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for ethylene chemisorbed alone on Pt(111).

The results suggest that the first C–H bond cleavage is the rate-determining step for ethylidyne formation from ethylene on Pt(111) and that vinyl is a facile intermediate in the conversion of ethylene to ethylidyne.

For high coverages of preadsorbed D, hydrogenation of vinyl to ethyl occurs and leads to TPD product distributions that are consistent with those measured when starting with ethyl iodide.[2] Moreover, isotope exchange is facile, leading to some perdeuterioethane desorption.

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Registry No. $H_2C{=}CHI$, 593-66-8; Pt, 7440-06-4; $H_2C{=}CH_2$, 74-85-1; ethylidyne, 67624-57-1; vinyl, 2669-89-8.

Activation of Alkanes by Cr^+: Unique Reactivity of Ground-State $Cr^+(^6S)$ and Thermochemistry of Neutral and Ionic Chromium–Carbon Bonds

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Abstract: Guided ion beam mass spectrometry is used to study the reactions of ground-state $Cr^+(^6S)$ with propane, butane, methylpropane, dimethylpropane, and selectively deuteriated propane and methylpropane. Thermal energy reactions of $Cr^+(^6S)$ with 4-octyne are also investigated. Ground-state Cr^+ ions undergo no bimolecular reactions at thermal energies with any of the alkanes, but do react at elevated kinetic energies. The only products formed at thermal energy in the alkane systems are the collisionally stabilized adduct complexes. Approximate lifetimes for these adducts are determined. Analyses of the endothermic processes in the alkane systems yield 298 K bond energies for several chromium–ligand species. These include the neutral and ionic chromium methyl species [$D^\circ(Cr{-}CH_3) = 37.9 \pm 2.0$ kcal/mol and $D^\circ(Cr^+{-}CH_3) = 30.3 \pm 1.7$ kcal/mol], several other chromium ion–alkyl species [$D^\circ(Cr^+{-}C_2H_5) = 35.0 \pm 2.1$ kcal/mol, $D^\circ(Cr^+{-}1{-}C_3H_7) = 32.1 \pm 1.4$ kcal/mol, $D^\circ(Cr^+{-}2{-}C_3H_7) = 28.5 \pm 1.3$ kcal/mol], and chromium ion–vinyl and –various alkylidenes [$D^\circ(Cr^+{-}C_2H_3) = 59.0 \pm 2.3$ kcal/mol, $D^\circ[Cr^+{=}CHCH_3] = 52 \pm 3$ kcal/mol, $D^\circ[Cr^+{=}CHCH_2CH_3] = 36 \pm 3$ kcal/mol, $D^\circ[Cr^+{=}C(CH_3)_2] = 39 \pm 3$ kcal/mol]. The observed reactivity requires unusual reaction mechanisms that are discussed in detail.

Introduction

Over the past decade, there has been extensive interest in examining the reactions of atomic transition-metal ions with small alkanes in order to provide insight into the means by which C–H and C–C bond activation processes might occur.[1-6] These studies show that of the first-row transition-metal ions, Sc^+, Ti^+, V^+, Fe^+, Co^+, and Ni^+ undergo exothermic reactions with alkanes larger than ethane, while Cr^+, Mn^+, Cu^+, and Zn^+ do not. Often, these differences in reactivity have been attributed to thermodynamic constraints.[3,7] This hypothesis has been tested explicitly by studies at elevated kinetic energies for Mn^+,[8] Cu^+,[9] and Zn^+.[10]

For the case of Cr^+, early studies of its reactions with butanes showed reactivity at thermal energies.[11] Detailed studies of the reaction of Cr^+ with methane suggest that such thermal reactivity is due to electronically excited states of the metal ion,[12-14] as confirmed by later studies of ground-state $Cr^+(^6S)$ that found no exothermic reactions with larger alkanes, alkenes, and cycloalkanes.[7] Schilling and Beauchamp[7] attribute this lack of reactivity to the very weak σ bonds formed by Cr^+, causing the insertion of Cr^+ into C–C and C–H bonds to be endothermic. Our studies on the reactions of ground-state Cr^+ with CH_4[14] and C_2H_6[15] confirmed this hypothesis and showed that the reactivity of $Cr^+(^6S)$ is similar to that for the other early first-row transition-metal ions once sufficient energy is supplied to overcome the reaction endothermicities. Cr^+ has been observed to react exothermically with 4-octyne,[16] although it has not been unequivocally demonstrated that this thermal reactivity is due to the ground state. Under multicollision conditions, Cr^+ is also seen to form collisionally stabilized adduct complexes at thermal energies with CH_4, C_2H_6, and C_3H_8.[17]

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In the present study, we examine the endothermic reactions of ground-state Cr^+ with a series of alkanes: propane, butane, methylpropane, and dimethylpropane. In order to gain additional mechanistic and structural information about the product ions, the reactions of ground-state Cr^+ with propane-*2,2-d*$_2$, propane-*1,1,1-d*$_3$, and methylpropane-*2-d*$_1$ are also examined. In addition, we briefly discuss the thermal energy reactions of $Cr^+(^6S)$ with 4-octyne. Thermochemical information for $CrCH_3^+$, $CrCH_3$, and several other species formed in these reactions are derived by quantitative analysis of the reaction thresholds. In a companion paper,[18] this work is further extended to the reactions of excited states of atomic chromium ions with the four alkanes studied here.

Mechanisms for Alkane Activation. We will find that the reactivity of ground-state Cr^+ is quite distinct from that of the other first-row transition-metal ions. In that context, it is useful to review the mechanism by which most transition-metal ions are believed to react with saturated alkanes. Two major pathways are observed at low kinetic energies: H_2 elimination and alkane elimination to yield metal ion alkene complexes. In general, dehydrogenation of alkanes is described as an initial C–H oxidative addition to the metal center followed by hydrogen atom transfer to the metal and reductive elimination of H_2 to form a metal ion–alkene complex.[1-4] The hydrogen transferred in the second step is often a β-H although γ-H and δ-H are also observed.[3] Transfer of an α-H has only been demonstrated for reactions of Sc^+, Ti^+, V^+, and Cr^+ with methane[14,19,20] and as a minor product in the reaction of Sc^+ with ethane.[21] In reactions with propane, methylpropane, and butane, dehydrogenation is exothermic for the following first-row transition-metal ions: Sc^+, Ti^+, V^+, Fe^+, Co^+, and Ni^+.[1,9,11,22-26] The metal ions Mn^+,[8] Cu^+,[9] and Zn^+ [10] do not undergo these reactions even at elevated energies. At higher kinetic energies, the reactive systems of Sc^+, Ti^+, and V^+ + alkanes also produce $MH^+ + R$ (where R = C_3H_7, C_4H_9, or C_5H_{11}) beginning at the thermodynamic threshold.[22,25,27] The late-transition-metal ions Fe^+, Co^+, and Ni^+ preferentially form MH + R^+ beginning at the thermodynamic thresholds.[9,28] Both of these processes are also generally considered to occur from decomposition of the initially formed C–H bond activation intermediate.

Alkane eliminations are postulated to occur either by (1) oxidative addition of a C–C bond to the metal followed by a β-H shift to the metal center and reductive elimination of the product alkane[1,4,29] or (2) oxidative addition of a C–H bond followed by a β-alkyl shift and reductive elimination of the product alkane.[29,30] The alkane elimination reactions that have been observed for the reactant alkanes studied here are the loss of methane in all cases and, in the case of butane, ethane loss. Similar to dehydrogenation, these alkane loss reactions are observed for Sc^+,[22] Ti^+,[27] V^+,[23,25] Fe^+,[11,31,32] Co^+,[9,11] and Ni^+.[9,11] These channels are minor ones for reactions of Sc^+, Ti^+, and V^+ and major ones for the late-transition-metal ions Fe^+, Co^+, and Ni^+. Thus, the early-transition-metal ions Sc^+, Ti^+, and V^+ have a tendency to react via C–H bond activation pathways, while the late-transition-metal ions react via both C–H and C–C bond activation processes, with the latter tending to dominate. These mechanisms describe the qualitative behavior of these reactions reasonably well; however, different metals do have distinctive behavior,[3] and details of the potential energy surfaces are still an active area of experimentation and theory.[30]

Experimental Section

General Procedures. The ion beam apparatus used in these experiments has been described in detail elsewhere.[33] For these experiments, ion beams of $^{52}Cr^+$ (83.76% natural abundance, ionization energy (IE) = 6.766 eV) are generated by surface ionization (SI) of Cr atoms produced by thermal decomposition of CrO_2Cl_2 on the SI filament. The electronic state distribution of the ions produced by SI should have a Maxwell–Boltzmann distribution if the metal ions reach equilibrium at the SI filament temperature. The validity of this assumption has been discussed previously.[20] Here, the filament temperature is 1800 ± 100 K such that the ion beam generated comprises 99.8% ground-state $Cr^+(^6S)$ ions and only 0.2% of the first excited-state $Cr^+(^6D)$, with an excitation energy of 1.52 eV.

The ions are extracted from the source, mass analyzed in a magnetic sector momentum analyzer, decelerated to a desired kinetic energy, and focused into an octopole ion guide. This device ensures efficient collection of all ionic products and transmitted reactant ions. The octopole passes through a reaction cell filled with a low pressure (0.02–0.08 mTorr) of the neutral reactant, such that multiple ion–molecule collisions are improbable. After exiting the reaction cell, the ions are extracted from the octopole, focused into a quadrupole mass filter for mass analysis, and detected by using a scintillation ion detector and standard ion counting techniques. Raw ion intensities are converted into absolute reaction cross sections with estimated uncertainties of ±20%.[33] Pressure-dependent studies verify that these cross sections are due to single ion–molecule collisions except where noted.

The absolute energy scale and the full width at half-maximum (fwhm) of the ion kinetic energy distribution are determined by using the octopole beam guide as a retarding potential analyzer.[33] The uncertainty in the absolute energy scale is 0.05 eV (laboratory). The distribution of ion energies is Gaussian with an average fwhm of 0.5 eV (laboratory) while the thermal motion of the gas in the reaction cell has a fwhm of $\sim 0.4E_{CM}^{1/2}$(eV).[34] Laboratory ion energies (lab) are converted to energies in the center-of-mass frame (CM) by using the conversion $E(\mathrm{CM}) = E(\mathrm{lab})M/(m + M)$, where m is the ion mass and M is the target molecule mass.

Thermochemical Analysis. Cross sections for endothermic reactions are analyzed by using eq 1. Here, E_T is the reaction endothermicity,

$$\sigma(E) = \sigma_0(E - E_T)^n/E \quad (1)$$

σ_0 is an energy-independent scaling factor, and n is an adjustable parameter. This form has been derived as a model for translationally driven reactions[35] and has been found to be quite useful in describing the shapes of endothermic reaction cross sections and in deriving accurate thermochemistry for a wide range of systems.[20-22,27,36,37] To analyze the experimental results, this model is convoluted over the kinetic energy distributions of the neutral and ion reactants, as described in detail previously.[33,38] The parameters n, σ_0, and E_T are then allowed to vary freely to best fit the data as determined by nonlinear least-squares analysis. Errors in threshold values are determined by the variation in E_T for the various models applied to several data sets and the absolute uncertainty in the energy scale, ~0.02 eV (CM). We assume that these thresholds

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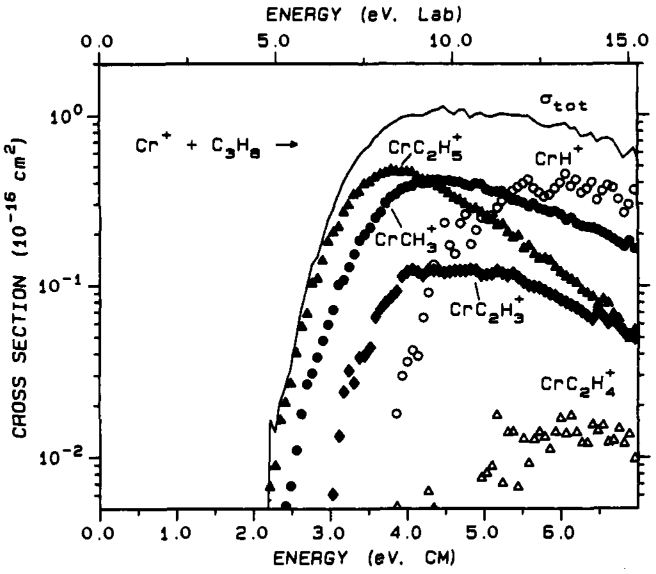


Figure 1. Variation of product cross sections with translational energy in the laboratory frame (upper scale) and the center-of-mass frame (lower scale) for the reaction of $Cr^+(^6S)$ with propane. The solid line represents the total cross section.

correspond to a temperature of 298 K, and so we make no correction for the energy available in internal modes of the neutral reactant.

The reaction cross section for an endothermic process may decline at higher energies due to dissociation of the product ion or competition with another process. For such systems, cross sections are analyzed by using a model that makes a simple statistical assumption within the constraints of angular momentum conservation.[39] For this model, two additional parameters are allowed to optimize: E_D, which is the energy at which dissociation or competition begins, and p, which is another adjustable parameter similar to n. The use of this model has been described in detail elsewhere.[9,39]

Results and Mechanism

As previously noted,[7,17] ground-state $Cr^+(^6S)$ is not very reactive with alkanes. We observe only adduct formation at thermal energies and find a limited number of products formed in endothermic reactions. All these reaction channels have rather high thresholds that exceed 1.5 eV and correspond to C–C bond cleavage reactions by Cr^+. Cr^+ fails to induce the loss of H_2 in any of the alkane systems studied here. These results are discussed for the individual systems in the sections that follow.

Cross sections for the endothermic reactions of $Cr^+(^6S)$ are subjected to detailed threshold analysis with eq 1 as described in the Experimental Section. Results of these analyses are summarized in Table I. Table II lists supplementary thermochemical data from the literature.

The CrH^+ cross sections are generally noisier than the other cross sections due to experimental difficulties in resolving the small intensities of these ions from the $\sim 10^5$ times larger reactant ion beam intensity. For this product and a few others, cross sections are corrected for mass overlap with other nearby ions when this correction is unambiguous. Cases where this correction cannot be made straightforwardly are noted below.

Propane. Experimental results for reaction of $Cr^+(^6S)$ with propane are shown in Figure 1. Five reaction pathways are observed (processes 2–6).

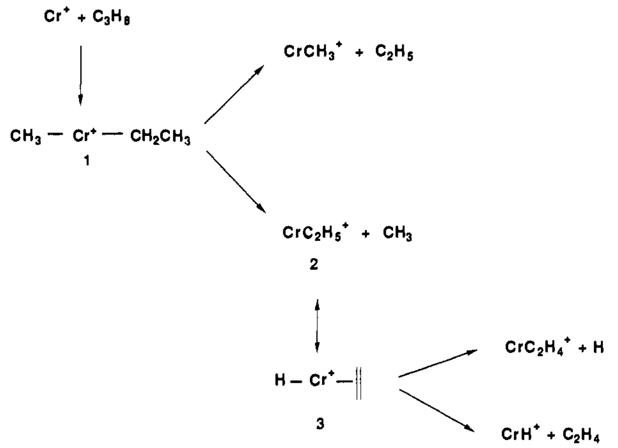
$$
Cr^+ + C_3H_8 \begin{cases} \rightarrow CrCH_3^+ + C_2H_5 & (2) \\ \rightarrow CrC_2H_5^+ + CH_3 & (3) \\ \rightarrow CrC_2H_3^+ + [CH_3 + H_2] & (4) \\ \rightarrow CrH^+ + [C_2H_4 + CH_3] & (5) \\ \rightarrow CrC_2H_4^+ + [CH_3 + H] & (6) \end{cases}
$$

The total cross section for the reaction of $Cr^+(^6S)$ with propane reaches a maximum of only ~ 1.0 Å^2 at ~ 4 eV and decreases steadily at higher energies. Dehydrogenation to form $CrC_3H_6^+$ and formation of alkyl ions are not observed at any energies studied, indicating that the cross sections for these processes are <0.005 Å^2. The cross section for $CrC_2H_4^+$ is quite small and is somewhat uncertain as it has been corrected for overlap with the much more intense $CrC_2H_5^+$ product ion.

Table I. Optimum Parameters Used in Equation 1

ionic product	n	E_T, eV	σ_0	E_D, eV	p
		Propane			
$CrCH_3^+$	2.4 ± 0.2	2.48 ± 0.07	1.18 ± 0.31	3.8	2
$CrC_2H_5^+$	2.3 ± 0.2	2.38 ± 0.04	3.32 ± 1.32	3.8	2
$CrC_2H_3^+$	2.9 ± 0.1	3.17 ± 0.15	2.62 ± 0.68	3.8	2
CrH^+	1.2 ± 0.1	4.18 ± 0.04	0.44 ± 0.04		
		Methylpropane			
$CrCH_3^+$	2.8 ± 0.4	2.52 ± 0.05	2.17 ± 0.50	4.2	3
$C_3H_7^+$	2.1 ± 0.2	2.77 ± 0.10	0.49 ± 0.10	4.1	2
$CrC_3H_7^+$	1.5 ± 0.3	2.59 ± 0.04	2.99 ± 0.10	3.5	1
$CrC_3H_6^+$	3.6 ± 0.1	2.10 ± 0.06	1.16 ± 0.32	3.4	3
$CrC_2H_4^+$	0.8 ± 0.2	2.32 ± 0.04	0.10 ± 0.02		
	1.9 ± 0.2	4.05 ± 0.15	0.49 ± 0.12	5.0	2
CrH^+	1.1 ± 0.3	4.18 ± 0.13	0.99 ± 0.27		
		Dimethylpropane			
$C_4H_9^+$	2.2 ± 0.1	2.05 ± 0.09	6.68 ± 2.27	4.1	2
$C_3H_5^+$	1.7 ± 0.3	4.07 ± 0.07	1.40 ± 0.26		
$C_2H_5^+$	1.0 ± 0.3	4.82 ± 0.11	1.27 ± 0.27		
$CrC_4H_8^+$	2.1 ± 0.4	2.02 ± 0.21	2.43 ± 1.10	4.5	2
$CrC_3H_6^+$	2.1 ± 0.3	2.28 ± 0.07	1.40 ± 0.54	3.7	3
$CrC_3H_4^+$	1.0 ± 0.1	4.86 ± 0.07	0.58 ± 0.23		
$CrC_2H_4^+$	1.5 ± 0.2	1.86 ± 0.04	0.07 ± 0.02	3.4	3
CrH^+	1.0 ± 0.1	4.57 ± 0.07	2.13 ± 0.21		
		Butane			
$CrCH_3^+$	2.5 ± 0.3	2.53 ± 0.04	0.56 ± 0.04	4.2	3
$CrC_2H_5^+$	3.0 ± 0.5	2.16 ± 0.13	0.80 ± 0.30	4.1	3
$CrC_3H_7^+$	2.0 ± 0.2	2.42 ± 0.05	0.09 ± 0.05	3.9	2
$CrC_2H_4^+$	1.6 ± 0.2	1.61 ± 0.13	0.22 ± 0.04	3.8	3
$CrC_3H_6^+$	2.8 ± 0.1	2.17 ± 0.04	0.43 ± 0.17	3.8	3
$CrC_2H_3^+$	3.8 ± 0.2	3.05 ± 0.05	0.48 ± 0.20	4.0	3
CrH^+	1.0 ± 0.1	4.08 ± 0.08	1.76 ± 0.17		

Scheme I



The simplest reaction mechanism that can be invoked to explain reactions 2 and 3 is shown in Scheme I. It involves the oxidative addition of a propane C-C bond to Cr^+ to form intermediate **1**. Subsequent loss of one of the ligands leads directly to formation of $CrCH_3^+$ and $CrC_2H_5^+$, the two major products at the lower energies. This mechanism suggests that the structure of $CrC_2H_5^+$ formed at threshold is the chromium–ethyl ion (**2**), consistent with the similar thresholds observed for processes 2 and 3. This structure is further indicated by the observation that the cross section for $CrC_2H_5^+$ peaks sharply near the energy required to decompose $CrC_2H_5^+$ to $Cr^+ + C_2H_5$, a process that can begin at $D^\circ(H_3C-C_2H_5)$ = 3.8 eV. The cross section for formation of $CrCH_3^+$ peaks at a slightly higher kinetic energy, probably because

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Table II. Thermochemistry at 298 K (kcal/mol)[a]

species	$\Delta_f H°$	IE, eV	species	$\Delta_f H°$	IE, eV
H	52.1		C_3H_6	4.8 (0.2)	9.73 (0.02)
Cr	94.8	6.766	$C(CH_3)_2$	72 (2)[b]	
CrH^+	270.4 (2.0)[c]		$CHCH_2CH_3$	74 (2)[b]	
CH_2	92.4 (1.0)[d]		2-C_3H_7	21.3 (0.7)[e]	7.36 (0.02)
CH_3	34.8 (0.2)[e]		1-C_3H_7	23.1 (0.8)[f]	8.09 (0.01)
CH_4	−17.8 (0.1)		C_3H_8	−25.0 (0.1)	10.95 (0.05)
C_2H_2	54.5 (0.2)		$CH_2C(CH_3){=}CH_2$	29	7.90 (0.02)
C_2H_3	71.7 (0.8)[g]		1-C_4H_8	−0.0 (0.2)	9.58 (0.02)
C_2H_4	12.5 (0.1)	10.51 (0.01)	$CH_2{=}C(CH_3)_2$	−4.0 (0.2)	9.24 (0.01)
$CHCH_3$	79 (2)[h]		$CH_2CH(CH_3)_2$	16	7.93
C_2H_5	28.3 (0.4)[e]	8.13 (0.06)	$C(CH_3)_3$	11.6 (0.4)[e]	6.70 (0.03)
C_2H_6	−20.0 (0.1)	11.52 (0.01)	2-C_4H_9	17.0 (0.4)[e]	
$HC{\equiv}CCH_3$	44.2 (0.2)		C_4H_{10}	−30.0 (0.2)	10.53 (0.10)
$H_2C{=}C{=}CH_2$	45.5 (0.3)		$HC(CH_3)_3$	−32.1 (0.2)	10.57
C_3H_5	39	8.13 (0.06)	$CH_2C(CH_3)_3$	8	7.88 (0.05)
			$C(CH_3)_4$	−40.2 (0.2)	≤10.21 (0.04)

[a] Except where noted, radical $\Delta_f H$s and IEs from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. $\Delta_f H$s for closed-shell species from: Pedley, J. M.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986. [b] These values are calculated by assuming that $D°[H-C(CH_3)_2] \approx D°(H-CHC_2H_5) \approx D°(H-CHCH_3)$. [c] Reference 42. [d] Reference 55. [e] Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347–1353. [f] Average of three values from: Marshall, R. M.; Rahman, L. *Int. J. Chem. Kinet.* **1977**, *9*, 705. Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872–2880. Holmes, J. L.; Lossing, F. P.; Maccoll, A. *J. Am. Chem. Soc.* **1988**, *110*, 7339–7342. [g] Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750–5759. [h] Based on ab initio calculations of: Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkly, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389. Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. This value agrees with a recent experimental determination of 73 ± 7 kcal/mol from: Schultz, R. H.; Armentrout, P. B. *Organometallics*, in press.

the neutral C_2H_5 product carries away some of the excess energy in internal degrees of freedom, while the CH_3 product of process 3 carries away relatively less energy.

The lack of substantial amounts of $CrC_3H_6^+$ and $CrC_2H_4^+$ products in this system contrasts with the observations made for most other first-row transition-metal ions.[5,9,22,24,27,30,40] This difference demonstrates that C–H bond activation is hindered with Cr^+ or that β-H transfer for intermediates such as **1** is constrained.

Formation of $CrC_2H_3^+$ and $CrC_2H_4^+$ is also explained by the mechanism of Scheme I since these products are probably formed by decomposition of $CrC_2H_5^+$. For instance, formation of $CrC_2H_3^+$ must occur via a sequential dissociation process since the only possible neutral products consistent with the observed threshold are $CH_3 + H_2$ or $CH_4 + H$. The only primary product ion that can account for such a sequential dissociation event is $CrC_2H_5^+$, such that the neutral products are $CH_3 + H_2$. For process 6, the apparent threshold is sufficiently high that it probably corresponds to the energy needed to form $CrC_2H_4^+ + H + CH_3$, 4.0 ± 0.2 eV given $D°(Cr^+-C_2H_4) = 32 \pm 5$ kcal/mol.[15] This is again a process that can only occur by decomposition of $CrC_2H_5^+$. The observation that reaction 6 is a minor decomposition pathway for $CrC_2H_5^+$ may imply that structure **2** can isomerize to a hydridochromium–ethene ion (**3**) at elevated energies.

For CrH^+, the measured threshold of 4.18 ± 0.04 eV (Table I) is more than 1.0 eV above the thermodynamic threshold for production of CrH^+ + 2-C_3H_7, 2.86 ± 0.09 eV, or CrH^+ + 1-C_3H_7, 2.94 ± 0.09 eV.[41,42] It is possible that this corresponds to a direct abstraction reaction, but the measured threshold corresponds nicely with the energy needed to form $CrH^+ + C_2H_4 + CH_3$, 3.98 ± 0.09 eV. This process can only occur by decomposition of $CrC_2H_5^+$ and is also consistent with the existence of structure **3**.

Deuteriated Propanes. In order to help confirm the reaction mechanism of Scheme I, the reactions of Cr^+ with the selectively deuteriated propanes $CH_3CD_2CH_3$ and $CD_3CH_2CH_3$ have also been examined. In both of these systems, no new types of reaction products are observed. For propane-*2,2-d*$_2$ the only Cr^+–methyl and Cr^+–ethyl products observed are $CrCH_3^+$ and $CrCD_2CH_3^+$, as expected for a $CH_3-Cr^+-CD_2CH_3$ intermediate. For propane-*1,1,1-d*$_3$ all products consistent with $CH_3-Cr^+-CH_2CD_3$ and $CD_3-Cr^+-CH_2CH_3$ intermediates are observed. The branching ratio for $CrCH_3^+:CrCD_3^+$ is 55:45, and that for $CrC_2H_5^+:CrC_2H_2D_3^+$ is 60:40. These results show that deuteriated ligands are lost more easily than perprotiated ligands of the same structure.

On the basis of the mechanism of Scheme I, we might not expect to see such an isotope effect since the C–C bond insertion step should not be affected by deuteriation. The branching ratios in the propane-*1,1,1-d*$_3$ system are, however, consistent with conservation of angular momentum ideas which have been discussed previously for both endothermic[19,22,43] and exothermic reactions.[44] Using these concepts, conservation of angular momentum predicts a branching ratio of 52:48 for $CrCH_3^+:CrCD_3^+$ and 54:46 for $CrC_2H_5^+:CrC_2H_2D_3^+$, in rough agreement with the experimental results.

For the analogue of reaction 4 in the propane-*2,2-d*$_2$ system, nearly equal amounts of $CrC_2H_2D^+$ and $CrC_2HD_2^+$ are formed at high energies, consistent with dehydrogenation of a $CrCD_2CH_3^+$ species. In the threshold region, the branching ratio is ~30:70, consistent with a primary isotope effect. In the propane-*1,1,1-d*$_3$ system, both $CrC_2H_3^+$ and $CrC_2HD_2^+$ are formed although the exact size and shape of the cross section for the latter species are obscured since this product has the same mass as the much larger $CrC_2H_5^+$ species. Neither $CrC_2D_3^+$ nor $CrC_2H_2D^+$ is formed in this system, showing that the $CrC_2H_2D_3^+$ species loses HD exclusively.

For reaction 5, the $CrH^+:CrD^+$ branching ratio is 75:25 in the d_2 system and 40:60 in the d_3 system. Since decomposition of $CrCD_2CH_3^+$ might be expected to yield CrH^+ almost exclusively, these results suggest either that scrambling is occurring (which seems unlikely at these elevated energies) or that direct stripping reactions contribute to CrH^+ product formation. This is consistent with the analysis of the CrH^+ product formed in the reaction of Cr^+ with methane, which showed that ~75% of the CrH^+ was formed via a direct reaction.[14]

The cross sections for the analogous of reaction 6 in the deuteriated propane systems are too small to determine unambiguously.

Methylpropane. Processes 7–12 are the major pathways observed in the reaction of Cr^+ ions with methylpropane (Figure 2). The only product observed at thermal energy is the adduct

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(40) Schultz, R. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 729–730.

(41) This threshold value is based on $D°(Cr^+-H) = 32.5 \pm 2.0$ kcal/mol.[42]

(42) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *86*, 1868–1877.

(43) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1985**, *89*, 5626–5636.

(44) Burley, J. D.; Ervin, K. M.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *80*, 153–175.

$$Cr^+ + CH(CH_3)_3 \rightarrow CrCH_3^+ + C_3H_7 \tag{7}$$
$$\rightarrow CrCH_3 + C_3H_7^+ \tag{8}$$
$$\rightarrow CrC_3H_6^+ + CH_4 \tag{9}$$
$$\rightarrow CrC_3H_7^+ + CH_3 \tag{10}$$
$$\rightarrow CrC_2H_4^+ + C_2H_6 \tag{11}$$
$$\rightarrow CrH^+ + [C_3H_6 + CH_3] \tag{12}$$

ion, $CrC_4H_{10}^+$, which is the result of collisional stabilization as verified by the linear pressure dependence of the cross section over a range of 0.01–0.20 mTorr. In addition to the products shown in Figure 2, small amounts of the alkyl ions $C_3H_5^+$ and $C_2H_5^+$ are observed at higher energies but are not shown in Figure 2 for clarity. Dehydrogenation of methylpropane to form $CrC_4H_8^+$ is not observed at any energy, indicating that the cross section for this process is <0.005 Å^2. The total cross section in the methylpropane system is larger than that seen in the propane system, with a maximum cross section of nearly 4 Å^2 occurring between 4 and 5 eV.

Scheme II, directly analogous to that for the propane system, shows the simplest mechanism consistent with the products observed for reaction of $Cr^+(^6S)$ with methylpropane. C–C bond activation leads to intermediate **4** which can lose the neutral propyl ligand (reaction 7), the ionic propyl ligand (reaction 8), or the neutral methyl ligand (reaction 10). This mechanism is consistent with the observation that reaction of $Cr^+(^6S)$ with methylpropane-*2-d*$_1$ yields only $CrCH_3^+$, $C_3H_6D^+$, and $CrC_3H_6D^+$.[45]

The cross section for formation of the other major product, $CrC_3H_6^+$, rises from a threshold slightly below that for $CrCH_3^+$ production. For most metal ions, such a product is generally a metal ion–propene complex, here $Cr(C_3H_6)^+$ (**5**). Because of the very high threshold observed for this product, we also consider two alternative structures: the chromium–propylidene ion, $Cr^+{=}C(CH_3)_2$ (**6**), and the metallocyclobutane ion, $Cr^+{-}CH_2CH_2CH_2$ (**7**). These three possibilities can be tested by examining the reaction of Cr^+ with methylpropane-*2-d*$_1$. Scheme II shows that production of structure **5** would be expected to retain the *d* label, while formation of **6** would not. Any mechanism that produces structure **7** must be fairly complex and also predicts that the $CrC_3H_6^+$ product would probably retain the *d* label. We find that Cr^+ reacts with $DC(CH_3)_3$ to form $CrC_3H_6^+$ exclusively, thus indicating that this product has structure **6**. Production of **6** via the mechanism in Scheme II suggests that reactions 7 and 9 should compete since they share the common intermediate **4**. This is consistent with the observation that the $CrC_3H_6^+$ cross section decreases as that for $CrCH_3^+$ rises.

The observation that CH_3D is eliminated exclusively from **4** is in stark contrast to the behavior of most first-row transition-metal ions, which eliminate CH_4 exclusively instead.[1,25,29] This demonstrates that, similar to the propane system, the commonly invoked β-H transfer to the metal ion center is not facile for Cr^+ such that structure **5** is not readily produced. The elimination of CH_3D involves what is formally an α-H pathway (Scheme II). This probably should not be thought of as α-H transfer to the metal center since that produces an intermediate with a formal oxidation state of +5, $(CH_3)(H)Cr^+{=}C(CH_3)_2$. Rather, we envision this process as a concerted four-center elimination of CH_4 (CH_3D) from intermediate **4**. This type of mechanism has been discussed previously as a likely pathway to formation of $CrCH_2^+$ in the reaction of Cr^+ with CH_4.[14] On the basis of the d-orbital occupancy in Cr^+, this type of four-center elimination is symmetry allowed.[46]

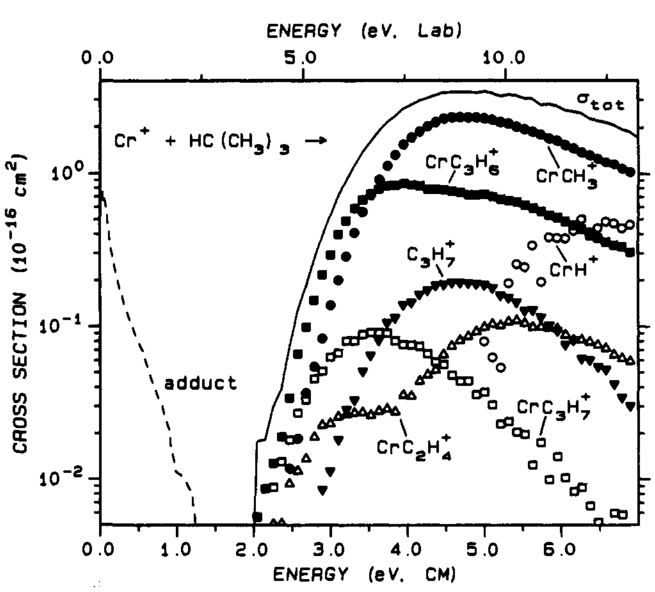
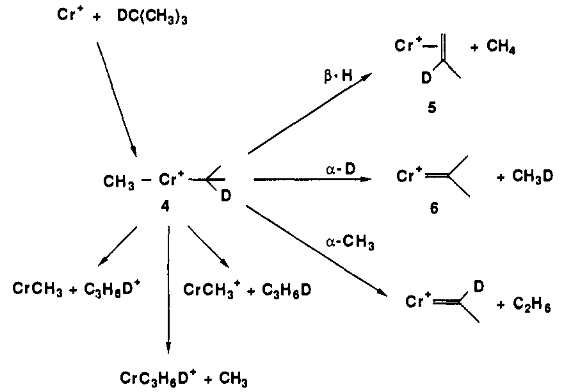


Figure 2. Variation of product cross sections with translational energy in the laboratory frame (upper scale) and the center-of-mass frame (lower scale) for the reaction of $Cr^+(^6S)$ with methylpropane. The cross section for the $Cr^+{\cdot}CH(CH_3)_3$ adduct is shown for a neutral pressure of 0.018 mTorr. The solid line represents the total cross section.

Scheme II



The $CrC_2H_4^+$ cross section displays interesting behavior with two distinct features (Figure 2). The low-energy feature has a measured threshold of 2.32 ± 0.04 eV and reaches a maximum of only 0.03 Å^2. The second feature rises from a threshold of ~4 eV to a maximum of 0.1 Å^2. The difference in these thresholds is close to the energy required for dehydrogenation of ethane, 1.4 eV. According to the mechanism of Scheme II, the most likely structure for $CrC_2H_4^+$ in this system is the chromium–ethylidene ion, $Cr^+{=}CHCH_3$, formed from **4** by transfer of an α-CH_3 group and elimination of ethane. In the reaction with $DC(CH_3)_3$, the low-energy feature is predominantly $CrC_2H_4^+$, with a 25% contribution from $CrC_2H_3D^+$, and the high-energy feature is about 70% $CrC_2H_3D^+$.[47] These observations are not completely consistent with Scheme II, which predicts that ethane elimination from methylpropane-*2-d*$_1$ should yield the deuteriated chromium–ethylidene ion. This indicates either that hydrogen scrambling is occurring for the lower energy feature or that the mechanism is substantially more complicated.

The final reaction product is the metal–hydride ion, CrH^+. As in the propane system, the cross section for this process has a threshold (Table I) that is much higher than the thermodynamic threshold for formation of $CrH^+ + C(CH_3)_3$, 2.74 ± 0.09 eV, or $CrH^+ + CH_2CH(CH_3)_2$, 2.94 ± 0.09 eV.[41] Thus, formation of CrH^+ may be the result of decomposition of one of the other reaction products or may be due to a stripping reaction. The measured threshold of 4.18 ± 0.13 eV is comparable to the

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(45) Small amounts (<10% compared to $C_3H_6D^+$) of signal at a mass corresponding to $C_3H_7^+$ were also seen, but this product appears to be due to mass overlap from the much larger $C_3H_6D^+$ product.

(46) Goddard, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 793–807. Steigerwald, M. L.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 308–311. Rappe, A. K. *Organometallics* **1987**, *6*, 354–357.

(47) The uncertainties in these percentages are about 10% due primarily to mass overlap.

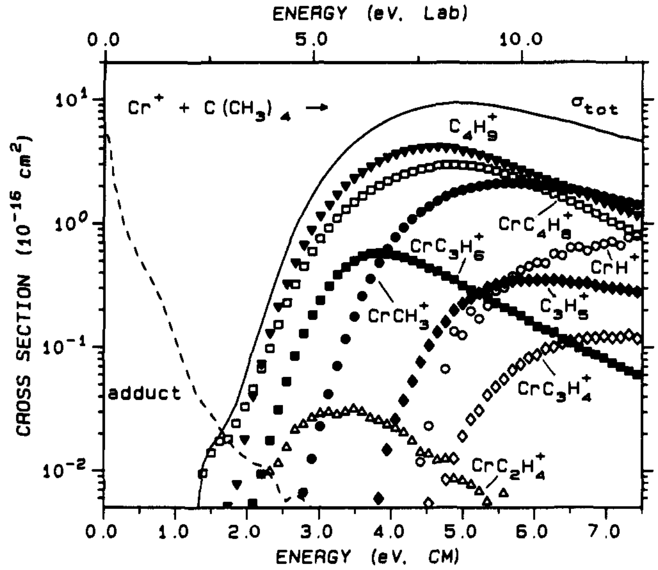


Figure 3. Variation of product cross sections with translational energy in the laboratory frame (upper scale) and the center-of-mass frame (lower scale) for the reaction of $Cr^+(^6S)$ with dimethylpropane. The cross section for the $Cr^+{\cdot}C(CH_3)_4$ adduct is for a neutral pressure of 0.043 mTorr. The solid line represents the total cross section.

calculated threshold for formation of $C_3H_6 + CH_3$ as neutrals, 3.96 ± 0.09 eV. In the deuteriated system, formation of CrH^+ is favored over CrD^+ by 86:14, close to the random statistical limits of 90:10 for the parent methylpropane or of 86:14 for decomposition of $CrC_3H_6D^+$. This branching ratio helps verify that oxidative addition of C–H bonds to $Cr^+(^6S)$ does not occur easily; otherwise, we would expect that CrD^+ formation would be preferred since the tertiary C–H bond is much weaker than the primary C–H bonds in methylpropane. It is also possible that direct stripping reactions contribute to the CrH^+ product formation.

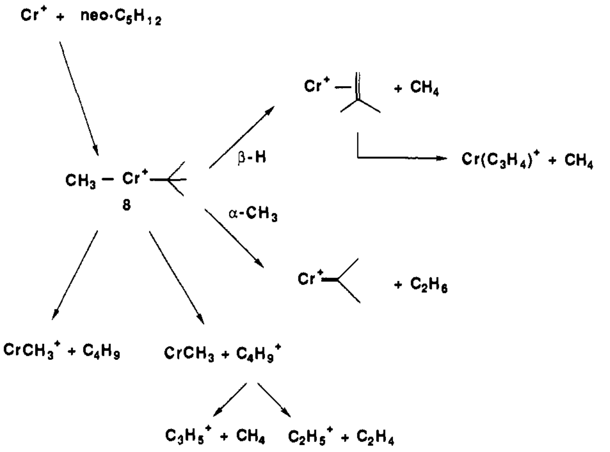
Dimethylpropane. The reaction of $Cr^+(^6S)$ with $C(CH_3)_4$ is the most efficient of the alkanes studied here, with a maximum total cross section of close to 10 Å² (Figure 3). This increased reactivity is presumably due to the increased number of degrees of freedom and the increased polarizability of dimethylpropane, which both lead to a longer lived intermediate. Reactions 13–20

$$Cr^+ + C(CH_3)_4 \rightarrow CrCH_3^+ + C_4H_9 \tag{13}$$
$$\rightarrow CrCH_3 + C_4H_9^+ \tag{14}$$
$$\rightarrow CrCH_3 + C_3H_5^+ + CH_4 \tag{15}$$
$$\rightarrow CrC_4H_8^+ + CH_4 \tag{16}$$
$$\rightarrow CrC_3H_6^+ + C_2H_6 \tag{17}$$
$$\rightarrow CrC_3H_4^+ + [CH_4 + CH_3 + H] \tag{18}$$
$$\rightarrow CrC_2H_4^+ + [C_3H_8] \tag{19}$$
$$\rightarrow CrH^+ + [C_2H_6 + C_3H_5] \tag{20}$$

are the major processes observed in this system (Figure 3). Also seen at high kinetic energies is formation of $C_2H_5^+$, not shown for clarity. Dehydrogenation to form $CrC_5H_{10}^+ + H_2$ is not observed, although this is not unusual for M^+ + dimethylpropane reactions.[8,9,10,25,29,31] The adduct ion, $CrC_5H_{12}^+$, is seen at the lowest energies. Its cross section is linearly dependent on pressure from 0.01 to 0.33 mTorr, establishing that this product is collisionally stabilized.

Scheme III shows a reaction mechanism for this system that is similar to the Scheme II mechanism for methylpropane. The first step is metal insertion into a C–C bond to form intermediate **8**. $Cr–CH_3$ bond cleavage leads to formation of either $CrCH_3^+$ (reaction 13) or $C_4H_9^+$ (reaction 14). At higher energies, the $C_4H_9^+$ product decomposes to $C_3H_5^+ + CH_4$ (reaction 15) and to $C_2H_5^+ + C_2H_4$. Using thermochemistry from Table II, reaction

Scheme III



15 should have a threshold that is 1.85 ± 0.07 eV higher than that of reaction 14, in agreement with the difference measured, 2.02 ± 0.11 eV (Table I). Similarly, formation of $C_2H_5^+ + C_2H_4$ from $C(CH_3)_3^+$ requires 2.70 ± 0.08 eV, in good agreement with the difference in thresholds measured, 2.77 ± 0.14 eV (Table I). An alternate route to formation of $C_3H_5^+$ would be via decomposition of $CrC_3H_6^+$ to give $CrH + C_3H_5^+$. Given $D°(Cr–H)$ = 53 ± 4 kcal/mol,[48] this process should have E_T = 3.88 ± 0.17 eV, within experimental error of the measured threshold (Table I).

In most metal ion reactions with $C(CH_3)_4$, the $MC_4H_8^+ + CH_4$ product channel is the only exothermic reaction observed.[8,9,25,29] This ionic product almost certainly has the structure of a metal ion–methylpropene complex as formed via the mechanism shown in Scheme III for Cr^+. This reaction involves a β-H transfer, a reaction step not evident in the reactions of Cr^+ with propane and methylpropane. However, alternative structures for $CrC_4H_8^+$ seem very unlikely given the observation that initial C–H bond activation is not observed in the other Cr^+–alkane systems. If we assume that $D°(Cr^+–C_4H_8) \approx D°(Cr^+–C_2H_4)$ = 32 ± 5 kcal/mol,[15] then formation of this product should be exothermic. This suggests that either the β-H transfer step from intermediate **8** or an initial C–H bond activation step has a considerable barrier. Further discussion of this species and its structure is found below.

Formation of $CrC_3H_6^+$ in reaction 17 is most straightforwardly explained via an α-CH_3 shift from intermediate **8** followed by reductive elimination of C_2H_6 (Scheme III). Similar to the methylpropane system, this is probably best considered as a four-center elimination of C_2H_6. This mechanism suggests that the structure of the $CrC_3H_6^+$ ion is the chromium-2-propylidene ion, a suggestion which is verified below by the agreement between the heats of formation of this ion as measured here and in the methylpropane system.

Formation of $CrC_3H_4^+$ must occur via a sequential dissociation process since the products must have the formula C_2H_8. Two possibilities are dehydrogenation of the $CrC_3H_6^+$ ion or methane loss from $CrC_4H_8^+$. Based on the size and shapes of the cross sections involved, the latter process seems more likely (Scheme III). The most reasonable structures for this molecule are Cr^+–propyne and Cr^+–allene.

Formation of $CrC_2H_4^+$ in the dimethylpropane system must involve extensive rearrangement. Similar to the methylpropane system, however, it seems likely that the structure is the chromium–ethylidene, $Cr^+{=}CHCH_3$.

Production of CrH^+ is only observed at high kinetic energies (Figure 3). The measured threshold of 4.57 ± 0.07 eV (Table I) is much higher than the thermodynamic threshold for the lowest energy process, formation of $CrH^+ + CH_2C(CH_3)_3$, 2.94 ± 0.11 eV.[41] It is also above those calculated for formation of $CrH^+ + C_2H_6 + C_3H_5$, 3.4 eV (which could result from decomposition of $CrC_3H_6^+$), $CrH^+ + C_4H_7 + CH_4$, 3.1 eV (from decomposition

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(48) Chen, Y.; Clemmer, D. E.; Armentrout, P. B. Unpublished results.

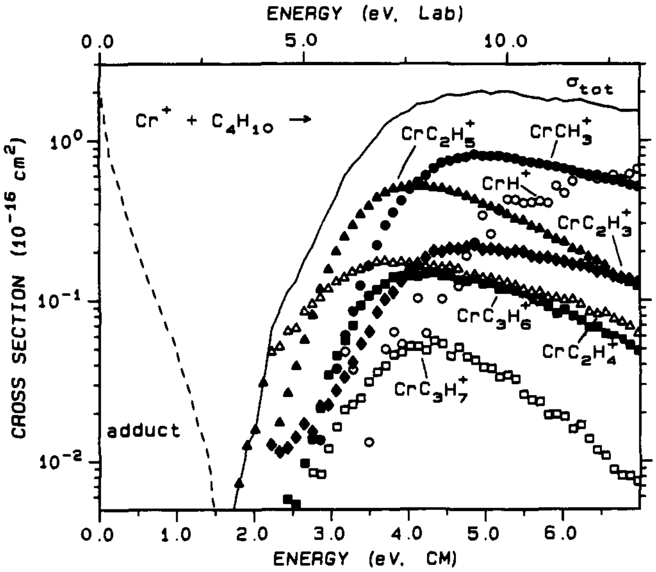


Figure 4. Variation of product cross sections with translational energy in the laboratory frame (upper scale) and the center-of-mass frame (lower scale) for the reaction of $Cr^+(^6S)$ wuth butane. The cross section for the $Cr^+{\cdot}C_4H_{10}$ adduct is shown for a neutral pressure of 0.030 mTorr. The solid line represents the total cross section.

of $CrC_4H_8^+$), and $CrH^+ + i\text{-}C_4H_8 + CH_3$, 3.9 eV, but lower than for $CrH^+ + C_3H_4 + CH_4 + CH_3$, 5.2 eV. Again, it is possible that direct stripping reactions contribute to the formation of CrH^+ in this system.

Butane. Processes 21–27 are seen in the reaction of $Cr^+(^6S)$ with butane (Figure 4). Formation of alkyl ions and dehydrogenation to form $CrC_4H_8^+$ are not observed, even at high energies, indicating that the cross-section magnitudes for these processes are <0.005 Å². The total cross section in this system is between

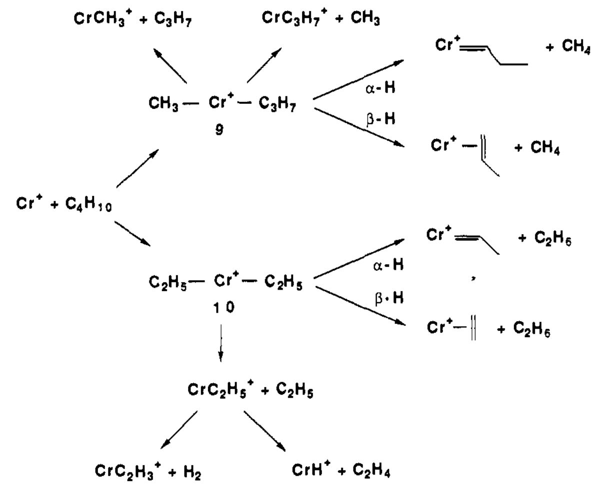
$$Cr^+ + C_4H_{10} \rightarrow CrCH_3^+ + C_3H_7 \quad (21)$$
$$\rightarrow CrC_3H_7^+ + CH_3 \quad (22)$$
$$\rightarrow CrC_2H_5^+ + C_2H_5 \quad (23)$$
$$\rightarrow CrC_2H_4^+ + C_2H_6 \quad (24)$$
$$\rightarrow CrC_3H_6^+ + CH_4 \quad (25)$$
$$\rightarrow CrC_2H_3^+ + C_2H_5 + H_2 \quad (26)$$
$$\rightarrow CrH^+ + C_2H_5 + C_2H_4 \quad (27)$$

that of the propane and methylpropane systems, with a maximum cross section of ~2 Å² between 4 and 5 eV. The only product observed at thermal energies is the adduct ion, $CrC_4H_{10}^+$. Adduct formation is the result of collisional stabilization as verified by the linear dependence of the cross section on pressure over a range of 0.01–0.20 mTorr.

The butane system is unique among the alkanes studied here in that it has two types of C–C bonds. Similar to the other alkanes, the observed products can be easily explained via C–C bond activation mechanisms. Scheme IV depicts the two possible pathways for C–C bond insertion in the butane system. Insertion into a primary C–C bond gives intermediate **9**, which leads directly to formation of $CrCH_3^+$ (reaction 21) and $CrC_3H_7^+$ (reaction 22). Likewise, intermediate **10** leads directly to the $CrC_2H_5^+ + C_2H_5$ (reaction 23). In contrast to the observation of $C_3H_7^+$ in the methylpropane system, this product is not observed here since intermediate **9** would lead to $1\text{-}C_3H_7^+$ as a product but the IE of $1\text{-}C_3H_7$ is much higher than that of $2\text{-}C_3H_7$ (Table II). Also, formation of $C_2H_5^+$ is not observed from intermediate **10** because of the high IE of C_2H_5 (Table II).

Both intermediates **9** and **10** can rearrange via α-H or β-H elimination (Scheme IV). Reductive elimination of C_2H_6 from **10** yields $CrC_2H_4^+$ (process 24). As shown in Scheme IV, the $CrC_2H_4^+$ ion observed in this system could be either the chromium–ethene ion or the chromium–ethylidene ion. Since in the other alkane systems β-H shifts appear to be hindered, we expect the structure to be $Cr^+{=}CHCH_3$ (Scheme IV). Reductive elimination of CH_4 from intermediate **9** produces the $CrC_3H_6^+$ ion, which could be either the chromium–propene ion or the chromium-1-propylidene. If we again assume that α-H shifts are more facile, the expected structure is $Cr^+{=}CHCH_2CH_3$ (Scheme IV). These structural conclusions are supported by the thermochemistry discussed below.

Scheme IV



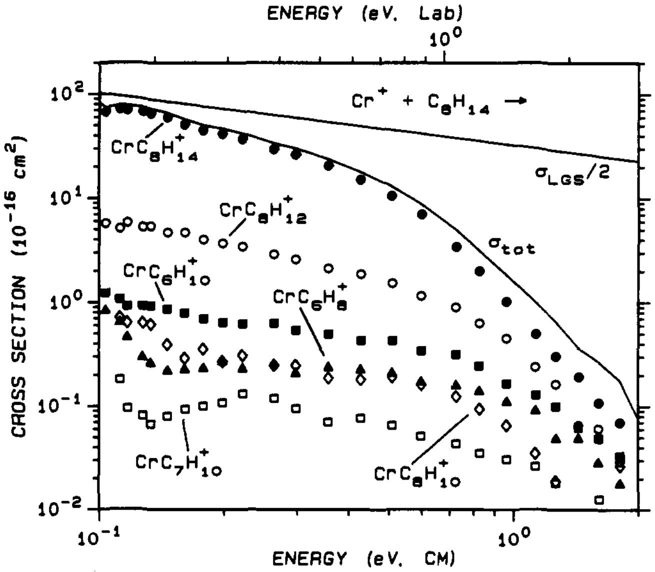


Figure 5. Variation of product cross sections with translational energy in the laboratory frame (upper scale) and the center-of-mass frame (lower scale) for the thermal energy reactions of $Cr^+(^6S)$ with 4-octyne. The cross section for the $Cr^+{\cdot}C_8H_{14}$ adduct is for a neutral pressure of 0.017 mTorr. The solid lines represent the total cross section and half the LGS collision cross section.

As in the propane system, it seems likely that formation of $CrC_2H_3^+$ and CrH^+ results from decomposition of $CrC_2H_5^+$. Indeed, the threshold for reaction 26 leads to a heat of formation for $CrC_2H_3^+$ in good agreement with that derived from the propane system. Formation of CrH^+ has a threshold (Table I) that is significantly higher than the thermodynamic threshold for formation of $CrH^+ + 2\text{-}C_4H_9$, 2.89 ± 0.09 eV, but comparable to the threshold expected for decomposition of $CrC_2H_5^+$ to $CrH^+ + C_2H_4$, 3.92 ± 0.09 eV.[41]

4-Octyne. The thermal energy reactions of $Cr^+(^6S)$ with 4-octyne were examined to see if ground-state Cr^+ is responsible for the previously observed reactivity with this molecule.[16] Our results, presented in Figure 5, show that ground-state Cr^+ does indeed react at thermal energies with 4-octyne. The reaction is fairly efficient, proceeding at ~40% of the collision limit at the lowest energies.[49] The most probable product in this reaction is the adduct ion, $CrC_8H_{14}^+$, accounting for ~90% of the total product cross section at the lowest energies. These results were obtained at a neutral pressure of 0.017 mTorr, which corresponds to a collision probability of ~9%, and a probability of stabilizing secondary collisions of ~1%. Other thermal energy products observed (Figure 5) are formed in reactions 28–32, and all release stable neutral molecules.

$$Cr^+ + C_3H_7C{\equiv}CC_3H_7 \rightarrow CrC_8H_{12}^+ + H_2 \tag{28}$$

$$\rightarrow CrC_6H_{10}^+ + C_2H_4 \tag{29}$$

$$\rightarrow CrC_7H_{10}^+ + CH_4 \tag{30}$$

$$\rightarrow CrC_6H_8^+ + C_2H_6 \tag{31}$$

$$\rightarrow CrC_8H_{10}^+ + 2H_2 \tag{32}$$

In previous work on this system, Schulze, Weiske, and Schwarz (SWS) observed the fragment ions generated in the unimolecular dissociation of the Cr(4-octyne)$^+$ adduct ions.[16] They did not observe reaction 32 and found that the branching ratio between reactions 28–31 was 75:17:6:2. For reactions 28–32, we observe a branching ratio of 75:13:2:4:6, in reasonably good agreement with SWS's results. This would seem to indicate either that SWS's ions were in their ground state or that the reaction is not sensitive to the electronic state of the chromium ions. Such insensitivity to electronic excitation has been observed previously for reactions of late-transition-metal ions with alkanes.[32,52]

Thermochemistry

Threshold energies for endothermic reactions are converted to thermochemical values of interest by assuming that the thresholds listed in Table I represent the enthalpy difference between reactants and products, that is, that there are no activation barriers in excess of the reaction endothermicity. This assumption is generally true for ion–molecule reactions and has been explicitly tested a number of times.[36–39,53] In the present work, exceptions to this are found and the origins of this behavior are discussed. In cases where thermochemical information is obtained, the bond energies are measured in more than one system to ensure that the results are free of the effects of activation barriers, kinetic shifts, and systematic errors. Table III summarizes the thermochemical data derived in this study by combining the E_T values of Table I with the supplementary literature in Table II.

$D°(CrCH_3^+)$ and $D°(CrCH_3)$. As observed previously for other metal ions,[9,10] the present study finds that reactions 33 and 34, where R is any alkyl group, compete directly. As R increases

$$M^+ + RCH_3 \rightarrow MCH_3^+ + R \tag{33}$$

$$\rightarrow MCH_3 + R^+ \tag{34}$$

in size, its IE decreases and consequently reaction 34 becomes more favorable compared to reaction 33. In the present work, this competition leads to the observation that the cross section for process 13 (reaction 33 in the dimethylpropane system) rises slowly from threshold, making analysis difficult. For this reason, we do not report $\Delta_fH(CrCH_3^+)$ from this system in Table III, although analysis can yield a value consistent with those derived in the other systems.

The other three alkane systems lead to comparable heats of formation for $CrCH_3^+$ and $Cr^+–CH_3$ bond energies (Table III). The values are in good agreement with a value measured previously in the reaction of ground state Cr^+ with ethane (Table III) and with preliminary results for reactions 7 and 13.[15] The average of the values derived from the ethane, propane, methylpropane, and butane systems is 30.3 ± 1.7 kcal/mol, nearly identical to the previously reported value of 30.2 ± 2.3 kcal/mol.[15]

Table III. Heats of Formation and Bond Dissociation Energies[a]

species	reactant	other products	Δ_fH, kcal/mol	$D°$, kcal/mol
$Cr^+—CH_3$	C_2H_6	CH_3	254.9 ± 3.5[b]	
	C_3H_8	C_2H_5	254.7 ± 1.8	
	$HC(CH_3)_3$	2-C_3H_7	255.5 ± 1.5	
	C_4H_{10}	1-C_3H_7	256.1 ± 1.4	
	av		255.3 ± 1.7	30.3 ± 1.7
$Cr—CH_3$	$HC(CH_3)_3$	2-$C_3H_7^+$	91.6 ± 2.5	
	$C(CH_3)_4$	t-$C_4H_9^+$	91.8 ± 2.3	
	av		91.7 ± 2.0	37.9 ± 2.0
$Cr^+—C_2H_5$	C_3H_8	CH_3	245.9 ± 1.2	
	C_4H_{10}	C_2H_5	242.3 ± 3.0	
	av		244.1 ± 2.1	35.0 ± 2.1
$Cr^+—2\text{-}C_3H_7$	$HC(CH_3)_3$	CH_3	243.6 ± 1.1	28.5 ± 1.3
$Cr^+—1\text{-}C_3H_7$	C_4H_{10}	CH_3	241.8 ± 1.2	32.1 ± 1.4
$Cr^+{=}C(CH_3)_2$	$HC(CH_3)_3$	CH_4	285.0 ± 1.5	
	$C(CH_3)_4$	C_2H_6	283.2 ± 1.8	
	av		284.2 ± 1.5	39 ± 3
$Cr^+{=}CHCH_2CH_3$	C_4H_{10}	CH_4	288.8 ± 1.1	36 ± 3
$Cr^+—C_4H_8$	$C(CH_3)_4$	CH_4	<275.0 ± 4.9	>–28 ± 5[c]
$Cr^+{=}CHCH_3$	C_4H_{10}	C_2H_6	278.0 ± 3.1	
	$C(CH_3)_4$	C_3H_8	278.5 ± 1.2	
	av		278.3 ± 1.9	52 ± 3
	$HC(CH_3)_3$	C_2H_6	292.2 ± 1.1	38 ± 3[c]
$Cr^+—C_2H_3$	C_3H_8	CH_3, H_2	264.1 ± 3.5	
	C_4H_{10}	C_2H_5, H_2	262.9 ± 1.2	
	av		263.5 ± 2.2	59.0 ± 2.3
$Cr^+—C_3H_4$	$C(CH_3)_4$	CH_3, H, CH_4	253.6 ± 1.8	42 ± 2[c]

[a] Ion heats of formation are based on the stationary electron convention. [b] Reference 15. [c] See text for a discussion of this thermochemistry.

This bond energy can be compared to theoretical results after converting from our 298 K value to 0 K. This is done by assuming that the system is an ideal gas with only translational and rotational degrees of freedom. Vibrational degrees of freedom contribute less than 0.1 kcal/mol.[54,55] This correction reduces our 298 K bond energy by 1.5 kcal/mol, giving $D°_0(Cr^+–CH_3)$ = 28.8 ± 1.7 kcal/mol. This value compares favorably with theoretical results for this bond energy of 25.5 kcal/mol.[56] Harrison and co-workers have calculated $D_e(CrCH_3^+)$ = 18 kcal/mol, a value that is too low due to the poor representation of the polarizability of the CH_3 ligand.[57]

The neutral Cr–methyl bond energy has not been measured before, although preliminary results from this laboratory have been reported.[58] From the data of Table I, we derive an average value from the methylpropane and dimethylpropane systems of $\Delta_fH(CrCH_3)$ = 91.7 ± 2.0 kcal/mol (Table III). This value leads to a 298 K bond energy, $D°(Cr–CH_3)$ = 37.9 ± 2.0 kcal/mol, which can be corrected to 0 K, $D°_0(Cr–CH_3)$ = 36.4 ± 2.0 kcal/mol. This latter value is in excellent agreement with a theoretical calculation of this bond energy, 37.7 kcal/mol,[56] and with the prediction of 35 kcal/mol from a correlation between metal–ligand bond energies and metal ion promotion energies, discussed in detail elsewhere.[58]

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(49) The collision cross section for ion–molecule reactions at low energies is predicted by the Langevin–Gioumousis–Stevenson (LGS) model,[49] $\sigma_{LGS} = \pi e(2\alpha/E)^{1/2}$, where e is the electron charge, α is the polarizability of the target molecule, and E is the relative kinetic energy of the reactants. The polarizability of 4-octyne is calculated as 14.4 Å^3 by using the method of Miller and Savchik.[50]

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(54) Vibrational frequencies of CH_3 are taken from the JANAF Tables.[55] Vibrational frequencies of $CrCH_3^+$ are estimated from a comparison to the methyl halides and from the stretching frequency calculated in ref 56.

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$D°(CrC_2H_5^+)$ and $D°(CrC_3H_7^+)$. $CrC_2H_5^+$ is formed in both the propane and butane systems. The two systems yield similar heats of formation (Table III) that average to $\Delta_fH(CrC_2H_5^+)$ = 244.1 ± 2.1 kcal/mol. This leads to a bond energy of $D°(Cr^+-C_2H_5)$ = 35.0 ± 2.1 kcal/mol, slightly stronger than $D°(Cr^+-CH_3)$. As noted above, it is possible that $CrC_2H_5^+$ has the chromium-hydridoethene structure 3. In this case, the heat of formation derived above and $D°(Cr^+-H)$ = 32.5 ± 2.0 kcal/mol[42] yield $D°(HCr^+-C_2H_4)$ = 39 ± 3 kcal/mol. This value is somewhat stronger than $D°(Cr^+-C_2H_4)$ as measured from the reaction of Cr^+ with c-C_2H_4O, 32 ± 5 kcal/mol,[15] but not unreasonable. The derived thermochemistry for $CrC_2H_5^+$ is consistent with either structure.

Formation of $CrC_3H_7^+$ is observed in the butane and methylpropane systems, although different structures are presumably involved, $Cr^+-CH_2CH_2CH_3$ (chromium-1-propyl ion) and $Cr^+-CH(CH_3)_2$ (chromium-2-propyl ion), respectively. The heats of formation measured lead to $D°(Cr^+-1\text{-}C_3H_7)$ = 32.1 ± 1.4 kcal/mol and $D°(Cr^+-2\text{-}C_3H_7)$ = 28.5 ± 1.3 kcal/mol, which compare nicely with $D°(Cr^+-CH_3)$ = 30.1 ± 1.8 kcal/mol. Similar to the $CrC_2H_5^+$ ion, the $CrC_3H_7^+$ ions could have a chromium-hydridopropene structure. This assumption leads to $D°(HCr^+\text{-propene})$ = 31.6 ± 2.2 and 33.4 ± 2.3 kcal/mol from the methylpropane and butane reactions, respectively. The average of these values, 32.5 ± 1.9 kcal/mol, is in excellent agreement with $D°(Cr^+-C_2H_4)$.[15] Again, thermochemistry cannot differentiate between the likely structures for the $CrC_3H_7^+$ species.

$D°(CrC_3H_6^+)$. The $CrC_3H_6^+$ ion is formed in three systems: methylpropane, dimethylpropane, and butane. As discussed above, the structure of this ion is believed to be the chromium-2-propylidene ion for the methylpropane and dimethylpropane systems and the chromium-1-propylidene ion in the butane system. In the former two systems, comparable heats of formation are obtained (Table III). The heats of formation of the $C(CH_3)_2$ and $CHCH_2CH_3$ carbenes are not known but are estimated in Table II. These values lead to $D°[Cr^+{=}C(CH_3)_2]$ = 39 ± 3 kcal/mol and $D°[Cr^+{=}CHCH_2CH_3]$ = 36 ± 3 kcal/mol (Table III). These values are smaller than the previously measured $Cr^+{=}CH_2$ double-bond strength of 54 ± 3 kcal/mol.[15]

$D°(CrC_4H_8^+)$. Since formation of methylpropene + CH_4 from dimethylpropane requires only 0.78 ± 0.03 eV, the threshold measured for reaction 16 (Table I) leads to a negative bond energy for $Cr^+-C_4H_8$ if the neutral product is methane. If the neutral products are instead assumed to be CH_3 + H, then $D°(Cr^+-C_4H_8)$ = 3.3 eV = 77 kcal/mol, much higher than other metal ion-alkene bond energies.[22,27] As mentioned above, the possibility that other $CrC_4H_8^+$ structures (such as a metallomethylcyclobutane or metal butylidene) are involved is rejected since formation of these species would require extensive rearrangement. Species such as $H-Cr^+-C_4H_7$ or $CH_3-Cr^+-C_3H_5$ are possibilities that would imply $D°(HCr^+-C_4H_7)$ = 24 ± 5 kcal/mol and $D°(H_3CCr^+-C_3H_5)$ = 19 ± 5 kcal/mol, which seem rather weak for metal ion-allyl species. We are unable to definitively conclude anything about the structure of the $CrC_4H_8^+$ product, but it seems likely that there is a substantial barrier to reaction 16.

$D°(CrC_2H_4^+)$. $CrC_2H_4^+$ is formed in all of the alkane systems. The result that is the most easily interpreted is in the butane system, where the low threshold observed for this product indicates that the neutral lost must be C_2H_6. This leads to the heat of formation $\Delta_fH(CrC_2H_4^+)$ = 278.0 ± 3.1 kcal/mol. If the structure of $CrC_2H_4^+$ is the chromium ethene ion, then this heat of formation leads to a negative $Cr^+-C_2H_4$ bond energy. As for the isobutene bond energy, this may mean that there is a barrier to reaction 24, which would be 47 ± 6 kcal/mol given $D°(Cr^+-C_2H_4)$ = 32 ± 5 kcal/mol.[15] Alternatively, if the C_2H_6 is lost by α-H transfer and a concerted four-center elimination process as shown in Scheme IV, then $CrC_2H_4^+$ has the chromium-ethylidene structure. This means that $D°(Cr^+{=}CHCH_3)$ = 52 ± 4 kcal/mol, very close to $D°(Cr^+{=}CH_2)$ = 54 ± 3 kcal/mol.[15]

In the dimethylpropane system, analysis of the threshold for reaction 19 leads to $\Delta_fH(CrC_2H_4^+)$ = 278.5 ± 1.2 kcal/mol if we assume that C_3H_8 is the neutral molecule formed. This heat of formation agrees very well with that derived from the butane system, suggesting that this product also corresponds to the chromium-ethylidene ion, although the mechanism that allows this ion and propane to be made from $C(CH_3)_4$ is unclear.

In the methylpropane system, a heat of formation of 292.2 ± 0.9 kcal/mol is derived if the neutral product is ethane, considerably above the values obtained in the other two systems. This could be an indication that there is an activation barrier to the α-CH_3 shift in this system. The heat of formation derived from the methylpropane system would mean that $D°(Cr^+{=}CHCH_3)$ = 38 ± 3 kcal/mol, lower than $D°(Cr^+{=}CH_2)$ or $D°(Cr^+{=}CHCH_3)$ derived in the other two systems.

Since the results from the deuteriated methylpropane system were ambiguous regarding the structure of this product ion, we consider the heat of formation and bond energy derived in the butane system and confirmed by the dimethylpropane system to be our best determination of these values. In all likelihood, these values correspond to the chromium-ethylidene ion. In the propane system, the threshold cannot be determined with sufficient accuracy to provide any reasonable thermodynamic information.

$D°(CrC_2H_3^+)$. The heats of formation for $CrC_2H_3^+$ measured in the propane and butane systems are in good agreement (Table III). The average of these values leads to $D°(Cr^+-C_2H_3)$ = 59.0 ± 2.3 kcal/mol. This is considerably larger than the $Cr^+-C_2H_5$ single-bond energy, possibly due to enhancement by the delocalization of the C-C π bond. A similar result is obtained for $VC_2H_3^+$ and $TiC_2H_3^+$, where $D°(V^+-C_2H_3)$ = 88 ± 5 kcal/mol[23] and $D°(Ti^+-C_2H_3)$ = 80 kcal/mol.[27] In these cases, the metal ion-vinyl bond strengths are 1.8 and 1.5 times stronger than the metal ion-methyl bond energies. For comparison, the chromium ion-vinyl bond energy is 1.9 times larger than the chromium ion-methyl bond energy. While it is conceivable that this ion could correspond to a $Cr^+{\equiv}CCH_3$ structure instead, the measured heat of formation would then yield $D°(Cr^+-CCH_3) \approx$ 119 kcal/mol (where we assume that $D°(HC{\equiv}CH) \approx D°(HC{\equiv}CCH_3)$). This bond energy is considerably higher than $D°(Cr^+-CH)$ = 75 ± 8 kcal/mol,[15] discounting this structural possibility.

$D°(CrC_3H_4^+)$. The cross section for formation of $CrC_3H_4^+$ in reaction 18 has a threshold (Table I) that yields $\Delta_fH(CrC_3H_4^+)$ = 358.8 ± 1.6 kcal/mol if the neutral products are two CH_4 molecules. This heat of formation yields a $Cr^+-C_3H_4$ bond energy that is negative by ~64 kcal/mol. While this could be due to a barrier in excess of the endothermicity, a barrier of over 64 kcal/mol seems excessive. A simpler explanation is that the neutral products of reaction 18 are CH_4 + CH_3 + H, leading to $\Delta_fH(Cr_3H_4^+)$ = 253.6 ± 1.8 kcal/mol. This value leads to the reasonable thermochemistry $D°(Cr^+-C_3H_4) \approx$ 42 ± 2 kcal/mol for either the propyne or allene isomers.

Discussion

Lifetimes of Adduct Intermediates. The lifetimes of reaction intermediates are measured by a method which parallels one introduced by Tolbert and Beauchamp.[24] We have previously discussed our implementation of this model for metal ion-ammonia systems.[59] Briefly, the pressure-dependent cross section for adduct formation can be expressed by $\sigma_a(P) = \sigma_c k_s P / k_d k_B T$, where k_B is the Boltzmann constant, σ_c is the cross section for formation of the energized Cr^+-alkane intermediate, k_s is the bimolecular rate of stabilization of this intermediate by additional collisions with the alkane, k_d is the unimolecular rate constant for dissociation of this intermediate back to reactants, and P and T are the neutral pressure and temperature, respectively. For the present systems, the LGS rate model[45] is used to calculate upper limits for k_s and σ_c, and these values for k_s are given in Table IV. When the cross sections for adduct formation are plotted as a function of neutral pressure at a given kinetic energy, the slopes of these data yield $k_s\sigma_c/k_d$. These slopes are determined by a linear regression analysis and are given in Table IV. In all cases, the intercepts are zero within our experimental error, indicating there

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Table IV. Lifetimes and Rate Constants for Stabilization of $Cr^+{\cdot}$Alkane Adducts

species	$k_s\sigma_c/k_d$,[a] 10^{-30} cm^5	k_s,[b] 10^{-9} cm^3/s	k_d,[c] 10^5 s^{-1}	τ,[d] μs
$Cr^+{\cdot}CH_4$			8×10^5	1×10^{-5} [e]
$Cr^+{\cdot}C_2H_6$			2.2×10^4	5×10^{-4} [e]
$Cr^+{\cdot}C_3H_8$			1600	0.006[d]
$Cr^+{\cdot}CH_3CD_2CH_3$	5.0	1.18	10.6	0.94
$Cr^+{\cdot}CH_3CH_2CD_3$	2.2	1.18	21.0	0.48
$Cr^+{\cdot}HC(CH_3)_3$	12.9	1.26	4.45	2.2
$Cr^+{\cdot}DC(CH_3)_3$	18.4	1.26	3.03	3.3
$Cr^+{\cdot}C_4H_{10}$	21.9	1.26	2.61	3.8
$Cr^+{\cdot}C(CH_3)_4$	91.8	1.35	0.74	13.5

[a] Experimentally measured slope of the adduct cross section vs pressure. [b] These values are upper limits calculated by using the strong-collision assumption. [c] These values are upper limits calculated as described in the text. [d] These values are lower limits calculated as described in the text. [e] Reference 17.

are no obvious radiative contributions to the lifetimes of these species. By combining the calculated values for k_s and σ_c with the measured values of the slopes, we find upper limits to k_d and lower limits to the lifetimes ($\tau = k_d^{-1}$) of the adduct intermediates. These are also listed in Table IV.

Tonkyn, Ronan, and Weisshaar[17] have determined the lifetimes of the $Cr^+{\cdot}CH_4$, $Cr^+{\cdot}C_2H_6$, and $Cr^+{\cdot}C_3H_8$ complexes, and these values are also listed in Table IV. We did not observe adduct formation in the C_3H_8 system here, presumably due to its considerably shorter lifetime (Table IV). The data of Table IV clearly indicate that the lifetimes for $Cr^+{\cdot}$alkane adducts increase with increasing alkane size. This is consistent with the increasing number of degrees of freedom and a deeper ion-induced dipole well for the larger, more polarizable alkanes. The adduct lifetimes also tend to increase with deuteration, an effect that has been seen previously[24,30,59] and attributed to lower vibrational frequencies and thus higher density of states for deuteriated adduct species.

One interesting observation is that the lifetime for the $Cr^+{\cdot}$butane adduct is longer than that for the $Cr^+{\cdot}$methylpropane adduct even though both C_4 alkanes have the same polarizability and the same number of degrees of freedom and the C–C bond energies and various Cr^+–alkyl bond energies are fairly similar. A possible explanation comes from the electrostatic potential calculations of Hankinson and Allison on the interactions of Cr^+ and butane.[60] These calculations indicate that Cr^+ binds to butane more weakly when it is close to a terminal C–C bond than when it is close to the interior C–C bond, in part because in the latter case it can interact with more than one C–C bond. Since all the C–C bonds in methylpropane are terminal, this calculation may provide an explanation for a more strongly bound $Cr^+{\cdot}$butane adduct compared with the $Cr^+{\cdot}$methylpropane.

Comparison of Mechanism and Reactivity. As discussed in the Introduction, two major reaction pathways are usually observed in the reactions of atomic transition metal ions with alkanes: dehydrogenation and alkane elimination to yield metal ion–alkene complexes. Dehydrogenation of alkanes involves an initial C–H oxidative addition to the metal center and reductive elimination of H_2 to form the metal ion–alkene complex.[1-4] Alkane elimination reactions are postulated to occur either by (1) oxidative addition of a C–C bond to the metal followed by a β-H shift to the metal center and reductive elimination of the alkane or (2) oxidative addition of a C–H bond followed by a β-alkyl shift and reductive elimination of the alkane.

The present results show that $Cr^+(^6S)$ is unique among the first-row transition-metal ions. We do not observe dehydrogenation processes with any of the alkanes studied here. In addition, although we do observe formation of the CrH^+ ion in these systems, in all cases the observed threshold is much higher than the thermodynamic threshold for C–H bond insertion processes. Consequently, we conclude that CrH^+ is formed exclusively by decomposition of other primary product ions or stripping reactions. Further, we also do not observe any hydride abstraction reactions to form $CrH + R^+$ ($R = C_3H_7, C_4H_9, C_5H_{11}$) in any of the alkane systems. As noted in the Introduction, all three of these processes (dehydrogenation, hydrogen atom transfer, and hydride transfer) are considered to proceed via C–H bond activation pathways. Thus, these observations are clear evidence that $Cr^+(^6S)$ does *not* react via initial C–H bond activations of alkanes. Further, all of the reaction products observed can be rationalized with mechanisms that use C–C bond activation processes exclusively (Schemes I–IV).

In addition, although methane loss is observed in the reactions of $Cr^+(^6S)$ with methylpropane, dimethylpropane, and butane, a distinct barrier to this reaction is seen in the dimethylpropane system. Like this latter reaction, other pathways in the methylpropane and butane systems that involve a β-H transfer step (which is the preferred mechanism for most metal ions) also appear to be constrained for Cr^+. This means that the systems studied here must find alternate reaction pathways. These kinetically favored pathways include α-H and α-CH_3 transfers, which lead to isomeric products that are considerably less stable than the isomers ordinarily formed by other metal ions. In the dimethylpropane system, an α-H is unavailable and hence a barrier to methane elimination, which presumably must then proceed via a β-H transfer, is observed. In the butane system, loss of C_2H_6 appears to be the result of an α-H reaction pathway rather than β-H transfer. From these reactions and failure to observe methane elimination in the propane system, we conclude that β-H transfer to Cr^+ is hindered in the alkane systems. Again, this is clearly in contrast to reactions of other transition-metal ions with alkanes and demonstrates the unique reactivity of ground-state $Cr^+(^6S)$. The reasons for this highly specific behavior are not obvious. It is possible that reaction of the ^6S state of Cr^+ is driven primarily by thermodynamic considerations, such that the weaker C–C bonds of the alkanes are activated preferentially over C–H bonds. This is discussed in substantially more detail in the following paper.[18]

Reactivity of Cr^+ with 4-Octyne. In contrast to the alkanes, $Cr^+(^6S)$ does dehydrogenate 4-octyne, a reaction that presumably occurs by metal insertion into a C–H bond. The reaction efficiency in this system (excluding adduct formation), however, never exceeds ~4% of the collision cross section, as given by the LGS model. Ground-state Cr^+ ions have also been seen to insert into C–H and N–H bonds of methylamines, but do so with cross sections that are also less than 5% of the collision cross section.[48] These results indicate that C–H bond insertion becomes allowed for $Cr^+(^6S)$ when the neutral molecule has a group with a high electron density such as the nitrogen lone pair of electrons on the methylamine or the triple bond in 4-octyne. The presence of such a group probably enhances reactivity by two means. First, it strengthens the initial interaction between the metal ion and neutral reactant such that the lifetime of the adduct complex increases and the energy of the transition state for reaction is lowered. Second, it weakens adjacent bonds making them more easily activated by the chromium ion.

Summary

The reactions of ground-state $Cr^+(^6S)$ ions with propane, butane, methylpropane, and dimethylpropane are studied by using guided ion beam mass spectrometry. The major result of this study is the proposed unusual reaction mechanisms for the interactions of $Cr^+(^6S)$ with alkanes that imply that ground-state Cr^+ reacts *exclusively* via C–C bond insertion pathways. These mechanisms are substantiated by the observation that the C–H bond activation processes of dehydrogenation and formation of $CrH^+ + R$ and of $CrH + R^+$ ($R = C_3H_7, C_4H_9, C_5H_{11}$) are not seen in any of the systems studied here. Further, barriers to β-H transfer processes are also observed in the present systems, and α-H and α-CH_3 transfers become the kinetically preferred pathways. These observations demand that many of the products formed in these reactions have structures that are more energetic than those formed in the reactions of other metal ions with the same alkanes. Such distinct reactivity is unprecedented and is very different from that

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of excited-state Cr$^+$ ions with alkanes, as discussed in the following paper.[18]

The thermochemistry for various chromium–ligand complex ions is also derived from the present results. Thermochemistry for CrCH$_3^+$ is found to be in good agreement with previous results.[15] New thermochemistry for CrCH$_3$, CrC$_2$H$_3^+$, Cr=CHCH$_3^+$, CrC$_2$H$_5^+$, CrC$_3$H$_4^+$, Cr=CHCH$_2$CH$_3^+$, Cr=C(CH$_3$)$_2^+$, and CrC$_3$H$_7^+$ is reported and tabulated in Table III.

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Electronic Effects in C–H and C–C Bond Activation: Reactions of Excited-State Cr$^+$ with Propane, Butane, Methylpropane, and Dimethylpropane

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Abstract: Guided ion beam mass spectrometry is used to study the reactions of excited states of Cr$^+$ with propane, butane, methylpropane, and dimethylpropane. The effect of electronic energy as well as kinetic energy on the reactivity of atomic chromium ions is examined and reveals several interesting aspects of Cr$^+$ chemistry. The present results include the first *direct* evidence for reaction of the Cr$^+$(^{6}D) first excited state. Most interesting is the observation that the excited quartet states of Cr$^+$ react with alkanes very differently than ground-state Cr$^+$(^{6}S). Previously we found that Cr$^+$(^{6}S) activates only C–C bonds of alkanes, while in the present study we find that the excited Cr$^+$(^{4}D, ^{4}G) states activate both C–H and C–C bonds of alkanes. The reactivity of the ^{6}D first excited state of Cr$^+$ is similar to that of the ^{6}S ground state. These reaction systems are currently the only examples where electronic excitation of a transition-metal ion drastically changes the products formed.

Introduction

The past decade has seen extensive investigation of the reactivity of the first-row transition-metal ions with small alkanes in order to gain insight into C–H and C–C bond activation processes.[1-7] Cr$^+$ has been one of the least studied metal ions, largely because the stable half-filled shell of the Cr$^+$(^{6}S, 3d^5) ground state renders it relatively unreactive.[8,9] This further suggests that excited states of Cr$^+$ having either 4s3d^4 or low-spin 3d^5 configurations should be much more reactive than the ground state. Early work by Ridge and co-workers[10] and Halle et al.[11] and later work in our laboratories[12,13] demonstrated this for reaction of electronically excited Cr$^+$ with H$_2$ and methane. Indeed, based on their studies, Halle et al. concluded that electronic but *not* translational excitation is effective in promoting certain reactions of Cr$^+$, particularly the production of CrCH$_2^+$ in the methane system. In contrast, our subsequent studies demonstrated that both translational and electronic energy are capable of promoting all reaction channels in these systems.[12,13]

For the systems studied in the present work, the earliest studies are those on the reactions of Cr$^+$ with butane and methylpropane by Freas and Ridge.[14] They found that EI-generated Cr$^+$ reacted with these molecules at thermal energies, a result that they speculated was due to ions in long-lived excited states. Later, Schilling and Beauchamp found that ground-state Cr$^+$ did not react at thermal energies with any of the title alkanes.[8] The present results are consistent with both studies and confirm that the previously observed reactivity at thermal energies is due to excited-state ions.

One interesting aspect of the previous work in our laboratory on the reactions of Cr$^+$ with H$_2$, HD, D$_2$, and CH$_4$[12,13] was the failure to observe any reaction attributable to the ^{6}D state of Cr$^+$. In both studies, reactivity due to the ^{6}S ground state and to the a^{4}D second and a^{4}G third excited states of Cr$^+$ (Table I) was clearly identified. There are two possible explanations for this behavior: Either the ^{6}D state is unreactive with H$_2$ and CH$_4$, or it is not formed appreciably. The present results will show that the former explanation for this behavior is correct.

In the present study, we complement our companion paper on the reactions of alkanes with ground-state Cr$^+$(^{6}S)[15] by examining the reactions of propane, butane, methylpropane, and dimethylpropane with Cr$^+$ formed via electron impact (EI) ionization, a source known to produce significant quantities of excited-state ions. The primary results of these studies include the first direct evidence for reaction of the Cr$^+$(^{6}D) first excited state and the characterization of the reactivity of the excited quartet states of Cr$^+$. These excited states are found to activate reaction

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