the electronic state(s) of $Cr^{\oplus}$ generated by electron impact ionization of $[Cr(CH_3COCH_2COCH_3)_3]$ at ion-source pressures compatible to those used to make $[CrC_8H_{14}]^{\oplus}$ two different kinds of experiments were performed. Firstly, by using charge stripping mass spectrometry (CSMS)[7, 8] the ionization energy $IE(Cr^{\oplus})$ for the process $Cr^{\oplus} \rightarrow Cr^{2\oplus} + e^{\ominus}$ was determined. To this end, mass-selected $Cr^{\oplus}$ ions of 8 keV translational energy were collided in the field-free region between B(1) and E with oxygen, and the minimal translational energy loss, Q_{min}, which corresponds to a first approximation to $IE(Cr^{\oplus})$, was measured from the displacement from E/2 as described in detail in Ref.[8]. The energy scale was calibrated by determining Q_{min} for the charge-stripping reaction $C_7H_8^{\oplus\odot} \rightarrow C_7H_8^{2\oplus}$ ($IE = 15.7$ eV)[9].

In a second experiment, the electronic state of $Cr^{\oplus}$ was probed by using high-resolution translational energy loss spectroscopy (HRTELS)[1i, 10]. Briefly, $Cr^{\oplus}$ ions of 8 keV are mass-selected by B(1) and focussed in a collision cell (housing pressure $10^{-4.7}$ mbar; collision gas helium). Translational energy analysis of the unscattered main ion beam and its scattered components is accomplished by scanning E. In the absence of the collision gas, the energy resolution of the $Cr^{\oplus}$ beam is < 0.4 eV (fwhm). During the collision between He and 8 keV $Cr^{\oplus}$, the internal energy of the ion may be altered due to excitation of ground or de-excitation of excited states of $Cr^{\oplus}$. The former event will result in peaks at lower and the latter in signals at higher energies relative to the kinetic energy of the unscattered $Cr^{\oplus}$ beam. The experimental set-up is such that only collision occuring at small scattering angles will be recorded, for which translational energy losses of the ion correspond to changes in the ion's internal energy[10].

Results and Discussion

Let us begin with the question as to whether the reactions described in Scheme 1 are truly unimolecular processes (driven by the energy gained in the formation of the $[CrC_8H_{14}]^{\oplus}$ complex from isolated reactants) or whether they are due to collisional activation. The results, given in Fig. 1, are unambiguous. Over the entire pressure range of collision gas (10^{-8} to 10^{-5} mbar), the loss of C_2H_4 is, within experimental error, insensitive to pressure. The same applies for the elimination of CH_4 which, for the sake of clarity, is not shown in Fig. 1. Similarly, hydrogen loss is over nearly two orders of magnitude insensitive to the pressure of the collision gas. The relative decrease of H_2 loss at pressures of 10^{-6} mbar is quite likely to reflect the normalization procedures as this decrease corresponds to an increase in the ligand detachment reaction, i.e. the process $[CrC_8H_{14}]^{\oplus} \rightarrow Cr^{\oplus} + C_8H_{14}$. As the latter reaction is known [1o, p, r] to be affected by collisions, we conclude that the products formed by $Cr^{\oplus}$-induced CH- and CC-activations are practically free of any major collision-induced contributions.

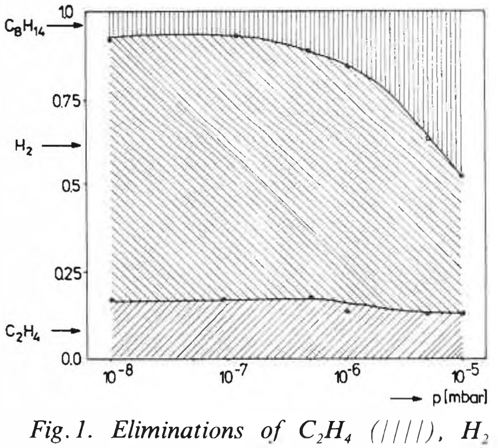

Fig. 1. Eliminations of C_2H_4 (////), H_2 (\\\\\\\\), and C_8H_{14} (||||) from $[CrC_8H_{14}]^{\oplus}$ as a function of collision gas (helium) pressure. Intensities are expressed as Σ 100%.

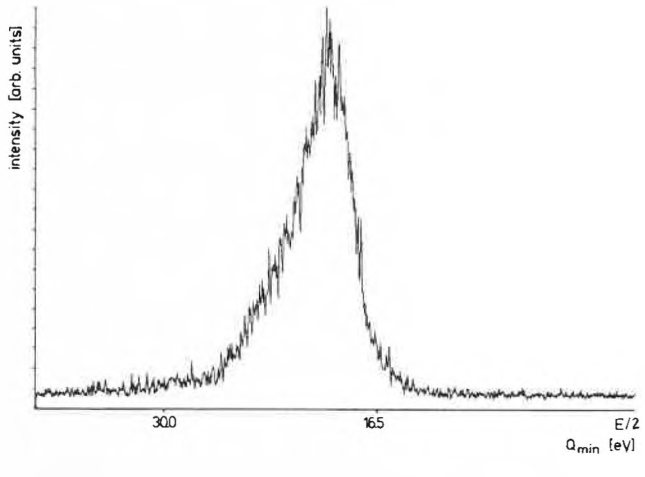

Fig. 2. Charge stripping spectrum of the reaction $Cr^{\oplus} \rightarrow Cr^{2\oplus}$. $Cr^{\oplus}$ is generated by 100 eV electron impact ionization of $[Cr(CH_3COCH_2COCH_3)_3]$; $p_{O_2} = 10^{-6}$ mbar.

We have also considered the possibility that in the course of acceleration to 8 keV the ion-source formed complex $[CrC_8H_{14}]^{\oplus}$ might be activated by collisions with neutral molecules in the ion source. If this were the case, the product distribution shown in Scheme 1 should be affected by varying the acceleration voltage. Over the range 8–1.5 kV there is no change discernible with regard to the products and their distributions.

Next, we discuss the results of the CSMS and HRTELS experiments aimed at providing information on the electronic state(s) of Cr$^{\oplus}$. In Fig. 2 the loss in kinetic energy, Q_{min}, is given for the process $Cr^{\oplus} \rightarrow Cr^{2\oplus} + e^{\ominus}$. From the onset we determine a $Q_{min} = 16.5 \pm 0.2$ eV which is (i) identical with *Beynon*'s Q_{min} value of 16.5 ± 0.5 eV[11] for Cr$^{\oplus}$ generated by fast atom bombardment and (ii) and most importantly, is in excellent agreement with the vacuum UV spectroscopic ionization energy of 16.49 eV for removing an electron from ground-state Cr$^{\oplus}$ ($3d^5$, a^6S)[12].

In line with the charge stripping results, the HRTELS experiment (Fig. 3) does not contain a signal at the «high energy» side of the main beam, thus ruling out the presence of a long-lived excited state of Cr$^{\oplus}$. In addition to the main peak at zero translational energy loss, we only observe the excitation peak around 1.5 eV which is due to the spin-allowed collisional excitation Cr$^{\oplus}$($a^6S \rightarrow a^6D$).

In conclusion, the present experiments demonstrate the following for the remarkable gas-phase ion chemistry of Cr$^{\oplus}$/4-octyne[2]:

1) CH- and CC-activations followed by reductive elimination of H_2, C_2H_4, and CH_4 are unimolecular in nature.
2) There is no experimental evidence that under the reaction conditions used, long-lived excited Cr$^{\oplus}$ is generated which was previously suggested[1] to account for the reactivity of Cr$^{\oplus}$ with organic substrates.
3) It is likely that the internal energy gained in the complexation of the CC triple bond by bare Cr$^{\oplus}$ is sufficient to overcome the barriers associated with the activation of CH- and CC-bonds.

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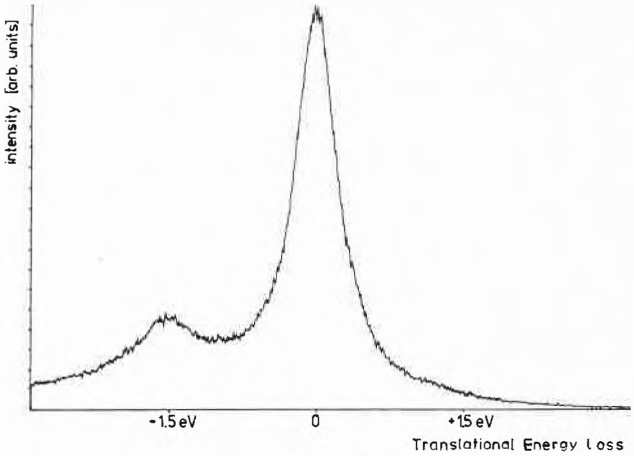

Fig. 3. Translational energy loss spectrum of Cr$^{\oplus}$ *(generated by 100 eV electron impact ionization of* $[Cr(CH_3COCH_2COCH_3)_3]$*) scattered by He* ($p_{He} = 10^{-4.7}$ *mbar).*

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