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.

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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Table I. Low-Lying Electronic States of Cr⁺

state (confign)	E (eV)[a]	population (%)				
		SI[b]	30[c]	32[c]	35[c]	50[c]
a⁶S(3d⁵)	0.0	99.83 (0.06)	80 (2) 80, 75 (5)[d] 86 (5)[e]	72 (4)	63 (2)	56 (4) ~60[d] 46 (5)[e]
a⁶D(4s3d⁴)	1.52	0.17 (0.06)	19 (2) 13 (5)[e]	27 (3)	36 (3)	39 (4) 47 (5)[e]
a⁴D(4s3d⁴)	2.46 ⎤	≪0.01	1 (1) 1.4 (0.5)[d] 1[e]	1 (1)	3 (1)	5 (2) 6 (2)[d] 7 (3)[e]
a⁴G(3d⁵)	2.54 ⎦					
higher states	≥2.71	≪0.01	~0[f]	f	f	f

[a] Statistical average of all J levels. Energies are taken from: Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1977**, *6*, 317. [b] Surface ionization. Populations are based on a Maxwell–Boltzmann distribution at a filament temperature of 2200 ± 100 K. [c] Electron energies in electronvolts for electron impact ionization. [d] References 12 and 13. [e] Reference 25. [f] These states are not obviously present at Ee = 30 eV, but are at Ee = 50 eV[13] although the absolute quantities are unknown. No direct information on their presence is available at intermediate electron energies, although there are some indications that these states are populated; see text.

channels not observed for ground-state ions, such as formation of CrCH₂⁺ and dehydrogenation of the alkane in all four reaction systems. In the propane, methylpropane, and butane systems, formation of CrH + R⁺ (R = C₃H₇, C₄H₉) is also observed. Formation of these reaction products indicates that the quartet excited states of Cr⁺ activate C–H as well as C–C bonds of alkanes, in contrast to the ground state which activates C–C bonds exclusively.[15]

Experimental Section

General Procedures. The ion beam apparatus used in these experiments has been described in detail elsewhere.[16] Briefly, 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 low pressures (0.02–0.08 mTorr) of the neutral alkane, 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 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%.[16] Pressure-dependent studies verified that all reaction cross sections are the result of single ion–molecule collisions, unless stated otherwise.

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.[16] 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 width of ~ $0.4E_{CM}^{1/2}$(eV).[17] Laboratory ion energies (lab) are converted to energies in the center-of-mass frame (CM) by using the conversion $E_{CM} = E_{lab}M/(m + M)$, where m is the ion mass and M is the target molecule mass.

The collision cross section for ion-molecule reactions at low energies is predicted by the Langevin–Gioumousis–Stevenson (LGS) model[18] (eq 1), where e is the electron charge, α is the polarizability of the target

$$\sigma_{LGS} = \pi e(2\alpha/E)^{1/2} \qquad (1)$$

molecule, and E is the relative kinetic energy of the reactants. Many exothermic reaction cross sections follow this type of energy dependence, although deviations are commonly seen.[19] For the alkanes studied here, we use $\alpha[C_3H_8] = 6.23$ Å³, $\alpha[C_4H_{10}] = \alpha[HC(CH_3)_3] = 8.0$ Å³, and $\alpha[C(CH_3)_4] = 10.0$ Å³.[20]

Ion Source. An electron impact ionization source is used to produce the Cr⁺ ions from CrO₂Cl₂. Ions are formed when the electron energy (Ee) exceeds the appearance energy of Cr⁺ from CrO₂Cl₂, 19.15 ± 0.07 eV.[21] For the present experiments, data are taken at Ee = 30, 32, 35, and 50 eV. Past experiments demonstrate that the degree of electronic

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Table II. Cr⁺ + Propane Product Distributions at 0.1 eV

product	⁶S[a]	30 eV[b]	50 eV[c]	⁶D[a]
CrH⁺	+	0	9	+
CrCH₂⁺	–	9	26	+
CrCH₃⁺	+	23	17	+
CrC₂H₃⁺	+	2	7	?
CrC₂H₄⁺	+	16	5	+
CrC₂H₅⁺	+	31	11	+
CrC₃H₆⁺	–	16	20	–
C₃H₇⁺	–	3	5	?

[a] A plus sign indicates that the product is formed in the reaction of the specified state at elevated kinetic energies. A minus sign indicates that the product is not formed. A question mark indicates that the size of the cross section was too small to make a clear determination of the reactivity. [b] Uncertainties are estimated to be about ±10. [c] Uncertainties are estimated to be about ±3.

excitation in the Cr⁺ beam can be varied by adjusting the Ee over this range.[12,13]

Results

Cross sections were obtained for reaction of all four alkanes with Cr⁺ produced at several electron energies. All ionic products seen in the reactions of Cr⁺(⁶S) with propane, methylpropane, dimethylpropane, and butane[15] are also observed in the present work, although the kinetic energy dependence of the cross sections for Cr⁺ produced by EI is markedly different from that for Cr⁺(⁶S). In addition, Cr⁺(EI) yields a number of products in each system that are *not* formed by Cr⁺(⁶S). These are shown by reactions 2–4. In the following sections, we highlight specific examples of the data from the four alkane systems to illustrate the major results of these studies.

$$Cr^+ + C_nH_{2n+2} \longrightarrow CrC_nH_{2n}{}^+ + H_2 \qquad (2)$$
$$\longrightarrow CrH + C_nH_{2n+1}{}^+ \qquad (3)$$
$$\longrightarrow CrCH_2{}^+ + C_{n-1}H_{2n} \qquad (4)$$
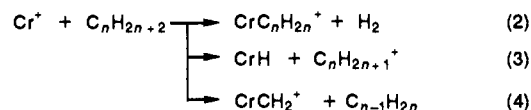
Propane. Table II lists the product distributions at a kinetic energy of 0.1 eV for reaction of propane with Cr⁺ produced by EI at Ee = 30 and 50 eV. This table shows that the same products observed for reaction of Cr⁺(⁶S) are observed here[15] but that processes 2–4 are also observed in the reactions of Cr⁺(EI) + C₃H₈. At the lowest kinetic energies, the total cross sections for reaction of propane with Cr⁺(EI) are ~0.4 and ~3% of σ_{LGS} for Ee = 30 and 50 eV, respectively. At the lowest kinetic energies, most reaction cross sections increase with decreasing energy, indicative of exothermic reactions, and fall off somewhat faster than predicted by eq 1. Cross sections for formation of C₃H₇⁺ (process 3) and CrH⁺ + C₃H₇ are fairly flat over the energy range examined for both the 30- and 50-eV data.

Methylpropane. Table III lists the product distributions at a kinetic energy of 0.1 eV for reaction of methylpropane with Cr⁺ produced by EI at Ee = 32 and 50 eV. The same products observed for reaction of Cr⁺(⁶S) with methylpropane[15] are observed here, and we also see formation of the new processes 2–4.

Table III. Cr$^+$ + Methylpropane Product Distributions at 0.1 eV

product	$^6S^a$	32 eV^b	50 eV^c	$^6D^a$
CrH$^+$	+	0	0	+
CrCH$_2^+$	−	3	7	+
CrCH$_3^+$	+	6	9	+
CrC$_2$H$_4^+$	+	45	18	?
CrC$_3$H$_6^+$	+	32	26	+
CrC$_4$H$_8^+$	−	6	38	−
C$_4$H$_9^+$	−	5	1	?
C$_3$H$_7^+$	+	3	1	+
C$_3$H$_5^+$	+	0	<1	?

^{a} A plus sign indicates that the product is formed in the reaction of the specified state at elevated kinetic energies. A minus sign indicates that the product is not formed. A question mark indicates that the size of the cross section was too small to make a clear determination of the reactivity. ^{b} Uncertainties are estimated to be about ±10. ^{c} Uncertainties are estimated to be about ±3.

Table IV. Cr$^+$ + Dimethylpropane Product Distributions at 0.1 eV

product	$^6S^a$	30 eV^b	50 eV^c	$^6D^a$
CrH$^+$	+	0	0	+
CrCH$_2^+$	−	<1	3	+
CrCH$_3^+$	+	0	4	+
CrC$_2$H$_4^+$	+	37	14	−
CrC$_3$H$_4^+$	+	0	4	+
CrC$_3$H$_6^+$	+	10	10	+
CrC$_4$H$_8^+$	+	28	58	+
CrC$_5$H$_{10}^+$	−	2	3	−
C$_4$H$_9^+$	+	21	3	+
C$_3$H$_5^+$	+	1	<1	?

^{a} A plus sign indicates that the product is formed in the reaction of the specified state at elevated kinetic energies. A minus sign indicates that the product is not formed. A question mark indicates that the size of the cross section was too small to make a clear determination of the reactivity. ^{b} Uncertainties are estimated to be about ±10. ^{c} Uncertainties are estimated to be about ±3.

At the lowest kinetic energies, the total cross sections for reaction of HC(CH$_3$)$_3$ with Cr$^+$(EI) are ~0.5%, ~0.7%, ~2%, and ~5% of σ_{LGS} for Ee = 30, 32, 35, and 50 eV, respectively. The cross section for reaction 2 increases monotonically with decreasing energy at all Ees, indicative of an exothermic reaction, and has an energy dependence of $E^{-0.5}$ at the lowest kinetic energies (<0.5 eV). The adduct ion, CrC$_4$H$_{10}^+$, was also observed in the EI data and was found to be collisionally stabilized, as for the ground-state reaction.

Dimethylpropane. Table IV contains the product distributions at a kinetic energy of 0.1 eV for reaction of C(CH$_3$)$_4$ with Cr$^+$ produced by EI at Ee = 30 and 50 eV. In addition to those products observed in the Cr$^+$(^6S) system,[15] processes 2 and 4 are observed for Cr$^+$(EI) at all four Ees. At the lowest kinetic energies, the total reaction cross sections are ~0.7%, ~2%, ~4%, and ~15% of σ_{LGS} at Ee = 30, 32, 35, and 50 eV, respectively. Dehydrogenation of dimethylpropane (process 2) is not often observed with first-row transition-metal ions.[4,22] In all four EI data sets, the cross section for this process decreases as $E^{-1.0}$, much faster than predicted by eq 1. Similar to results in the ground-state system,[15] the adduct ion, CrC$_5$H$_{12}^+$, was observed in the EI data at all four Ees and was found to be a collisionally stabilized reaction product.

Butane. The product distributions at a kinetic energy of 0.1 eV for reaction of butane with Cr$^+$ produced by EI at Ee = 32 and 50 eV are listed in Table V. As in the other systems, processes 2–4 are observed for Cr$^+$(EI) in addition to those products observed for reaction of Cr$^+$(^6S) with butane.[15] At the lowest kinetic energies, the total cross sections for reaction of butane with Cr$^+$(EI) are ~0.5%, ~2%, ~4%, and ~7% of σ_{LGS} for Ee = 30, 32, 35, and 50 eV, respectively. The adduct ion, CrC$_4$H$_{10}^+$, was

Table V. Cr$^+$ + Butane Product Distributions at 0.1 eV

product	$^6S^a$	32 eV^b	50 eV^c	$^6D^a$
CrH$^+$	+	0	0	+
CrCH$_2^+$	−	1	5	+
CrCH$_3^+$	+	1	5	+
CrC$_2$H$_3^+$	+	3	NC	+
CrC$_2$H$_4^+$	+	47	4	+
CrC$_2$H$_5^+$	+	5	22	+
CrC$_3$H$_6^+$	+	40	29	+
CrC$_4$H$_8^+$	−	<1	29	−
C$_4$H$_9^+$	+	<1	3	?
C$_3$H$_7^+$	+	2	2	?

^{a} A plus sign indicates that the product is formed in the reaction of the specified state at elevated kinetic energies. A minus sign indicates that the product is not formed. A question mark indicates that the size of the cross section was too small to make a clear determination of the reactivity. NC indicates that the product was not collected. ^{b} Uncertainties are estimated to be about ±10. ^{c} Uncertainties are estimated to be about ±3.
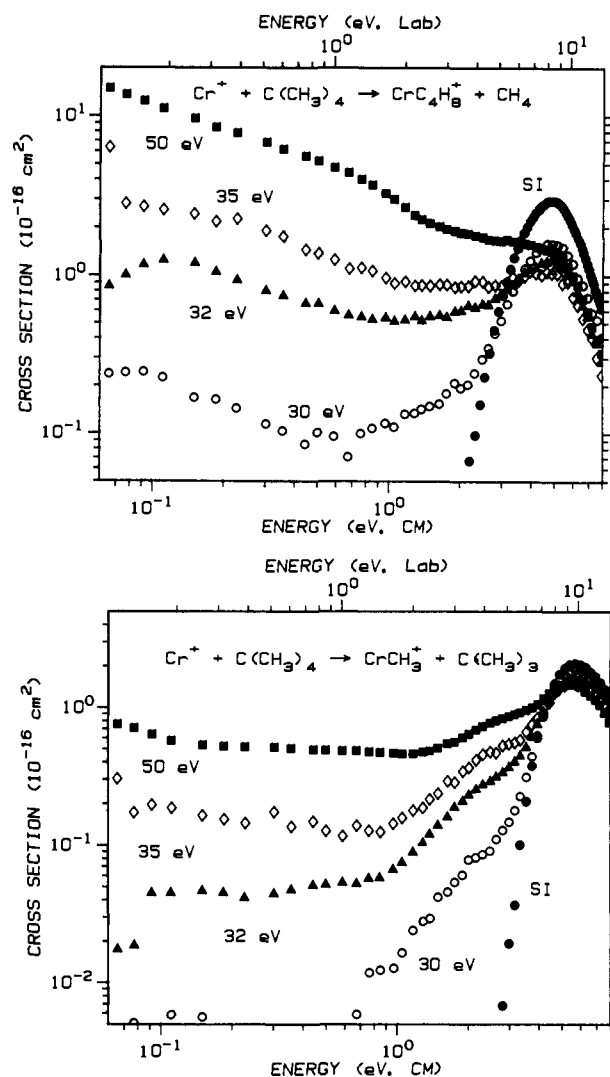

Figure 1. Cross sections for the production of CrCH$_3^+$ (a, top) and CrC$_4$H$_8^+$ (b, bottom) from reaction of dimethylpropane with Cr$^+$ produced by surface ionization (SI) and by electron impact (EI) with Ee = 30, 32, 35, and 50 eV as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) of reference.

also observed in the EI data at all four Ees and was found to be a collisionally stabilized reaction product, as was true in the Cr$^+$(^6S) + C$_4$H$_{10}$ system.[15]

Dependence on Electron Energy. Figure 1 illustrates the variation in reaction cross sections with electron energy for two reaction channels in the dimethylpropane system and compares these results with those for reaction of Cr$^+$(^6S) produced by surface

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ionization (SI). It can be seen that the energy dependence of the cross sections for $Cr^+(SI)$ and $Cr^+(EI)$ are similar at elevated kinetic energies but that the magnitudes generally decrease with increasing Ee. Thus, the reactions at these energies are due primarily to ground-state $Cr^+(^6S)$. At low kinetic energies, the cross sections increase with increasing Ee. This behavior clearly indicates that this low-energy reactivity is due to electronically excited Cr^+ states.

The electronic states responsible for the observed reactivity can be assigned by using the thermochemistry determined previously for ground-state $Cr^+(^6S)$.[15] This is illustrated nicely by the results for the $CrCH_3^+$ reaction channel. Formation of this product requires 2.44 ± 0.08 eV for ground-state $Cr^+(^6S)$. As shown in Figure 1a, the threshold for forming this product when Ee = 30 eV has shifted down to 0.9 ± 0.2 eV,[23] 1.5 ± 0.2 eV lower in energy than the ground-state threshold. Quantitatively similar threshold shifts are obtained in all four alkane systems for the $CrCH_3^+$ product channel and other product channels as well. This is illustrated by the $CrC_4H_8^+$ product cross section in Figure 1b which exhibits an endothermic feature that begins near 0.6 eV, ~ 1.5 eV below the threshold for $Cr^+(SI)$. The 1.5-eV shift in threshold energies is in excellent agreement with the excitation energy of the $Cr^+(^6D)$ first excited state and clearly is not consistent with the excitation energies of any other electronic state (Table I). These results strongly suggest that $Cr^+(^6D)$ does indeed react with these alkanes.[24]

At kinetic energies lower than the threshold for reaction of $Cr^+(^6D)$, the cross sections in Figure 1 exhibit energy dependences that are characteristic of exothermic reactions. Based on the thresholds for reaction of the $Cr^+(^6S)$ ground state,[15] these exothermic features must be due to Cr^+ ions with $E_{el} \geq 2.4$ eV. As demonstrated elsewhere,[13] it is primarily the ^4D and ^4G excited states (Table I) that are populated at Ee = 30 eV. As the electron energy is increased further, additional electronic states are populated until those with excitation energies greater than 3 eV are present at Ee = 50 eV.

Figure 2 illustrates the variation in reaction cross sections with electron energy for two reaction channels in the dimethylpropane system that were not observed for reaction of $Cr^+(^6S)$. The absolute magnitudes for $\sigma(CrC_5H_{10}^+)$ in the 30-, 32-, and 35-eV EI data are nearly identical (Figure 2a) with that for the 50-eV EI data approximately 1 order of magnitude larger. This dependence on electron energy is not consistent with the change in populations of either the ^6D or ^4D, ^4G states (Table I). We therefore think that this product may be due primarily to reaction of a small population of excited states above the ^4D and ^4G states. In contrast, cross sections for the dehydrogenation channels in the other three alkane systems have magnitudes that increase as the electron energy is increased in a fashion that is consistent with reactivity due to the quartet states *and* to these higher lying excited states.

Cross sections for formation of the chromium–methylidene ion from dimethylpropane (reaction 4) are shown in Figure 2b. For the $Cr^+(^6S)$ ground state, this reaction is endothermic by 2.03 or 2.86 eV when the neutral products are methylpropane or propene + methane, respectively. A rough analysis of the relatively small 30-eV data yields a reaction threshold of 1.1 ± 0.2 eV. This is consistent with the thermodynamic threshold for $Cr^+(^6D)$, ~ 0.5–1.3 eV, although an assignment of the neutral products cannot be made unambiguously. We therefore attribute this endothermic reactivity observed at all four Ees to reaction of the first excited state of Cr^+. The exothermic portion of the $CrCH_2^+$ cross section increases with small increases in Ee (Figure 2b) consistent with reactivity due to the excited quartet states of Cr^+ if methylpropane is the neutral product.

Figure 2. Cross sections for the production of $CrC_5H_{10}^+$ (a, top) and $CrCH_2^+$ (b, bottom) from reaction of dimethylpropane with Cr^+ produced by electron impact (EI) with Ee = 30 (not shown in part a for clarity), 32, 35, and 50 eV as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) of reference.

Cross sections for many of the other reaction products display dependences on electron energy that are similar to one of those illustrated in Figures 1 and 2. Some of these cross sections contain features that can be attributed to reaction of the $Cr^+(^6D)$ first excited state, while others do not. The CrH^+ reaction cross sections are an exception in that they do not display multiple features, but rather have reaction thresholds that simply shift to lower energies as the Ee is increased.

$Cr^+(^6D)$ **Reactivity.** Following the procedure outlined above, a comparison of the data for different Cr^+ source conditions allows us to discern whether the ^6D first excited state is forming the reaction products in these four systems. Tables II–V tabulate the results of this analysis. While there are a few ambiguous cases, $Cr^+(^6D)$ generally produces all of the same reaction products observed for ground-state $Cr^+(^6S)$. As for the ground state, $Cr^+(^6D)$ also does not undergo reaction 2. Thus, these products must be due entirely to the excited quartet states and higher lying states. However, $Cr^+(^6D)$ does react to form $CrCH_2^+$ (process 4) in all four alkane systems, while this product is not observed for $Cr^+(^6S)$. Results for reaction 3 are not clearcut in that the electron energy dependence for these minor products is consistent with reactivity due to the ^4D and ^4G states but contributions from the ^6D state cannot be unequivocally eliminated.

(23) For a detailed description of the cross-section modeling employed, see ref 15.

(24) The only other possible explanation is that such reactivity is due to high-lying excited states reacting with a barrier, but cross-section features attributable to these states are also present. Further, if barriers are involved, it seems unlikely that they would all be exactly the same for several different reaction channels in four different alkane systems.
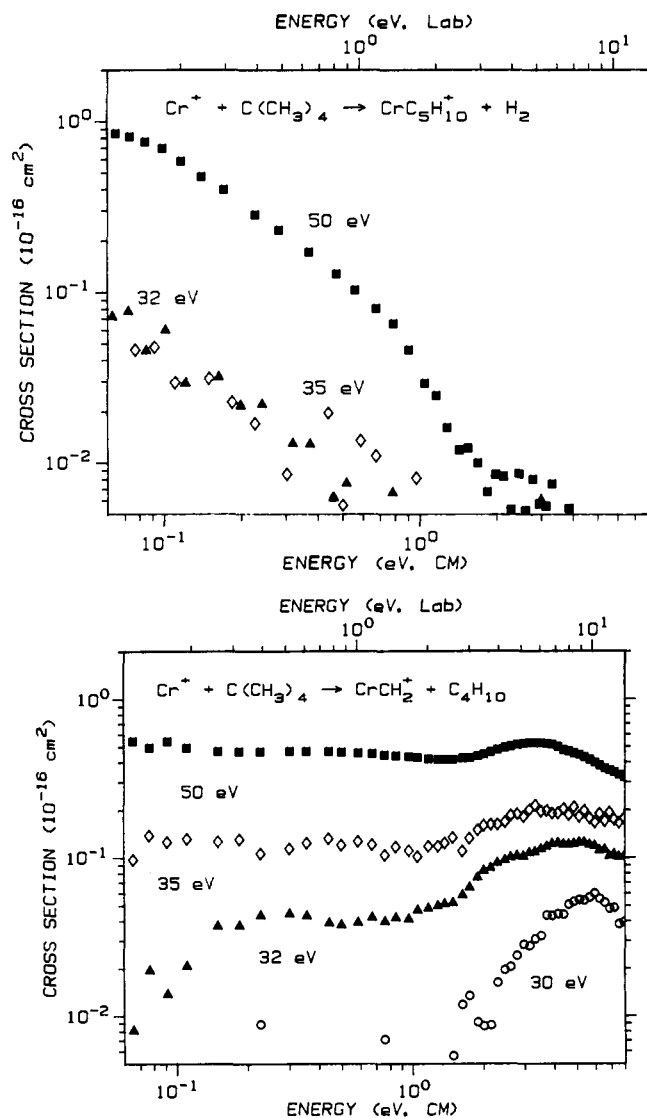
EI Beam Populations. Comparison of the various features in the cross sections for the four EI data sets and the single feature in the SI data provides additional information about the populations of the ^6D and quartet states at all four electron energies. To make this comparison, we analyze the $CrCH_3^+$ cross sections in detail (Figure 1) since the various features are well defined in all four reaction systems. We have, however, confirmed this analysis with other reaction product cross sections in all four systems.

Comparison of the highest energy features in the $CrCH_3^+$ cross sections indicates that, for the 30- and 50-eV EI data, these features are 0.80 ± 0.02 and 0.56 ± 0.04 times the cross section for $Cr^+(^6S)$, respectively. These populations are in good agreement with the ^6S populations found previously in the H_2 and CH_4 systems, ~0.8 and 0.75 ± 0.05 for the 30-eV EI beam and ~0.60 for the 50-eV EI beam.[12,13] Similar operations on the 32- and 35-eV EI data yield ground-state populations in these beams of 72 ± 4% and 63 ± 2%, respectively (Table I).

By subtracting these ground-state contributions from the EI data, it is straightforward to obtain cross sections corresponding only to excited states. These cross sections can then be analyzed further to determine the reactivity due exclusively to the ^6D state. In all systems, the exothermic portions of the 30-eV EI data attributable to the excited quartet states never exceed 1 ± 1% of σ_{LGS}. If we assume that these states react on every collision, then this equals the percentage of these states in the beam. This is consistent with results in the $Cr^+ + H_2$ and CH_4 studies,[12,13] where it was estimated that ~1.3 and 1.4 ± 0.5% of the 30-eV EI beam were in the reactive ^4D and ^4G excited states. We therefore attribute the remaining 19 ± 3% of the beam to the ^6D first excited state. In the H_2 and CH_4 systems, this same fraction of the beam was unreactive and therefore could not be assigned to any particular state.

This population information can then be used to further analyze the data obtained at higher electron energies. This analysis applied to several different reaction channels yields the populations and uncertainties given in Table I. The populations found in these experiments agree nicely with the previous results from the H_2 and CH_4 experiments in our laboratories. In addition, the trends in the beam populations found here agree with the results of "ion chromatography" experiments by Kemper and Bowers,[25] also given in Table I.

As noted above, the thermal energy reactivities observed in the four systems for excited-state Cr^+ ions produced at $Ee = 30, 32, 35$ and 50 eV are 0.5 ± 0.1%, 1.6 ± 0.7%, 3.3 ± 1.1%, and 9 ± 5% of the LGS collision cross section, respectively. These values are the same within experimental error as the excited-state populations derived here for these EI beams (Table I). This is a clear demonstration that the excited quartet states of Cr^+ react with near unit efficiency.

Using all of this population information, state-specific cross sections for reaction of $Cr^+(^6D)$ and $Cr^+(^4D, ^4G)$ can be obtained. The results for the two reaction channels of Figure 1 are compared with the ground-state cross sections in Figure 3. It is evident that the quartet states are much more reactive than the sextet states and that the ground state is somewhat more reactive than the first excited state. This is qualitatively true of all reaction channels, except for reaction 4 where the ^6D is more reactive than the ^6S.

Discussion

Mechanism. In our paper on the interaction of ground-state Cr^+ with large alkanes, we discussed in detail the unique reaction mechanisms found in these systems.[15] It was proposed that ground-state $Cr^+(^6S)$ ions react with alkanes exclusively via C–C bond activation pathways and that alkane elimination reactions proceed via concerted four-center elimination processes. In the present systems, we find that excited states of Cr^+ form the same products observed in the ground-state systems but also react along C–H bond activation pathways. Indeed, while dehydrogenation

(25) Kemper, P. R.; Bowers, M. T. *J. Phys. Chem.* **1991**, *95*, 5134–5146.
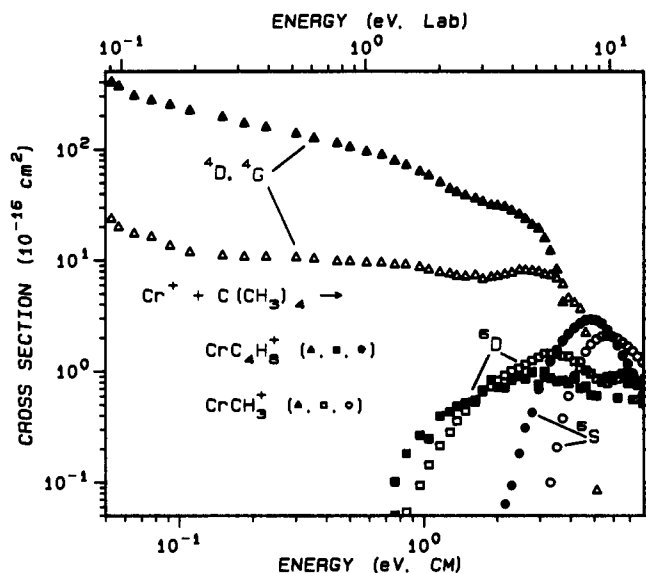
Figure 3. State-specific cross sections for the production of $CrCH_3^+$ (open symbols) and $CrC_4H_8^+$ (solid symbols) from reaction of dimethylpropane with Cr^+ as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale) of reference. Triangles indicate results for reaction of $Cr^+(^4D, ^4G)$; squares, those for $Cr^+(^6D)$; and circles, those for $Cr^+(^6S)$.

of the alkanes is not observed for reaction of $Cr^+(^6S)$, it is a dominant process for Cr^+ excited quartet states in the butane, methylpropane, and propane systems. It is even seen in the dimethylpropane system, a rather unusual observation for reaction of first-row transition-metal ions,[4,22] although this may be due to very high-lying excited states of Cr^+.

In the propane system, the intermediate used to explain formation of all reaction products in the ground-state system[15] was I, $CH_3–Cr^+–C_2H_5$, corresponding to C–C bond activation by the Cr^+. Here, we propose that primary or secondary C–H bond activation to produce II, $H–Cr^+–C_3H_7$, is also accessible to excited states of Cr^+. These types of intermediates have been proposed previously for reactions of transition-metal ions with alkanes.[1–10,22b,26] Intermediate II can rearrange by β-H transfer and reductive elimination to form $CrC_3H_6^+ + H_2$ (reaction 2) or it can cleave the Cr–C bond to yield $CrH + C_3H_7^+$ (reaction 3) (which occurs more readily for 2-propyl than for 1-propyl due to the lower ionization energy of the former radical). Reaction 3 can also occur by a more direct H^- transfer between Cr^+ and $C_3H_7^+$. If II has the $H–Cr^+–CH_2C_2H_5$ structure formed by activation of the primary C–H bond of propane, then reaction 4 to form $CrCH_2^+$ can occur by a four-centered reductive elimination of C_2H_6. Such four-center eliminations by Cr^+ have been observed for dehydrogenation of methane,[13] for elimination of CH_4 from ethane,[9] and for production of chromium alkylidene ions in the reactions of ground-state Cr^+ with these alkanes.[15]

Similarly, in the methylpropane, dimethylpropane, and butane systems, excited Cr^+ ions have access to the C–C bond activation intermediates proposed in the $Cr^+(^6S)$ study[15] as well as to the C–H bond activation intermediates, $H–Cr^+–R$ (where R = $C(CH_3)_3$ or $CH_2CH(CH_3)_2$ in the methylpropane system, $CH_2C(CH_3)_3$ in the dimethylpropane system, and $CH_2(C_3H_7)$ or $CH(CH_3)(C_2H_5)$ in the butane system). These latter intermediates can lead to dehydrogenation reactions and formation of CrH + R^+, $CrH^+ + R$, and $CrCH_2^+$ as described above. In these systems, an alternate pathway for reaction 4 is subsequent decomposition of another primary channel, for example, propene loss from $CrC_4H_8^+$ in the dimethylpropane system.

(26) van Koppen, P. A. M.; Brodbelt-Lustig, J.; Bowers, M. T.; Dearden, D. V.; Beauchamp, J. L.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 2359–2369. van Koppen, P. A. M.; Brodbelt-Lustig, J.; Bowers, M. T.; Beauchamp, J. L.; Fisher, E. R.; Armentrout, P. B. Unpublished results.
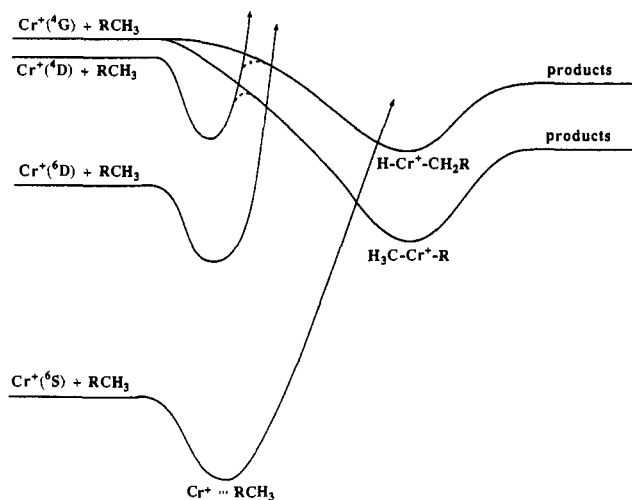
Figure 4. Semiquantitative potential energy surfaces for the reaction of Cr^+ with alkanes.

This leads to a further distinction between the reaction mechanisms in the ground-state and excited-state systems. For $Cr^+(^6S)$, we observed that β-H and β-alkyl transfer pathways were hindered in all of the alkane systems. These barriers led to alternate reaction pathways such as the four-centered alkane elimination (α-H and α-alkyl transfer) reactions mentioned above. Although kinetically favored, these reactions form product ions that are high-energy isomers. For example, in the reaction of $Cr^+(^6S)$ with methylpropane and butane, elimination of methane yields $CrC_3H_6^+$ with $Cr^+=C(CH_3)_2$ and $Cr^+=CHCH_2CH_3$ structures, respectively. In contrast, there is no evidence for such barriers to β-H transfer processes in the excited-state systems. Therefore, we presume that the alkane elimination processes are "normal" for these states and lead to Cr^+–alkene structures, e.g., Cr^+–propene for methane elimination from methylpropane and butane. This mechanism is outlined in detail in the preceding paper.[15]

Electronic State-Specific Reactivity. In order to further understand the reactivity of Cr^+ in its various electronic states, there are two major factors that we need to consider in some detail: the electronic character of the intermediates and products and the relative energies of these species. A primary consideration is the electronic character of the proposed reaction intermediates I and II and their analogues in the other alkane systems. Given the reasonable assumption that the Cr–H and Cr–C bonds in all of these intermediates are covalent, there are three remaining non-bonding 3d electrons on the metal such that these species should have quartet spins. This has been confirmed by ab initio calculation for the $Cr(CH_3)_2^+$ species.[27] Thus, formation of C–C and C–H bond activation intermediates such as I and II is spin-forbidden from the Cr^+ sextet states and spin-allowed from the Cr^+ quartet states. This begins to explain why the sextet states are much less reactive than the excited quartet states.

Figure 4 shows a semiquantitative potential energy surface for the chromium ion–alkane systems based on these ideas. The initial interaction between all states of Cr^+ and the alkanes is attractive due to long-range ion-induced dipole forces. At closer distances, however, molecular orbital ideas discussed in detail elsewhere[4,5,13,28] suggest that the surfaces arising from the ^6D and ^4D states become fairly repulsive due to the 4s orbital occupation, while those states with empty 4s orbitals, the ^6S and ^4G, evolve into surfaces that are less repulsive. The ^4G is the lowest energy state having both the correct spin and electron configuration to correlate directly to the ground states of the C–C and C–H bond activation intermediates. Since the two quartet surfaces evolving from $Cr^+(^4D)$ and $Cr^+(^4G)$ cross one another and are close in energy, we presume

that they mix, thereby allowing the ^4D state to also react efficiently.

A pertinent feature of Figure 4 is the relative energetics of the C–H vs the C–C bond activation intermediates. While no experimental information on the thermochemistry is available for such R_1–Cr^+–R_2 species,[13] theoretical calculations of Rosi et al.[27] on $Cr(CH_3)_2^+$ indicate that the second chromium–methyl bond energy is nearly the same as the first. Thus, bond additivity can be used to approximate the thermochemistry of these species. Further, the thermochemistry obtained in the previous paper[15] shows that the Cr^+–R (where R = H, CH_3, C_2H_5, or C_3H_7) bond strengths are all roughly the same. Thus, differences in the energetics of the intermediates are just the differences in the C–C and C–H bond strengths of the alkanes, on average about 10 kcal/mol.[29] Overall, the sum of two Cr^+–R bond energies is considerably less than the C–H (by 35–40 kcal/mol) and C–C (by 20–30 kcal/mol) bond energies of the alkanes. Thus, the intermediates are unstable (or at best, metastable) with respect to reductive elimination of the starting alkane to form $Cr^+(^6S)$ but are stable with respect to the excited $Cr^+(^4D)$ and $Cr^+(^4G)$ states (by 18–38 kcal/mol) (Figure 4). These features of the potential energy surfaces provide an additional rationale for the efficient reactivity of the excited quartet states vs the sextet states. We presume that since the C–C bond activation intermediates are substantially lower in energy than the C–H bond activation intermediates, the probability of generating the former species from $Cr^+(^6S)$ is substantially enhanced. Thus, no evidence for products evolving from the latter intermediates such as II are observed in the reactions of $Cr^+(^6S)$.[15]

The ^6D first excited state behaves similarly to the ^6S ground state in that most of the products it forms are consistent with C–C bond activation pathways. The only exception is production of $CrCH_2^+$ (Tables II–V), and the pathway taken for this product is ambiguous. (While another possible exception is formation of R^+ in reaction 3, the contribution of the ^6D state to these hydride transfer reactions is not clearcut. However, even if the ^6D state were contributing, transfer of H^- from R^+ to Cr^+ does not require an insertion of the metal into the C–H bond of the alkanes.) This overall behavior is consistent with the observation that the C–H bond activation intermediates lie somewhat above the $Cr^+(^6D)$ + alkane asymptotic energy, while the C–C bond activation intermediates lie below this energy. As noted above, the surface evolving from the ^6D state should be fairly repulsive, a result that has been used to explain why no reactivity of this state with H_2 or CH_4 was observed in previous work[12,13] and helps explain why this state is less reactive than the ground state despite having 1.5 eV more energy available. Presumably, this state reacts with the larger alkanes studied here because as the neutral reactant increases in size, its polarizability and thus the depth of the ion-induced dipole well for the $Cr^+(^6D)$·alkane complex also increase. This lowers the energy where these sextet surfaces cross the quartet surfaces leading to the intermediates, allowing reaction to proceed.

Two final details regarding the electronic characteristics of these reactions are worth commenting on. The first concerns the formation of $CrH(^6\Sigma^+)$ + $R^+(^1A)$ (reaction 3) and formation of $CrH^+(^5\Sigma)$ + $R(^2A)$ in these systems. While both processes are spin-allowed from the sextet ground and first excited states, the ground state undergoes neither of these reactions and the first excited state probably does not. (While formation of CrH^+ is observed in the ground-state system, it is produced by decomposition of primary products and thus is not accompanied by R.) As explained above, this is presumably because the C–H bond activation intermediates are not accessible to these states. Both reactions are observed, however, for reaction of the quartet excited states, even though the former is spin-forbidden. This is consistent with the experimental observation that the cross sections for production of CrH + R^+ at energies above about 0.5 eV are significantly smaller than those for CrH^+ + R in all four systems. The reason that the former process is observed at all is probably because this channel is energetically more favorable than formation

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(29) Alkane thermochemistry is taken from ref 15.

of CrH$^+$ + R,[30] such that the surfaces leading to these two product channels must cross. This difference in energetics is illustrated by the observation that cross sections for CrH + R$^+$ are higher than those for CrH$^+$ + R at thermal energies (Tables II–V), the opposite of the results obtained at higher kinetic energies.

A second detail concerns the alkane elimination reactions mentioned in the mechanism section above. For demethanation in the methylpropane and butane systems, the ionic species formed in the reactions of Cr$^+$(^{6}S) have the Cr$^+$=C(CH$_3$)$_2$ and Cr$^+$=CHCH$_2$CH$_3$ structures.[15] The Cr=C double bond demands that these species have quartet spin ground states, as has been calculated for Cr$^+$=CH$_2$.[31,32] Since the CH$_4$ product is ^{1}A$_1$, formation of these products from Cr$^+$(^{6}S) is spin-forbidden. This explicitly demonstrates that the reactions of the Cr$^+$(^{6}S) ground

state with alkanes must involve a coupling of sextet and quartet surfaces. This coupling presumably occurs during the C–C bond activation step that forms intermediate I and its analogues. In contrast, the ionic species formed in the reactions of excited-state Cr$^+$ with methylpropane and butane presumably have the chromium ion–propene structure. Since the ground state of this species must be formed from a dative interaction of ground-state Cr$^+$(^{6}S) with propene, it should have sextet spin. However, excited states of Cr(C$_3$H$_6$)$^+$ can be formed by the interaction of propene with the other states of Cr$^+$. As long as the Cr$^+$(^{4}D, ^{4}G)–propene bond energy exceeds the energy required to remove methane from the alkanes (19 and 17 kcal/mol in the methylpropane and butane cases, respectively), as seems reasonable, reaction of the excited quartet states of Cr$^+$ with these alkanes to form excited states of Cr(C$_3$H$_6$)$^+$ can still be exothermic.

(30) This is based on an ionization energy for CrH of ~7.6 eV derived from $D°$(Cr$^+$–H) = 32.5 ± 1.8 kcal/mol[12] and $D°$(Cr–H) = 53 ± 4 kcal/mol (Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. Work in progress).
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An ab Initio MO/SD-CI Study of Model Complexes of Intermediates in Electrochemical Reduction of CO$_2$ Catalyzed by NiCl$_2$(cyclam)

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Abstract: Ab initio MO/SD-CI calculations of several Ni^I- and Ni^{II}–CO$_2$ complexes indicate that CO$_2$ can coordinate to Ni^{I}F(NH$_3$)$_4$, yielding a stable η^1-CO$_2$ complex, but cannot to [Ni^{II}F(NH$_3$)$_4$]$^+$, [Ni^I(NH$_3$)$_4$]$^+$, and [Ni^I(NH$_3$)$_5$]$^+$. The HOMO of Ni^{I}F(NH$_3$)$_4$(η^1-CO$_2$) is largely contributed from the O p$_\pi$ orbital and lies higher in energy than the HOMO (nonbonding π orbital) of the uncomplexed CO$_2$. At the same time, the electron density increases around the O atom upon CO$_2$ coordination. As a result, the coordinated CO$_2$ in Ni^{I}F(NH$_3$)$_4$(η^1-CO$_2$) is activated to electrophilic attack and is expected to undergo facile protonation. MO calculations show that the second one-electron reduction can easily occur in the protonated species [NiF-(NH$_3$)$_4$(CO$_2$H)]$^+$, yielding the triplet state of [NiF(NH$_3$)$_4$(CO$_2$H)], but cannot in the unprotonated species NiF(NH$_3$)$_4$(CO$_2$). The second reduction significantly weakens the C–OH bond, which suggests that OH$^-$ easily dissociates from [NiF(NH$_3$)$_4$(CO$_2$H)], yielding the triplet state of [Ni^{II}F(NH$_3$)$_4$(CO)]$^+$. The CO coordinate bond to Ni^{II} is calculated to be weak, which suggests that CO easily dissociates from Ni^{II}. All these results support Sauvage's reaction mechanism of electrocatalytic reduction of CO$_2$ by NiCl$_2$(cyclam).

Introduction

CO$_2$ conversion into useful substances is of great interest for a variety of reasons including a resource utilization problem.[1] Of many attempts of CO$_2$ conversion, electrochemical[2–15] and pho-

tochemical[16–20] reduction of CO$_2$ catalyzed by transition-metal complexes have been actively investigated. In those reactions,

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