dissimilar oxidation states, and reside in distinctly different ligand environments. The molybdenum atom is in a low valent state and is surrounded by a soft ligand field. The divalent nickel ion is surrounded by a hard ligand field. To our knowledge, there is no comparable analogous bimetal complex known. Metalla-β-diketonato complexes contain two transition metals in different ligand fields but can interact through the π system.[19] The recently reported zirconocene phosphines[20] are able to bind two different metals remotely, but both ligand sites are soft. A major impetus for the synthesis and characterization of bimetal complexes containing greatly dissimilar metal sites is the search for simple systems which might permit the controlled reduction of CO and N_2.[21,22]

Supplementary Material Available: A listing of positional and thermal parameters and structure factors (19 pages). Ordering information is given on any current masthead page.

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Formation of Chromium Carbene Ions by Reaction of Electronically Excited Chromium Ions with Methane in the Gas Phase

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Received October 6, 1980

The gas-phase reactions of singly charged chromium ions have been studied by using an ion beam tandem mass spectrometer[1] equipped with two different ion sources. One source produces singly charged chromium ions by thermal decomposition of $CrCl_3$ and surface ionization of the resulting Cr on a hot rhenium surface.[1] It is estimated that at the filament temperature used, ~2350 K, more than 99% of the chromium ions are in the ^6S ground state. The other source forms Cr^+ from $Cr(CO)_6$ by electron impact.[2] The metal ions are collimated, mass and energy selected, and allowed to interact with the target gas in a collision chamber. Product ions scattered in the forward direction are detected by using a quadrupole mass spectrometer.

Using the suface ionization source, chromium carbene ions are formed in the *endothermic* reactions of Cr^+ with ethylene and cyclopropane, processes 1 and 2. Analysis of the thresholds[3] yields

$$Cr^+ + C_2H_4 \rightarrow CrCH_2^+ + CH_2 \tag{1}$$

$$Cr^+ + \text{cyclo-}C_3H_6 \rightarrow CrCH_2^+ + C_2H_4 \tag{2}$$

a chromium carbene bond strength, $D°(Cr^+-CH_2) = 65 \pm 7$ kcal/mol.[4] Reaction of Cr^+ with methane yields CrH^+ as the only detectable product at high energies.

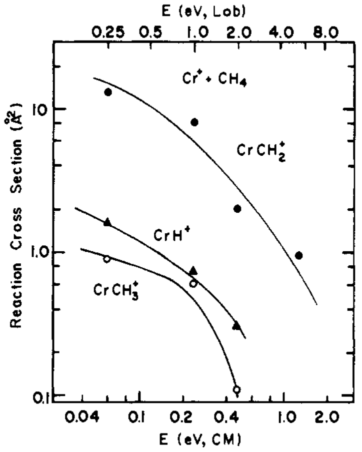


Figure 1. Variation in experimental cross section for the reactions of Cr^+ with methane as a function of kinetic energy in the center-of-mass frame (lower scale) and laboratory frame (upper scale). For the results illustrated, Cr^+ was produced by 30-eV electron impact from $Cr(CO)_6$.

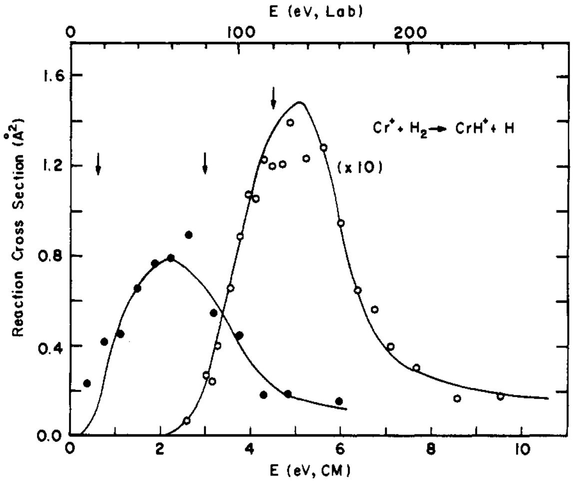
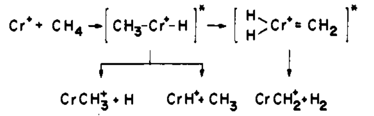


Figure 2. Variation in experimental cross section for reaction 3 as a function of kinetic energy in the center-of-mass frame (lower scale) and the laboratory frame (upper scale). Open circles depict data for beam of surface-ionized Cr^+, while closed circles depict data for Cr^+ produced by 30-eV electron impact from $Cr(CO)_6$. Curves drawn are theoretical fits to the data as described in ref 9. Arrows depict derived thresholds of 3.0 and 0.6 eV, and the bond energy of H_2, D = 4.5 eV.

Scheme I



Surprisingly, Cr^+ formed by electron impact from $Cr(CO)_6$ reacts with methane to produce $CrCH_2^+$ in abundance, and the behavior of the cross section as a function of energy (Figure 1) is characteristic of an *exothermic* reaction. Also observed are lesser amounts of $CrCH_3^+$ and CrH^+.[5] A mechanism for the formation of these products is suggested in Scheme I. On the basis of the measured bond energy, formation of $CrCH_2^+$ from reaction with CH_4 is endothermic by 45 kcal/mol.[6] Since the

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[1] For a more detailed description of the instrument, see: Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *50*, 21.

[2] This new source is of standard design in which an ion beam is extracted at right angle from a collimated electron beam.

[3] Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.*, in press.

[4] This value can be compared to other metal ion-carbene bond energies. (a) $D°(Mn^+-CH_2)$ is between 92 and 100 kcal/mol: Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (b) $D°(Co^+-CH_2) = 85 \pm 7$ kcal/mol.[3] (c) $D°(Ni^+-CH_2) = 86 \pm 6$ kcal/mol: Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L., unpublished results. In general, threshold experiments yield only a lower limit for the bond strength. However, studies with Co^+ (ref 3), which include results for $CoCH_2^+$ formed in *both* endothermic and exothermic processes, suggest that the threshold data yield the true bond energies rather than a lower limit.

[5] Analysis of the thresholds of the reactions of Cr^+ formed by surface ionization with H_2 and ethane yield, respectively, $D°(Cr^+-H) = 35 \pm 5$ kcal/mol and $D°(Cr^+-CH_3) = 37 \pm 7$ kcal/mol. Reactions forming these species from methane are thus endothermic by 69 and 67 kcal/mol, respectively.

[6] $\Delta H_f°(CH_4) = -17.9$ kcal/mol from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1975. $\Delta H_f°(CH_2) = 92.4$ kcal/mol from: Chase, M. W.; Curnutt, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data Suppl.* **1975**, *4*, No. 1.

0002-7863/81/1503-962$01.25/0

Table I. Low-Lying Excited States of Cr^+ [a]

configuration	state	energy[b] eV	energy[b] kcal/mol
$3d^5$	a ^6S	0	0
$3d^44s$	a ^6D	1.483	34.20
$3d^44s$	a ^4D	2.421	55.84
$3d^5$	a ^4G	2.543	58.65
$3d^5$	a ^4P	2.706	62.40
$3d^5$	b ^4D	3.104	71.58
$3d^44s$	b ^4P	3.714	85.64
$3d^5$	a ^2I	3.738	86.19

[a] Data from: Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1977**, *6*, 317. [b] Listed numbers are for the lowest energy *J* level of the term.

reaction appears to be exothermic (Figure 1), it must involve an electronically excited state of Cr^+.[7]

Two experiments confirm this hypothesis. The appearance potential of $CrCH_2^+$ is 2.5 ± 0.3 eV (58 kcal/mol) above the threshold for Cr^+ formation[8] from $Cr(CO)_6$. In addition, in the endothermic reaction of Cr^+ with H_2 to form CrH^+ (process 3), the threshold is shifted 2.4 eV to lower energy when Cr^+ is formed by electron impact (Figure 2).[9]

$$Cr^+ + H_2 \rightarrow CrH^+ + H \qquad (3)$$

The energies of low-lying excited states of Cr^+ are summarized in Table I. An excitation energy of 2.5 eV implicates one of the lowest quartet states (the energy resolution does not distinguish among the lowest ^4D, ^4G, or ^4P states). Since the spin multiplicity of these states differs from the ground state, they should be metastable and have relatively long lifetimes.

Reaction of excited Cr^+ to form $CrCH_2^+$ is efficient and may occur on every collision. The apparent cross section is ~13 Å^2 at low energies; the actual cross section is higher because only a fraction of the Cr^+ beam is in the reactive excited state.[10] It is of interest to note that the reaction with CH_4 is promoted by *electronic* and not *translational* excitation. As the relative kinetic energy is increased, it is expected that the reaction dynamics will become dominated by direct processes.[11] It is thus not surprising that ground-state Cr^+ reacts with CH_4 to form only CrH^+, probably in a stripping reaction.[12] Formation of $CrCH_2^+$ requires major rearrangement and a relatively long-lived intermediate. Hence electronic excitation is uniquely effective in promoting this reaction.

Transition-metal carbenes are believed to be intermediates in processes such as hydroformylation and the Fischer-Tropsch synthesis. Our results show that excited chromium ions produce chromium carbene ions exothermically from methane. This suggests that photochemical methods may provide an efficient way to form these highly reactive intermediates. For example, photoexcitation of metal atoms in a matrix containing methane might lead to carbene formation.[13]

We have observed numerous other examples where electronically excited metal ions exhibit modified reactivity in ICR and ion beam studies of organometallic chemistry.[14] This clearly indicates that caution be exercised in the inference of thermochemical data from the observation of reactions which *appear* to be exothermic.[15]

Acknowledgment. This research was supported in part by the U.S. Department of Energy. Graduate fellowship support from Bell Laboratories (L.F.H.) is gratefully acknowledged.

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[7] In a note added in proof, Freas and Ridge note that studies of the kinetics of the reaction of Cr^+ with $Cr(CO)_6$ examined by use of an ion cyclotron resonance spectrometer suggest two states of Cr^+ are produced by electron impact from $Cr(CO)_6$ (Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129).

[8] Appearance potential curves were taken on an ion cyclotron resonance spectrometer operating in the drift mode. The shift in threshold is calculated by using the extrapolated voltage difference method as described in: Warren, J. W. *Nature* (London) **1950**, *165*, 810. Variation of electron energy in the ion beam experiments produces the expected variation in cross sections; however, the intensity of the beam near threshold is too low to obtain accurate data. Earlier appearance potential measurements of Cr^+ produced by electron impact from $Cr(CO)_6$ suggested that chromium ions may be produced in an excited state. See: Winters, R. E.; Kiser, R. W. *Inorg. Chem.* **1965**, *4*, 157. However, subsequent measurements have not agreed well with this result nor with each other: Rosenstock, H. M.; et al., *J. Phys. Chem. Ref. Data Suppl.* **1977**, *6*, No. 1. If the appearance potential curve of Cr^+ that we have observed is due to an excited state, then the difference of 2.5 eV corresponds to a lower limit on the energy of the reactive excited state.

[9] Armentrout, P. B.; Beauchamp, J. L. *Chem. Phys.* **1980**, *48*, 315.

[10] The apparent cross section for reaction of excited Cr^+ with H_2 (process 3) is about 8 times the maximum cross section of ground-state Cr^+ (Figure 2), indicating that here, too, the excited state reaction is efficient.

[11] Levine, R. D.; Bernstein, R. B. "Molecular Reaction Dynamics"; Oxford University Press: New York, 1974.

[12] Henglein, A. *Adv. Chem. Ser.* **1966**, *No. 58*, 63.

[13] A recent study (Billups, W. E.; Konarski, M. M.; Hauge, R. H.; Margrave, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 7394) indicates that photoexcitation of metal atoms in a methane matrix yields the insertion product CH_3MH where M = *Mn*, *Fe*, *Co*, *Cu*, *Zn*, Ag, and Au. Ca, Ti, Cr, and Ni do not react. Further irradiation yields $(CH_3)_2M$. Although they might be difficult to characterize, no mention was made of carbenes in the systems studied. It appears that in the frozen matrix the first intermediate suggested in Scheme I is trapped. Further excitation results in reaction with a second methane molecule rather than an α-hydrogen shift which would yield a carbene. In a dilute system (e.g., methane in argon) it might be possible to observe the carbene.

[14] See, for example: Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808. We have observed reactions of excited-state Cr^+ as well as excited-state Mn^+ [produced by electron impact of $Mn_2(CO)_{10}$] with alkanes other than methane which differ markedly from the reactions of ground-state ions.

[15] For examples where this analysis has been used, see: Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. Allison, J.; Ridge, D. P. *Ibid.* **1979**, *101*, 4998 and ref 4a. In the latter study, thresholds for $MnCH_2^+$ product ions were checked and found to be identical with the threshold for Mn^+ formation.

First Evidence for Manganese Binding to Sulfur Donor Group in Metalloprotein, Mn(III)-Containing Acid Phosphatase

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Received November 5, 1980

Although the biological importance of iron-sulfur complex systems and the chemical similarity of Fe(III) and Mn(III) are well-known, manganese binding to sulfur donor groups in metalloproteins has never been demonstrated. In addition, the chemistry of manganese complexes with sulfur donor ligands is much less understood than that for oxygen and nitrogen donor ligand complexes.[1] The acid phosphatase purified from sweet potato contains one Mn(III) ion per molecule which is essential for enzymatic activity and the intense 515-nm visible band.[2,3] We reported the coordination of a tyrosine phenolate anion to the Mn(III) chromophore of this enzyme.[2] However, a Raman line due to the Mn-S streching mode was not detected because of the fluorescence of the native enzyme. The present study of the tryptophan-modified Mn(III)-containing acid phosphatase has demonstrated the first evidence for manganese binding to sulfur

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[1] Lawrence, G. D.; Sawyer, D. T. *Coord. Chem. Rev.* **1978**, *27*, 173-193. This is due mainly to the facile oxidation of sulfur in such ligands.

[2] Sugiura, Y.; Kawabe, H.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 6581-6582.

[3] Recently, the iron-containing acid phosphatase from pig allantoic fluid was purified to homogeneity and the violet enzyme showed an absorption maximum near 550 nm (ε 2000): Keough, D. T.; Dionysius, D. A.; Jersey, J.; Zerner, B. *Biochem. Biophys. Res. Commun.* **1980**, *94*, 600-605.

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