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What Is Wrong with Gas-Phase Chromium? A Comparison of the Unreactive Chromium(1+) Cation with the Alkane-Activating Molybdenum Cation

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We have studied the interaction of gas-phase Cr^+ and Mo^+ with small alkanes, cycloalkanes, and alkenes using ion beam mass spectrometric techniques. Although the two group 6 metal ions have the same ground electronic state (^6S, d^5) and similar excitation energies to the first excited electronic state (^6D, d^4s^1 with state splittings of 1.52 and 1.59 eV for Cr^+ and Mo^+, respectively), they behave quite differently. Unlike a majority of the metal ions which have been studied, Cr^+ ions are extremely unreactive. Cr^+ does not react with C_1–C_6 alkanes, cycloalkanes and alkenes. Even though the reaction cross sections are quite small, Mo^+, on the other hand, reacts with all alkanes, except methane, to give dehydrogenation products. Reactions of Mo^+ with the strained cycloalkanes, cyclopropane and cyclobutane, and with most alkenes are quite facile. This difference in reactivity is attributed to the difference in size of the Mo^+ orbitals with respect to Cr^+. The larger size of the d orbitals reduces the d–d exchange energy and increases the σ-bond energies between the metal and carbon or hydrogen, allowing exothermic insertion into C–H and C–C bonds.

I. Introduction

A growing number of experiments have shown that the unsaturated, gas-phase transition-metal cations are very reactive when it comes to activation of C–H and C–C bonds of alkanes and other small hydrocarbons. The largest number of studies have involved the first-row group 8–10 metal ions Fe^+, Co^+, and Ni^+,[1] although more recently, the early first row metals[2–4] as well as several second[5–7] and third[7–9] row species (Ru^+, Rh^+, Pd^+, Y^+, and La^+) have been investigated. Comparison of the reactivity of the second-row metals with their counterparts in the first row has shown some surprising differences. As one moves down a given column, dehydrogenation increases in importance relative to C–C bond cleavage processes. This is especially noticeable with Ru^+ and Rh^+ where dehydrogenation products are almost exclusively formed compared to Fe^+ and Co^+, where C–C bond cleavage products dominate. This paper is another study of the differences encountered between similar metals of the first and second transition-metal series. Previous work has shown that, although excited-state Cr^+ is reactive with alkanes[10] (even reacting exothermically with methane), ground-state Cr^+ is quite unreactive. This lack of reactivity is fairly unusual for a gas-phase metal cation. Theoretical calculations have indicated that differences in bonding and bond dissociation energies between Cr^+ and Mo^+ could be significant enough that Mo^+ would react exothermically with small hydrocarbons.[11] The present study confirms this hypothesis, and we discuss the differences between the two group 6 metal ions.

Experimental Section

The ion beam mass spectrometer used in this study of transition-metal ion reactivity has been described previously.[12] Briefly, singly charged, atomic metal ions are formed by thermal vaporization of a metal-containing compound and surface ionization on a hot rhenium ribbon filament. Cr^+ ions were formed from $Cr(CO)_6$ at approximately 1800 K while Mo^+ ions were formed by using $[CpMo(CO)_3]_2$ (Cp = cyclopentadienyl) and an approximate filament temperature of 2500 K. It is generally assumed that the internal temperature of the ions is the same as the filament surface temperature. It is thus possible, using a Maxwell–Boltzmann distribution, to estimate the population of ions in the ground and low-lying excited electronic states. Table I lists several of the low-lying electronic states for Cr^+ and Mo^+

Table I. Low-Lying M^+ Electronic States[a] and Beam Populations

ion	configuration	term	E_{rel}(low J),[b] eV	E_{rel}(av J),[c] eV	ion beam pop.,[d] %
Cr^+	$3d^5$	a^6S	0.00	0.00	99.97
	$3d^44s^1$	a^6D	1.48	1.52	0.03
	$3d^44s^1$	a^4D	2.42	2.46	0.00
	$3d^5$	a^4G	2.54	2.54	0.00
	$3d^5$	a^4P	2.70	2.71	0.00
Mo^+	$4d^5$	a^6S	0.00	0.00	99.52
	$4d^45s^1$	a^6D	1.46	1.59	0.34
	$4d^5$	a^4G	1.88	1.91	0.08
	$4d^5$	a^4P	1.94	1.95	0.02
	$4d^5$	a^4D	2.08	2.11	0.02

[a] Electronic state information taken from ref 13. [b] Relative energy determined by using the splitting between the lowest j level for each state. [c] Relative energy determined by using a weighted average over j levels for each state. [d] Populations determined by using a Maxwell–Boltzmann distribution over the energy levels at a temperature of 1800 K for Cr^+ and 2500 K for Mo^+.

[†] Contribution No. 7591.

(1) See, for example: (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (b) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (d) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (e) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492. (f) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

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Table II. Product Distributions for the Reactions of Mo^+ with Alkanes and Cycloalkanes

neutral reactant	percentages of neutral products,[a] %							cross section, Å^2	
	H_2	$2H_2$	$3H_2$	$4H_2$	$CH_4 + H_2$	$CH_4 + 2H_2$	C_2H_4	products[b]	adduct[c]
ethane	83	17						0.4	0.0
propane	46	54						0.7	0.8
n-butane		100						3.0	15.8
2-methylpropane	37	63						1.2	6.9
n-pentane	6	80	14					4.7	20.5
2,2-dimethylpropane	23	63			12	5		3.4	51.2
n-hexane	10	51	24	15				18.7	44.6
cyclopropane	100							54.8	0.0
cyclobutane	40	5					55	60.6	2.9
cyclopentane	3	97						26.8	2.5
cyclohexane	5	13	82					6.9	17.1

[a] Observed at a center-of-mass collision energy of approximately 0.25 eV. [b] Total reaction cross section for all observed products. [c] Apparent cross section observed for formation of adduct species. The neutral reaction gas pressure ranges from 1 to 1.5 mTorr.

along with their relative energies[13] (determined by two methods: from lowest *j* level to lowest *j* level of each state; and using weighted averages over the *j* levels for each state, the latter being useful for discussion of theoretical results pertinent to the present experiments) and relative populations at the filament temperatures used. Both ions have similar ground states (^6S, d^5) with the lowest excited state (^6D, d^4s^1) ~1.5 eV higher in energy. The Cr^+ ions are formed with greater than 99.9% of the ions in the ground electronic state. For Mo^+, greater than 99.5% of the ions are in the ground state. Thus, any reactions observed are likely to be reactions of ground-state metal ions.

After the metal ions are produced on the filament, they are accelerated, collimated into a beam, mass analyzed, and injected into a collision chamber containing the neutral reaction gas. The gas is at ambient temperature with a pressure that is maintained at less than 2 mTorr to yield single-collision conditions. By varying the kinetic energy of the ion beam, it is possible to study the reaction products as a function of the center-of-mass interaction energy between the ion and neutral. Unreacted ions and forward scattered products are extracted from the collision chamber and injected into a quadrupole mass spectrometer for mass analysis. The ions are detected by using a channeltron electron multiplier and pulse counting electronics. The quadrupole and ion detection circuits are controlled by an IBM-PC XT computer.

Results

Interaction of Cr^+ and Mo^+ with Alkanes. Previous experiments in our labs,[10] coupled with the present work, have shown that Cr^+ is unable to exothermically activate the C–H and C–C bonds of alkanes. These experiments have involved a variety of alkanes varying in size from methane to the C_7 hydrocarbons *n*-heptane and 2,4-dimethylpentane. Although many of these systems exhibit extensive adduct formation at collision energies of less than 1 eV and pressures of 1–2 mTorr (indicating long-lived interaction complexes are being formed), no reaction products are observed.

In marked contrast to Cr^+, Mo^+ reacts with alkanes larger than methane. Table II gives product distributions and total cross sections for these reactions measured at a center-of-mass collision energy of approximately 0.25 eV. It should be noted that the reaction cross sections for these processes are quite small, similar to those seen for reaction of V^+ in the first row,[3] indicating that Mo^+ is not as reactive as many of the other transition-metal ions that have been studied.

Methane, Ethane, and Propane. Very few metal ions have been observed to react with methane exothermically, and Mo^+ is no exception. Gas-phase reactions under single-collision conditions require formation of a neutral product to satisfy momentum and energy constraints. The most favorable pathway for reaction with methane is shown in eq 1. For this reaction to be exothermic, the bond dissociation energy, $D(M^+–CH_2)$, must exceed 111 kcal/mol[14] (this is seen to be the case for Ta^+).[8]

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 \qquad (1)$$

Mo^+ does react with ethane to eliminate both one and two molecules of H_2. This requires that the Mo^+–ethylene and Mo^+–acetylene bonds be greater than 32.7 and 74.6 kcal/mol, respectively. Similarly, reaction with propane also generates products corresponding to loss of one and two molecules of hydrogen, $Mo(C_3H_6)^+$ and $Mo(C_3H_4)^+$; the latter is either a metal–allene or a metal–propyne complex (the energetics of formation of allene and propyne from propane are 70.5 and 69.2 kcal/mol, respectively).

***n*-Butane and 2-Methylpropane.** As with the smaller molecules, Mo^+ reacts with *n*-butane and 2-methylpropane by dehydrogenation. $Mo(C_4H_6)^+$ is the only reaction product from *n*-butane while both $Mo(C_4H_8)^+$ and $Mo(C_4H_6)^+$ are formed in the reaction with 2-methylpropane. Formation of a metal–1,3-butadiene complex from 2-methylpropane requires rearrangement of the carbon skeleton. This structural rearrangement could account for the difference in product distribution for the two isomers. Reaction with *n*-butane to produce 1,3-butadiene can proceed with no rearrangement of the carbon skeleton. These reactions yield a lower limit for the molybdenum–butadiene bond energy of 58.5 kcal/mol.

***n*-Pentane, *n*-Hexane, and 2,2-Dimethylpropane.** As the size of the alkane increases, the amount of dehydrogenation is also seen to increase. The reaction of Mo^+ with *n*-pentane (eq 2–4) produces products corresponding to loss

$$Mo^+ + n\text{-}C_5H_{12} \xrightarrow{6\%} Mo(C_5H_{10})^+ + H_2 \qquad (2)$$

$$\xrightarrow{80\%} Mo(C_5H_8)^+ + 2H_2 \qquad (3)$$

$$\xrightarrow{14} Mo(C_5H_6)^+ + 3H_2 \qquad (4)$$

of up to three molecules of H_2, the latter possibly involving cyclization of the carbon chain to produce a Mo^+–cyclopentadiene complex with an interaction energy which must

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(14) Thermodynamic quantities used in this paper are taken from: (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York, 1970. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, Supp. 1. (d) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Supp. 2.

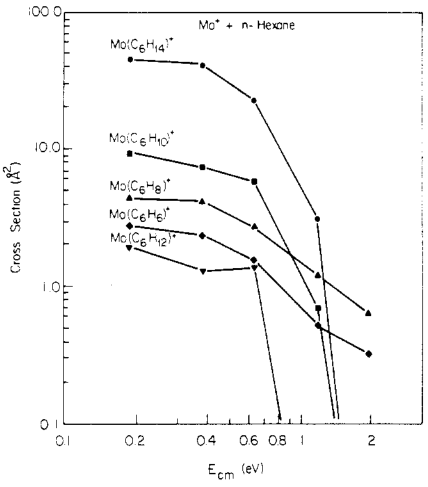


Figure 1. Reaction cross section versus center-of-mass collision energy, E_{CM}, for the reaction between Mo^+ and *n*-hexane. The neutral hexane pressure was approximately 1.4 mTorr. The most abundant product at low energy is the metal adduct $Mo(C_6H_{14})^+$, with the four dehydrogenation products at lower intensity. All products show exothermic behavior. Solid lines are a simple extrapolation between data points.

be ≥ 67 kcal/mol. In a similar fashion, reaction with *n*-hexane (eq 5–8) produces dehydrogenation of hexane

$$Mo^+ + n\text{-}C_6H_{14} \xrightarrow{10\%} Mo(C_6H_{12})^+ + H_2 \qquad (5)$$

$$\xrightarrow{51\%} Mo(C_6H_{10})^+ + 2H_2 \qquad (6)$$

$$\xrightarrow{24\%} Mo(C_6H_8)^+ + 3H_2 \qquad (7)$$

$$\xrightarrow{15\%} Mo(C_6H_6)^+ + 4H_2 \qquad (8)$$

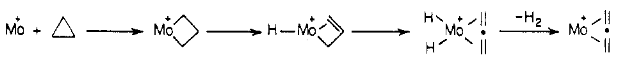
with the loss of up to four molecules of hydrogen in one ion–molecule encounter. The cross section versus collision energy data is shown in Figure 1. The products show the typical exothermic behavior with cross sections decreasing with increasing collision energy. If loss of four molecules of H_2 produces a metal–benzene complex, the reaction places a lower bound on the Mo^+–benzene interaction energy of 59.7 kcal/mol.

As seen in Table II, the products from reaction with 2,2-dimethylpropane are distinguished from the linear alkanes by the appearance of C–C bond cleavage processes. 1,2 H_2 elimination, which is prevalent in the reactions of many metal ions, is impossible. After initial insertion into a C–H bond, there are no β-hydrogens. Sc^+ is seen to undergo a very facile H_2 elimination reaction with 2,2-dimethylpropane,[2] part of the evidence put forth in support of a 1,3 dehydrogenation mechanism for that metal ion. For metals which do not react via this 1,3 mechanism, extensive rearrangement must take place before dehydrogenation and this allows other reaction pathways to compete, such as the elimination of CH_4 and H_2, as seen here.

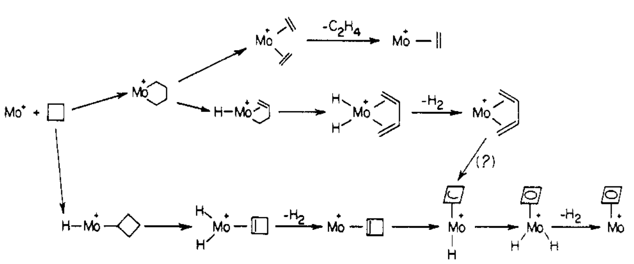
Interaction with Cycloalkanes. Cr^+ is unreactive with the C_3–C_6 cycloalkanes, as it is with the corresponding linear and branched alkanes. Table II contains the product distributions for the reactions of Mo^+ with cycloalkanes at a center-of-mass collision energy of approximately 0.25 eV.

Cyclopentane and Cyclohexane. These two reactive systems exhibit chemistry similar to that described for the linear alkanes. Both react via dehydrogenation and form almost exclusively $Mo(C_5H_6)^+$ and $Mo(C_6H_6)^+$, products which are also obtained with the loss of three and four molecules of hydrogen from the linear alkanes. The sequential dehydrogenation process favors formation of $Mo(C_6H_6)^+$ from $Mo(C_6H_8)^+$ due to the −5.5 kcal/mol enthalpic change on conversion of 1,3-cyclohexadiene to benzene and hydrogen.

Scheme I



Scheme II



Cyclopropane and Cyclobutane. The ring strain in these two cycloalkanes is seen to increase their reactivity over that of cyclopentane and cyclohexane. Although dehydrogenation products are seen for both of these molecules, it is unlikely that these products arise from a process involving initial C–H insertion, at least not for cyclopropane. The C–H bond strengths of cyclopropane and cyclobutane are 106.3 and 96.5 kcal/mol, respectively, while the C–C bonds are much weaker, being only approximately 54 and 55 kcal/mol.[15] Schemes I and II show the expected pathways for production of $Mo(C_3H_4)^+$ from cyclopropane and the three products (eq 9–11) formed in

$$Mo^+ + c\text{-}C_4H_8 \xrightarrow{40\%} Mo(C_4H_6)^+ + H_2 \qquad (9)$$

$$\xrightarrow{5\%} Mo(C_4H_4)^+ + 2H_2 \qquad (10)$$

$$\xrightarrow{55\%} Mo(C_2H_4)^+ + C_2H_4 \qquad (11)$$

the reaction with cyclobutane. We also show the C–H insertion process for cyclobutane since this process could account for the dehydrogenation products. Reaction with both cycloalkanes could proceed through initial insertion into a C–C bond to form a metallacycle. Two β-H transfers and H_2 elimination yield Mo^+–allene and Mo^+–butadiene complexes. Subsequent loss of H_2 from $Mo(C_4H_6)^+$ would yield Mo^+–cyclobutadiene. $Mo(C_2H_4)^+$ can come from symmetric cleavage of the metallacyclopentane to give a bis(ethylene) complex and then elimination of C_2H_4. This is a major product pathway and tends to indicate that the metal does indeed insert into one of the C–C bonds.

Interaction of Cr^+ and Mo^+ with Alkenes. Table III shows the product distributions for the reactions between Mo^+ with several small alkenes. Product cross sections are much larger than in the comparable alkane reactions. Although Mo^+ is much more reactive with alkenes than alkanes, Cr^+ remains unreactive. Reaction is only seen with cyclohexene, where very small amounts of $Cr(C_6H_8)^+$ and $Cr(C_6H_6)^+$ are observed.

Ethylene and Propene. Mo^+ was seen to doubly dehydrogenate ethane. Thus, it is no surprise that dehydrogenation of ethylene also takes place. The overall reaction cross section for the process is very small (0.5 Å^2 at a collision energy of 0.25 eV). The generally accepted

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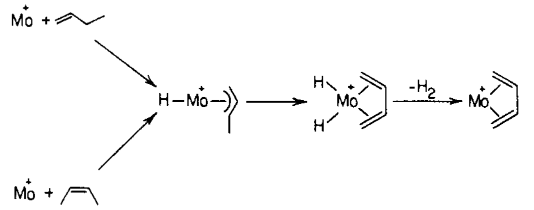
[15] The cyclopropane and cyclobutane C–C bond energies are determined as outlined in: Benson, S. W. *Thermochemical Kinetics*, Wiley: New York, 1976. Heats of formation of the diradical formed on ring opening are determined by using the terminal C–H bond dissociation energy for the corresponding linear alkane, assuming that breaking the C–H bonds at either end of the molecule are equivalent and that there is no interaction between the resulting radical electrons.

Table III. Product Distributions for the Reactions of Mo^+ with Alkenes

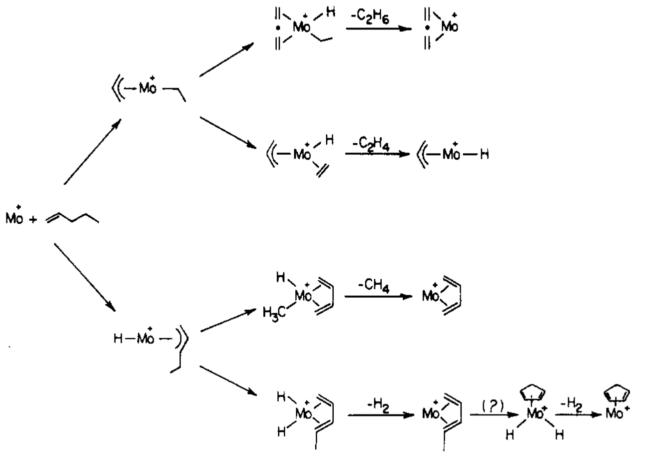
neutral reactant	percentages of neutral products,[a] %							reactn cross sectn,[b] Å^2
	H_2	$2H_2$	$3H_2$	CH_4	$CH_4 + H_2$	C_2H_4	C_2H_6	
ethylene	100							0.5
propene	100							46.5
1-butene	100							115.0
cis-2-butene	100							119.0
1-pentene	73	25		1		1	tr[c]	133.9
1-hexene	14	81	2		2		1	288.9
cyclohexene	7	93						216.2

[a] Observed at a center-of-mass collision energy of approximately 0.25 eV. [b] Total reaction cross section for all observed products. [c] Trace amount (<1%) observed.

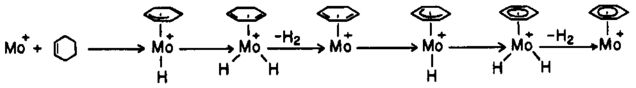
Scheme III



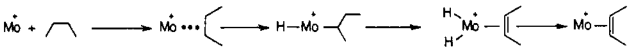
Scheme IV



Scheme V



Scheme VI



I II III IV

pathway for reaction of metal ions with alkenes[16] involves an initial metal insertion into one of the allylic C–H or C–C bonds. With ethylene this is not possible and the metal must interact with the stronger vinylic C–H bonds. Reaction of Mo^+ with propene *can* proceed through initial allylic C–H insertion to yield a hydrido–allyl complex. Subsequent β-H transfer to the metal and reductive elimination of H_2 gives Mo^+–allene. The cross section is approximately a hundred times greater than that for the ethylene reaction as well as the related reaction with propane.

1-Butene and *cis*-2-Butene. Reaction of Mo^+ with butane yielded Mo^+–butadiene as the only product. Reaction with the two butene isomers also gives this single product by elimination of H_2. Reaction cross sections for the two isomers are very similar, and the two reaction processes probably involve the same hydrido–allyl intermediate, Scheme III, after allylic C–H insertion.

1-Pentene, 1-Hexene, and Cyclohexene. Similar to the other cases already discussed, Mo^+ reacts with the C_5 and C_6 alkenes to give predominantly H_2-loss products. Contrary to the reactions with the comparable alkanes, however, there are also small amounts of C–C bond cleavage products. Scheme IV shows possible mechanisms for the products observed in the reaction with 1-pentene. Products are produced either by initial insertion into an allylic C–H bond followed by β-H or β-CH_3 shifts and elimination of H_2 or CH_4 or through allylic C–C bond insertion. Transfer of hydrogen from either the allyl ligand or the ethyl group then leads to elimination of either C_2H_4 or C_2H_6. In contrast to 1-pentene and 1-hexene, the reaction of Mo^+ with cyclohexene yields only dehydrogenation products (Scheme V).

Discussion

Reactivity differences between first- and second-row transition-metal congeners is not a fact unique to Cr^+ and Mo^+. Although the reaction types are similar, the group 3 metal ions, Sc^+, Y^+, and La^+ (to a certain extent), exhibit quite different product distributions.[2,7] The differences displayed by the group 8 (Fe^+ and Ru^+) and group 9 (Co^+ and Rh^+) metal ions is much greater than for Sc^+ and its congeners, with very different types of products.[5] While products in which C–C bonds are cleaved are prevalent with Fe^+ and Co^+, the interaction of Ru^+ and Rh^+ with hydrocarbons leads to almost exclusive elimination of one or more molecules of H_2. In all cases studied thus far, congeners are distinguished by differences in the relative importance of different reaction pathways. In the present case there is a difference in overall reactivity, where Cr^+ is totally unreactive while Mo^+ activates C–C and C–H bonds. For an explanation of this behavior, we must understand the differences between the metals in terms of (1) electronic structure, (2) bonding characteristics, and (3) the overall reaction mechanism for hydrocarbon activation. These points are by no means independent, and all interact to produce the observed results.

As an example of the alkane activation process, we will consider the reaction of a metal ion with n-butane (Scheme VI) to give 1,2 H_2 elimination and a M^+–2-butene product (eq 12). In the gas phase, for the reaction to occur and

$$M^+ + C_4H_{10} \rightarrow M(C_4H_8)^+ + H_2 \qquad (12)$$

exhibit exothermic behavior, the final product as well as all points on the reaction pathway must be lower in energy than the initial reactants (as shown for Mo^+ in Figure 2). The 1,2 mechanism for dehydrogenation of butane is assumed to take place in four steps. Initial approach of the

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[16] (a) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484. (c) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307.

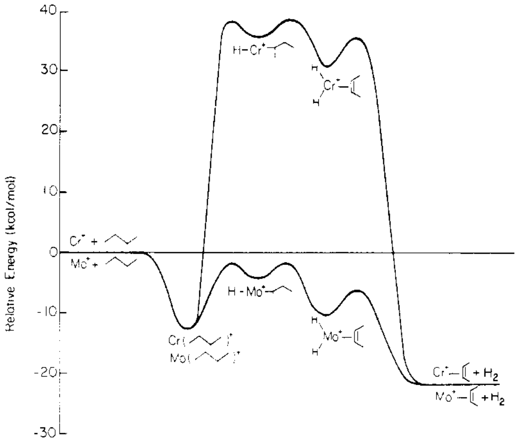

Figure 2. Estimated potential energy diagrams for the reactions of Cr^+ and Mo^+ with *n*-butane to produce H_2 and a metal-2-butene product, using the bond energies discussed in the text. The large endothermicity for insertion of Cr^+ into C–H bonds explains the lack of reactivity of this species with alkanes.

metal ion induces a dipole in the neutral butane. Interaction of this dipole with the metal ion allows formation of a loose collision complex (I in Scheme VI) with an interaction energy of possibly 10–15 kcal/mol. In many ion–molecule reactions, this interaction energy is sufficient to overcome any intrinsic barrier to further reaction. The second step involves insertion of the metal ion into one of the C–H bonds to produce new metal–carbon and metal–hydrogen bonds in place of the original C–H bond (II). Thirdly, transfer of a β-hydrogen to the metal center forms a dihydridometal–butene complex (III). Reductive elimination of H_2 then gives the final metal–butene product (IV).

Equations 16–18 give the overall energetics for production of the alkyl and hydrogen fragments in the two inserted intermediates and the final product. Thus, for

$$\begin{aligned} C_4H_{10} &\rightarrow C_4H_9 + H & \Delta H &= 96\ \text{kcal/mol} && (13)\\ &\rightarrow C_4H_8 + 2H & &= 132\ \text{kcal/mol} && (14)\\ &\rightarrow C_4H_8 + H_2 & &= 27\ \text{kcal/mol} && (15)\end{aligned}$$

the initial insertion step to be exothermic, the sum of the metal–carbon and metal–hydrogen bonds must be greater than 96 kcal/mol. For the next step, the sum of the two metal–hydrogen bonds plus the metal–alkene bond must be greater than 132 kcal/mol. Lastly, for the overall reaction to be exothermic, the metal–2-butene bond energy must be greater than 27 kcal/mol. Several estimates have been made on the bond strength between bare metal ions and ethylene. It has been estimated that the Sc^+–ethylene bond strength is on the order of 40 kcal/mol.[2] Aristov and Armentrout have indicated that V^+ binds ethylene with an energy of approximately 50 kcal/mol.[4] The M^+–ethylene bond strength has also been estimated, from kinetic energy release data for the reactions of the first-row Group 8–10 metals, as being between 40 and 45 kcal/mol.[17] We can thus assume that the metal–butene interaction is also this strong and that the overall dehydrogenation reaction of butane by Cr^+ and Mo^+ is exothermic. If we also assume that $D(H_2M^+–C_4H_8) = 50$ kcal/mol, then the sum of the two M^+–H bonds in the reaction intermediate must be greater than 82 kcal/mol.

If, as we have suggested, the overall dehydrogenation reaction is exothermic, then either the initial insertion step or the β-hydrogen transfer step must be endothermic for the reaction of Cr^+ and the difference between Cr^+ and Mo^+ must lie in the strengths of the bonds formed to the two metals. As shown in Table I, the ground and first excited electronic states for Cr^+ and Mo^+ are the same with almost identical state splittings. These two states have been shown to be important in the bonding between the metal ions and hydrogen.[11] The superficial similarity between the electronic states of the two metal ions might leads one to assume that the bonding in equivalent compounds would be very similar. This, however, is not the case. One must also take other factors into consideration such as the size of the orbitals, the intrinsic bond strengths of hydrogen and carbon to various orbitals, and the exchange energy between the high spin electrons. Elkind and Armentrout[18] have determined, using guided ion beam techniques, bond energies for the diatomic metal hydride ions CrH^+ and MoH^+ of $D_{298}(M^+–H) = 28.6 \pm 2$ and 42 ± 3 kcal/mol, respectively, a fairly substantial difference. Ab initio theoretical calculations on the two molecules[11] also indicate significant differences in the hybridizations of the bonding orbitals used by the two metals. In CrH^+, the metal bond orbital is hybridized 40.6% s, 12.5% p, and 46.9% d, building in a substantial amount of the ^6D excited state. For MoH^+, on the other hand, the hybridization is 19.7% s, 7.0% p, and 73.3% d, with a much greater amount of d (ground-state) character.

How does one account for the differences in bonding to the two metals? The major difference is in the principal quantum numbers for the valence electrons. The Mo^+ orbitals are larger than the corresponding Cr^+ orbitals. Hartree–Fock calculations[11] indicate a difference of ~0.29 Å in the radii of the 3d and 4d orbitals (0.75 Å versus 1.04 Å) and a 0.14-Å difference between the 4s and 5s orbitals (1.73 Å versus 1.87 Å). Calculations designed to show the trends in "intrinsic" bond energy of hydrogen to pure s or d orbitals indicate that the optimal size s orbital is smaller than that of Zn^+, 1.49 Å, and that the optimum size d orbital is larger than the 4d orbitals of Y^+, 1.47 Å. Thus, the intrinsic bond strengths predict stronger s bonding for Cr^+ and stronger d bonding for Mo^+.

Exchange energy losses are another important consideration. For unpaired electrons in orthogonal orbitals, high-spin coupling is best (Hund's rule) due to the energy stabilization from electron exchange. When one of these high-spin electrons is spin paired to another electron to form a bond, it is essentially high-spin coupled to the other metal electrons only one half of the time, causing a loss of one half of the high spin exchange stabilization due to that electron. For ^6S Cr^+, the average d–d exchange energy, K_{dd}, is 16.5 kcal/mol, while for ^6D Cr^+, $K_{sd} = 5.1$ kcal/mol and $K_{dd} = 18.2$ kcal/mol. The exchange terms are inversely proportional to the distance between the electrons. Thus, for Mo^+, with larger d orbitals and a smaller s–d size difference, K_{dd} is smaller than for Cr^+, 13.4 and 14.2 kcal/mol (^6S and ^6D states, respectively), while K_{sd} is larger, 8.5 kcal/mol. Since the electronic states of the two metal ions are the same, the number of exchange terms lost on bonding is also the same. Exchange arguments yield the same trends as the intrinsic bonding arguments, supporting more d bonding in Mo^+ compounds and more s bonding in Cr^+ compounds. For Cr^+, however, s bonding has the unfortunate energy penalty of involving an electronic state 1.52 eV above the ground state. Thus, exchange energy losses are high on bonding to the ground-state and promotion energy losses are high on bonding to the excited state, all of which causes the Cr^+–H

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[17] Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P.; Bowers, M. T., in press.

[18] Elkind, J. L.; Armentrout, P. B. *Inorg. Chem.* **1986**, *25*, 1080.

bond energy to be quite weak. Mo^+, on the other hand, loses less energy bonding with its ground state and forms stronger σ bonds.

All the reaction intermediates we are dealing with involve not one but two σ bonds to the metal ion. Experiments have not yielded bond energies for the second metal bond, and we must thus estimate the differences in the first and second bond dissociation energies. The simplest such case is the metal dihydride. We have previously published a theoretical study on the bonding in the two metal dihydrides CrH_2^+ and MoH_2^+.[11d] The second metal–hydrogen bond in the molybdenum case is very similar to the first from the standpoint of metal orbital hybridization. Since the number of high-spin coupled electrons is less, the second bond dissociation energy is found to be slightly higher than the first. In CrH_2^+, from an energy standpoint, the second bond can be thought of as being to an almost pure metal d orbital (although mixing creates two equivalent Cr^+–H bonds). As we have just discussed, d bonding in Cr^+ is not strong, and the second metal–hydrogen bond in chromium dihydride is indeed seen to be weaker than the first by up to 7 kcal/mol.

Activation of the C–H bonds in ethane by Mo^+ indicates that the sum of the metal–hydrogen and metal–ethyl bond energies is at least 98 kcal/mol. The very small cross section for this reaction suggests that the process may be very nearly thermoneutral. If we assume a difference of 7 kcal/mol in the bond energies of two metal–hydrogen bonds (the difference in exchange energy lost on bonding), this would yield a sum of 91 kcal/mol for two M^+–H bonds.[19] We must assume, then, that a metal–alkyl bond is on the order of 7–10 kcal/mol stronger than a metal–hydrogen bond. Making similar assumptions for Cr^+ leads to a sum of metal–hydrogen and metal–alkyl bond energies of approximately 59 kcal/mol, much below the C–C and C–H bond energies of alkanes. Thus, from a bond energy standpoint, the Mo^+ bond energies are just strong enough to activate C–H bonds and the reactions are seen to be exothermic with small cross sections. The bonds formed by Cr^+ are much too weak for the metal to be reactive with hydrocarbons. Estimated potential energy curves for the interaction of both Cr^+ and Mo^+ with *n*-butane are shown in Figure 2. A previous study[10b] supports the estimated energetics for the Cr^+–butane interaction. Collision induced dissociation of Cr^+–*n*-butane and Cr^+–2-methylpropane complexes yield, almost exclusively, Cr^+ and the neutral alkane. This indicates that the neutrals are only loosely bound to the metal ion and that the dissociation pathway is lower in energy than reaction pathways.

Replacing *n*-butane by 1-butene in the dehydrogenation reaction with Mo^+ is seen to make a large change in the reaction cross section (the cross section increases by a factor of almost 40). This change is brought about by the increased interaction energy between the ion and neutral due to the presence of the π system. We have seen that metal–ethylene bonds are on the order of 40–50 kcal/mol. Thus, the initial metal–butene interaction as well as the bonds in the hydrido–allyl metal insertion complex lower the energy of these species on the reaction surface and make the reaction more facile. Again, for Cr^+, the bond strengths must be too weak for the insertion process to take place.

The types of reaction products observed with Mo^+ are similar to those found in the reactions of Ru^+ and Rh^+, almost exclusive elimination of hydrogen and formation of metal–alkene complexes. First-row group 8–10 metals are seen to form many products that result from cleavage of C–C bonds. In all cases studied so far, as one proceeds down a column in the periodic table, the amount of dehydrogenation increases and the amount of C–C bond cleavage products decreases. It has been argued by Tolbert and Beauchamp that for the case of Ru^+ and Rh^+, this is not due to a difference in the bond dissociation energies to the metals but to the types of orbitals involved in bonding. If one assumes an initial interaction with and insertion into a C–H bond, then hydrogen loss products and alkane loss products must come from a competition between β-hydrogen versus β-alkyl migrations onto the metal followed by reductive elimination. The first-row metals are seen to use much more s character in bonding than the corresponding second-row metals. It is postulated that the highly directional nature of the second-row metal d bonds favor transfer of a spherically symmetric, nondirectional hydrogen atom while the less directional, s-containing, bonds of the first-row metals allow transfer of alkyl groups with their more directional carbon p orbitals. Mo^+, with its largely d-like bonds, falls into the same category as Ru^+ and Rh^+ and is seen to favor insertion into C–H bonds along with β-hydrogen transfer and formation of hydrogen loss products.

Summary

Previous studies have shown that excited-state Cr^+ is reactive, even with methane. The present work shows that ground-state Cr^+ is very unreactive with small hydrocarbons including alkenes. Mo^+, although quite similar to Cr^+ from the standpoint of low-lying electronic states, is seen to activate C–H bonds of alkanes, cycloalkanes, and alkenes. The reaction products are similar to those seen with other second-row metal ions, Rh^+ and Ru^+, although the overall reactivity is not as great. Theoretical calculations on CrH^+, MoH^+, CrH_2^+, and MoH_2^+ indicate that the differences observed between the two metal ions are the result of the very weak σ bonds formed by Cr^+, causing the insertion of Cr^+ into C–H bonds to be endothermic. The larger size of the d orbitals of Mo^+, and the resultant decrease in the d–d exchange energy lost on forming σ bonds to the metal, result in stronger bonds to Mo^+, just strong enough to activate the C–H bonds of alkanes.

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Registry No. $Cr(CO)_6$, 13007-92-6; $[CpMo(CO)_3]_2$, 12091-64-4; Cr^+, 14067-03-9; Mo^+, 16727-12-1; ethane, 74-84-0; propane, 74-98-6; *n*-butane, 106-97-8; 2-methylpropane, 75-28-5; *n*-pentane, 109-66-0; 2,2-dimethylpropane, 463-82-1; *n*-hexene, 110-54-3; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; ethylene, 74-85-1; propene, 115-07-1; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; 1-pentene, 109-67-1; 1-hexene, 592-41-6.

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[19] The calculated bond dissociation energy for MoH^+ is $D_e(M^+\text{–H}) = 33.8$ kcal/mol, which is over 8 kcal/mol weaker than the experimentally determined value. The bond energy, $D_e(HM^+\text{–H})$, is calculated to be 35.1 kcal/mol, yielding a sum for the two metal–hydrogen bonds of 68.9 kcal/mol. This value is not consistent with the observed reactivity of Mo^+, and we thus use experimental estimates for the bond strengths.