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Bare Transition Metal Atoms in the Gas Phase: Reactions of M, M$^+$, and M^{2+} with Hydrocarbons

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Introduction

Alkanes are abundant sources of carbon, but they are rather inert. Consequently, chemists have long sought means to selectively break, or *activate*, the C–H and C–C bonds of alkanes in low-energy conditions. Cracking of alkanes by metal catalysts, usually at a high temperature, has a long history.

In the past 10 years, two new classes of alkane-activation chemistry have developed in parallel. In solution-phase organometallic chemistry, certain coordinatively unsaturated (open-shell) transition metal centers insert in C–H bonds of alkanes in a chemical step known as "oxidative addition".[1] For example, following photolytic or pyrolytic removal of a ligand, many different Ru, Rh, Ir, and Pt compounds insert into C–H bonds of alkanes, including methane.[2] In the gas phase, the chemistry of bare transition metal cations (M$^+$ and M^{2+}) appears unique.[3] Certain M$^+$ and M^{2+} break the C–H or C–C bonds (or both) of alkanes at 300 K. For example, most of the 3d-series cations Sc$^+$ through Ni$^+$ react with propane and larger alkanes, leading to products from H_2 or CH_4 elimination. Ta$^+$, W$^+$, Os$^+$, Ir$^+$, Pt$^+$, Nb^{2+}, Ta^{2+}, and Zr^{2+} dehydrogenate CH_4 at 300 K.[4,5] Some of these atoms react with as many as *four* CH_4 molecules.

The key question that spans solid-phase, solution-phase, and gas-phase chemistry is how the electronic structure of the metal atom or metal center controls its chemical reactivity.[6] By *electronic structure* we mean orbital sizes, shapes, and relative energies; orbital occupancy, or electron configuration; electron spin; and the resulting overall *pattern* of low-lying electronic states. The chemical observations raise many broad questions. The most active metals in *all* phases appear to be those on the right-hand side of the 4d and 5d series, e.g., Ru, Rh, Pd, Ir, and Pt. What intrinsic properties of these atoms cause their special reactivity? Why are alkanes relatively inert to some metals in the gas phase and to many metals in solution phase? Certain gas-phase M$^+$ and M^{2+} break even *C–C bonds* of alkanes; why is there no analogous solution-phase chemistry? In the gas phase, how does the *charge* on the metal atom (M, M$^+$, M^{2+}) influence its reactivity? Why do gas-phase M$^+$ from the left-hand side of the 3d series preferentially attack C–H bonds, while those on the right-hand side attack both C–H and C–C bonds?

The gas phase provides a unique opportunity to study chemistry one bimolecular collision at a time. This Account focuses on gas-phase measurements and high quality ab initio calculations that are beginning to explain how metal atom electronic structure determines chemical reactivity. We have an enormous body of basic chemical reactivity data for M$^+$ and a growing body of data for M^{2+} and neutral M. Sophisticated experiments can control the kinetic energy and the electronic state of M$^+$ reactants.[6a,b] We can study the reactivity of Fe$^+$ in the 3d^{6}4s, high-spin ground state, the 3d^7, high-spin first excited state, or the 3d^{6}4s, low-spin second excited state.[7,8] Each electronic state is potentially a different chemical! We have learned to follow the elimination of H_2 and C_2H_6 from bimolecular Ni$^+$(*n*-butane) complexes *in real time*, on a 50-ns time scale.[9] In M$^+$ reactions, we can control the kinetic energy and the electronic state of the reactants.[6a,b]

A key advantage in interpreting these results is that we understand the electronic structure of the bare metal atom *reactants* very well. We are beginning to see how the different charges on M, M$^+$, and M^{2+} as well as the structure and energetics of low-lying electronic states determine whether or not specific atoms can approach hydrocarbons to close range and break chemical bonds.

Solution-phase chemists might well question the relevance of atomic species with genuine 1+ or 2+ charges and no ligands or solvent to the "real world" of organometallic chemistry. Yet connections surely exist, as witnesses the fact that Rh and Ir atoms are unusually

James C. Weisshaar was born in Cincinnati, OH, in 1952. He received a B.S. in chemistry from Michigan State University in 1974 and a Ph.D. in chemistry from U.C. Berkeley in 1979. His thesis "Non-radiative Decay of Single Rotational States of S_1 Formaldehyde", under the direction of C. Bradley Moore, won the ACS Nobel Laureate Signature Award in 1980. Postdoctoral work with Stephen Leone, Barney Ellison, and Veronica Bierbaum at the University of Colorado involved measurement of infrared chemiluminescence spectra from gas-phase ion–molecule reactions. Since 1981, he has served on the faculty of the Chemistry Department of the University of Wisconsin—Madison, presently as Professor. In addition to the chemistry of gas-phase transition metal species, current research interests include the spectroscopy of unstable species, such as metal clusters, ligated metal atoms and clusters, and organic free radicals, and the dynamics of molecular photoionization.

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reactive in *all* phases. Theoretical chemists are beginning to provide a conceptual framework[10-12] that will unify seemingly diverse branches of experimental chemistry. Of necessity, the ab initio quantum chemist works on model transition metal systems, draws experimental evidence from all available sources, and tries to abstract from the calculations what is robust and common to all phases. Gas-phase metal atoms are idealized model systems well matched to the capabilities of modern theory. Many new conceptual insights in the next 10 years will come from careful analysis of ab initio wave functions informed by incisive gas-phase experiments.[13]

Brief Overview of Electronic Structure

Bare transition metal atoms M, M^+, and M^{2+} are electronically complex but well understood.[14] An atomic state is labeled by its electron configuration (orbital occupancy), total electron spin S, orbital angular momentum L, and total angular momentum J, as embodied in the symbol $^{2S+1}L_J$. Both the size and energy of atomic orbitals influence the strength of metal–ligand chemical bonding. The order of low-lying states results from a competition between electron configuration stability, which often favors low-spin states, and quantum mechanical exchange effects, which always favor high-spin states.[12] For a given atomic charge, the effective nuclear charge felt by an nd or $(n+1)$s electron increases from left to right across a transition series, differentially stabilizing nd relative to $(n+1)$s. Changing the net charge from M to M^+ to M^{2+} has a similar effect. The exchange stabilization energy increases with the number of unpaired spins, and the d–d exchange interactions are larger than d–s.[15]

In the 3d series, Sc, Ti, V, Mn, Fe, Co, and Ni have $3d^{x-2}4s^2$ ground-state configurations.[14] The lowest excited states are high-spin $3d^{x-1}4s^1$. The 4s orbital is much larger than 3d. In the 4d series, the 5s orbital is more comparable in size to 4d, and the orbital energies are more similar as well. The ground states are either $4d^{x-2}5s^2$ (Y, Zr, Tc) or high-spin $4d^{x-1}5s^1$ (Nb, Mo, Ru, Rh), except for Pd, which has a unique $4d^{10}$ ground state. In both the 3d series and the 4d series, the M^+ ground states and low-lying excited states are either $3d^{x-1}4s^1$ or $3d^x$; the $3d^{x-2}4s^2$ states lie high in energy. For M^{2+}, almost all ground states are $3d^x$. These trends in orbital sizes and relative energies are directly reflected in the chemical reactivity.

Survey of M, M^+, and M^{2+} Reactivity

The neutral metal atoms are less well studied experimentally than the cations because of the inherent difficulty in detecting reactants and identifying products. Yet gas-phase neutrals may be more representative of condensed-phase species than cations. To a large extent, *long-range forces* between metal atom and hydrocarbon determine which atoms react and which do not.[6a,b,13] Like most solution-phase chemistry, neutral metal atom chemistry in the gas phase typically occurs in spite of potential energy barriers between reactants and products. Long-range M + hydrocarbon forces are typically *repulsive*.

As we will see, gas-phase M^{2+} and M^+ are probably less representative of condensed-phase species than neutral M. Regardless of nominal oxidation state, the net charge on ligated metal centers in the solution phase is seldom (if ever) as large as the genuine 1+ or 2+ charge on a gas-phase cation. At sufficiently long range, the force between any bare cation and any hydrocarbon is *attractive*. The positive charge *polarizes* the approaching hydrocarbon molecule, and the charge and the induced dipole attract each other. For M^+ and M^{2+}, these forces are really *physical* in nature, since they occur before orbitals begin to overlap and do not depend on the details of orbital occupancy, size, and shape.

In all phases, it is useful to think of reaction efficiencies in terms of a limiting rate constant that represents 100% reaction probability *every time reactants come in close contact*. In the solution phase, the fastest reactions are *diffusion-controlled*, with rate constants on the order of 10^{10} M^{-1} s^{-1}. The analogous gas-phase rate constants are called the *hard-spheres* rate constant k_{hs} for neutral M and the *Langevin* rate constant k_L for M^+ or M^{2+}. In the gas phase at 300 K, where no solvent molecules impede the approach of reactants, typical values are $k_{hs} = 3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} = 2×10^{11} M^{-1} s^{-1} and $k_L = 2 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} = 10^{12} M^{-1} s^{-1}. The Langevin rate is faster than the hard-spheres rate because M^+ or M^{2+} polarizes and attracts neutral collision partners that would have completely "missed" neutral M. The *reaction efficiency* k/k_{hs} or k/k_L is the fraction of close collisions that actually react.

Neutral Transition Metal Atoms. My own group has been surveying the gas-phase chemical kinetics of bare neutral transition metal atoms with alkanes and alkenes of fewer than five carbon atoms.[16] Mitchell and co-workers[17] are working in a similar vein; they have concentrated on smaller reactants such as CO, H_2O, and C_2H_4. We measure M + hydrocarbon reactivity in the multicollision environment of a fast flow reactor at 300 K with 0.5–0.8 Torr of He buffer gas.[18]

The total removal rate of ground-state atoms yields *effective bimolecular rate constants k* that may depend on pressure. These rate constants could include contributions from *bimolecular* chemistry, *termolecular* chemistry, or both. In thermal conditions at 300 K, the only energetically feasible bimolecular reactions involve *elimination* of H_2, CH_4, or a larger hydrocarbon molecule. Since M–H, M–alkyl, and M–alkene bonds are roughly half as strong as C–H and C–C bonds,[19] exothermic, bimolecular M + hydrocarbon reactions

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Table I. Selected Bimolecular Rate Constants (10^{-12} cm^3 s^{-1}) for Reactions of Neutral and Cationic Metal Atoms with Alkanes and Alkenes at 300 K in 0.8 Torr of He Buffer Gas[a,b]

metal atom (confign)	hydrocarbon reactant			
	ethene	1-butene	propane	*n*-butane
$Sc(3d^1 4s^2)$	NR	14 ± 1	NR	NR
$Ti(3d^2 4s^2)$	NR	7.1 ± 0.7	NR	NR
$V(3d^3 4s^2)$	NR	14 ± 1	NR	NR
$Cr(3d^5 4s^1)$	NR	NR	NR	NR
$Mn(3d^5 4s^2)$	NR	NR	NR	NR
$Fe(3d^6 4s^2)$	NR	NR	NR	NR
$Co(3d^7 4s^2)$	NR	0.09 ± 0.03	NR	NR
$Ni(3d^8 4s^2)$	0.5 ± 0.05	140 ± 30	NR	NR
$Cu(3d^{10} 4s^1)$	NR	NR	NR	NR
$Y(4d^1 5s^2)$	7.5 ± 0.8	130 ± 13	–	–
$Zr(4d^2 5s^2)$	54 ± 6	147 ± 15	NR	NR
$Nb(4d^4 5s^1)$	296 ± 15	368 ± 37	NR	NR
$Mo(4d^5 5s^1)$	–	1.9 ± 0.5	NR	NR
$Pd(4d^{10})$	14.5 ± 1.5	357 ± 36	1.15 ± 0.12	4.4 ± 0.4
$Ti^+(3d^2 4s^1)$	–	–	760 ± 230	–
$Cr^+(3d^5)$	–	–	210 ± 60	–
$Mn^+(3d^5 4s^1)$	–	–	19 ± 10	–
$Ni^+(3d^9)$	–	–	1200 ± 400	–
$Cu^+(3d^{10})$	–	–	950 ± 290	–

[a] Rate constants in 10^{-12} cm^3 s^{-1}; NR means no reaction ($k \leq 3 \times 10^{-14}$ cm^3 s^{-1}); dash (–) means not studied. Error limits are ±2 standard deviations of the mean or ±10%, whichever is larger. These refer to the precision of the data; the absolute accuracy is ±30%. Data from refs 16 and 20. [b] The reactivity of the Ni ground state $3d^8 4s^2(^3F_4)$ and the low-lying excited state $3d^9 4s^1(^3D_3)$ at 205 cm^{-1} were identical.

must make more new bonds than they break. Abstraction of H or CH_3 is quite endothermic. Termolecular chemistry involves formation of internally hot M(hydrocarbon) *complexes* that are sufficiently long-lived (~100 ns at 0.8 Torr of He) to be stabilized by a collision with the third body He.[18] Statistical theories predict that the lifetime of a hot complex increases rapidly with the number of atoms in the hydrocarbon reactant and with the M–hydrocarbon bond energy (potential well depth).

Neutral metal atoms are generally less reactive than metal cations. Table I provides a representative sample of effective bimolecular rate constants at 300 K in 0.8 Torr of He for ground-state M and M^+. So far most neutral transition metal atoms do not react with alkanes, and only a subset react with alkenes. In the 3d series,[16] we find that *none* of the neutral atoms react with alkanes at 300 K, and only Sc, Ti, V, and Ni react with alkenes. The Sc, Ti, and V reactions are quite *inefficient*, with $k/k_{hs} \leq 0.05$. The reason is simple. Most of the neutral 3d-series atoms have $3d^{x-2}4s^2$ ground-state configurations, and the 4s orbital is much larger than 3d. The $4s^2$ configuration of the outermost subshell looks much like an unusually large helium atom to the approaching hydrocarbon, which is also closed-shell. A substantial potential energy barrier usually prevents close approach of metal atom and hydrocarbon at 300 K.

In the 4d series, the 5s and 4d orbitals are more similar in size and orbital energy. This enhances the strength of metal–ligand bonds.[15] In addition, while Y, Zr, and Tc have $4d^{x-2}5s^2$ ground states, Nb, Mo, Ru, and Rh have $4d^{x-1}5s^1$ ground states and Pd has a $4d^{10}$ ground state. We thus anticipated greater chemical reactivity of the 4d neutral metals. At present, we know that Y, Zr, and Nb react *rapidly* with alkenes but do not react with alkanes at 300 K (Table I). Efficiencies are greater than in the 3d series. In addition, Mo reacts slowly with larger alkenes, while its congener Cr is inert. Pd reacts very rapidly with alkenes (~30 times faster with C_2H_4 than Ni) and surprisingly rapidly even with *alkanes*.[20] The Pd + alkane products are collisionally stabilized complexes whose structure may well be an unusual long-range, η^2-complex **2**, which is distinct from the transition state **3** en route to the bond insertion complex **4**. Recent ab initio calculations found the η^2-complex to be stable by 4 kcal mol^{-1} for $Pd(CH_4)$ relative to ground-state Pd + CH_4 reactants.[21]

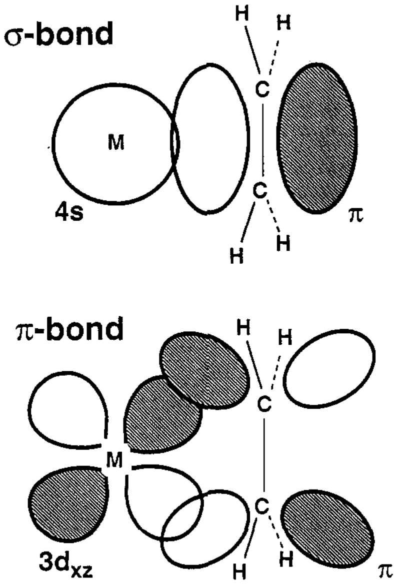
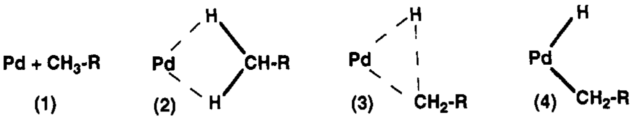


Figure 1. Donor–acceptor model of M–C_2H_4 bonding, showing both σ- and π-bonds.



Potential Energy Surfaces from a Model of Chemical Bonding. The Ni + C_2H_4 reaction provides a simple example of how we can combine known atomic energy levels and a model of metal–hydrocarbon bonding to infer the nature of the potential energy surfaces that govern chemical reactivity. We assume that the key step along the reaction path is formation of a strong Ni–alkene bond. Ni has a *triplet* $3d^8 4s^2$ ground state ill-suited for bonding. However, the unusually low-lying $3d^9 4s^1(^1D)$ excited state at 7 kcal mol^{-1} has the proper orbital occupancy and electron spin to form a strong bond to alkene. The simplest description of metal–alkene bonding is the donor–acceptor model originally due to Dewar, Chatt, and Duncanson.[22] Bonding occurs via the simultaneous formation of *two* donor–acceptor bonds (Figure 1). The σ-bond involves donation of electrons from the alkene 2pπ orbital to the metal 4s orbital along the axis of approach. The π-bond involves "back-donation" from the metal $3d_{xz}$ orbital to the empty alkene 2pπ* orbital. It will usually be necessary to form hybrid orbitals on the metal atom.

The Ni ground state has the wrong orbital occupancy ($4s^2$ instead of empty 4s) and the wrong spin (triplet

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(20) Carroll, J.; Weisshaar, J. C. *J. Am. Chem. Soc.*, submitted.

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instead of singlet) to form a strong bond to alkene. As discussed by Langhoff and Bauschlicher[12] and Siegbahn and co-workers,[23] promotion from triplet $3d^84s^2$ to singlet $3d^94s^1$ permits sd hybridization, which forms the new orbitals $|sd_+\rangle = |4s\sigma\rangle + |3d\sigma\rangle$ and $|sd_-\rangle = |4s\sigma\rangle - |3d\sigma\rangle$. The $|sd_+\rangle$ hybrid concentrates probability density along the approach axis, making a good σ-acceptor orbital. The $|sd_-\rangle$ hybrid concentrates density near the *xy* plane in a smaller, torus-shaped orbital, which decreases repulsion between the nonbonding pair and the approaching alkene. Recent ab initio calculations[23a] show sd hybridization in the $^1A_1$ ground state of NiC_2H_4. As Ni and alkene approach, electron density flows first from $|4s\rangle$ into $|sd_-\rangle$ and from $|\pi\rangle$ into $|sd_+\rangle$ and subsequently from $|3d_{xz}\rangle$ into $|\pi^*\rangle$, leaving Ni with a net positive charge of +0.18*e* in the NiC_2H_4 complex.

As a measure of the energy required for promotion and sd hybridization, we use the excitation energy to the lowest $3d^94s^1$ term with the singlet spin necessary for double occupancy of the $|sd_-\rangle$ orbital.[15] Ni reacts efficiently because ΔE_{sd} is only 6 kcal mol^{-1}, compared with 67 kcal mol^{-1} for Mn, 34 kcal mol^{-1} for Fe, and 20 kcal mol^{-1} for Co. Mn, Fe, and Co are accordingly inert at 300 K. This is a simple example of how atomic structure controls chemical reactivity.

We can go beyond simple models of chemical bonding to infer the nature of the *potential energy surfaces* that govern the outcome of bimolecular collisions.[6,13] By combining the donor–acceptor model with atomic state energies, we can discern the underlying cause of the potential energy *barriers* that make 3d-series neutral metal atoms so inert at 300 K. In approach geometries like that of Figure 1, the repulsive forces between the $4s^2$ electrons on Ni and the π^2 electrons on alkene lead to repulsive *diabatic* potential energy surfaces correlating with ground-state reactants (Figure 2). Here diabatic means conserving both the electron spin of the full Ni + alkene system and the $4s^2$ orbital occupancy of the metal atom. The $3d^94s^1(^1D)$ excited state of Ni, which *is* well suited to bind to alkene, provides diabatic potential energy surfaces that are *attractive*. The attractive and repulsive diabatic surfaces *intersect*, or *cross*. For certain NiC_2H_4 geometries, the potential energy is the same when the Ni atom has triplet spin and $3d^84s^2$ configuration or singlet spin and $3d^94s^1$ configuration.

During the collision, hybridization and changes of electron spin occur in the vicinity of diabatic curve crossings. For the polyatomic systems of interest, it not completely clear what will happen to the collision complex near *multidimensional* surface intersections.[24] While simple models help us to sketch reasonable diabatic surfaces, low-energy collisions tend to remain on the same *adiabatic* surface. Quantum mechanics tells us that the crossing of two diabatic surfaces of different spin will be *weakly avoided.* Spin–orbit interaction leads to two new adiabatic surfaces, shown as the bold lines in Figure 2. On the lower adiabatic surface, the electron configuration and electron spin change from triplet Ni + alkene reactants to the singlet Ni(alkene) complex.

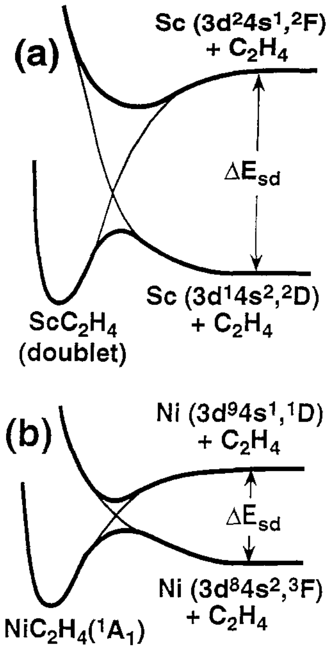

Figure 2. Potential energy curves describing approach of Sc (a) and Ni (b) to C_2H_4. Bold lines are adiabatic curves; light lines are diabatic curves that conserve electron spin and metal configuration. The two diabatic curves have the *same* spin for Sc but *different* spin for Ni.

This is really just the sd hybridization mechanism with concomitant change of electron spin, described in the language of potential energy surfaces. The height of the barrier on the adiabatic surface correlating to ground-state reactants should be roughly proportional to the excitation energy ΔE_{sd}. Collisions with sufficient kinetic energy and favorable approach geometry overcome the barrier and form long-lived NiC_2H_4 complexes, which may eventually break C–H bonds.

Quantitative experimental information is emerging for the Ni + C_2H_4 potential surfaces. Mitchell and co-workers[17] estimate the binding energy of NiC_2H_4 to be 35 kcal mol^{-1} relative to Ni(^{3}F) + C_2H_4. Observation of chemical reaction at 300 K implies an *adiabatic* barrier height no larger than 5 kcal mol^{-1}. The best ab initio calculations[23a] find NiC_2H_4 bound by 10 kcal mol^{-1} relative to ground-state Ni + C_2H_4 and the *diabatic* curve crossing 8 kcal mol^{-1} above ground-state reactants.

Mn, Fe, and Co are unreactive because their promotion energies ΔE_{sd} are too large. On the other hand, ΔE_{sd} is quite large for Sc (43 kcal mol^{-1}), Ti (33 kcal mol^{-1}), and V (24 kcal mol^{-1}), but they *do* react with alkenes, albeit more slowly than Ni. The Sc, Ti, and V ground states need not change electron spin to bind to alkene (Figure 2a). The crossing of diabatic surfaces of the *same spin* will be *more strongly avoided* than crossings between surfaces of different spin. For a given value of ΔE_{sd}, we expect smaller adiabatic barrier heights for Sc, Ti, and V than for Mn, Fe, and Co (Figure 2). All else being equal, ground-state metal atoms that can bond to the hydrocarbon without changing spin react more efficiently.

Finally, recall that the 4d-series neutrals are more reactive than the 3d-series neutrals (Table I). For example, Y and Zr are much more reactive than their congeners, Sc and Ti. Yet the values of ΔE_{sd} are very

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(23) (a) Widmark, P. O.; Roos, B. O.; Siegbahn, P. E. M. *J. Phys. Chem.* **1985**, *89*, 2180. (b) Blomberg, M. R. A.; Siegbahn, P. E. M.; Nagashima, U.; Wennerberg, J. *J. Am. Chem. Soc.* **1991**, *113*, 424.

(24) Tully, J. In *Dynamics of Molecular Collisions, Part B*; Miller, W. H., Ed.; Plenum: New York, 1976.

similar for Sc and Y and for Ti and Zr. This suggests smaller adiabatic barrier heights in the 4d series. The larger d orbitals in the 4d series overlap better with alkene orbitals, producing a stronger M–alkene bond, which pulls down the energy of the curve crossing. We also find that Mo reacts with alkenes but Cr does not, even though the promotion energy to a $d^{x-1}s$ state of the correct spin is 8 kcal mol^{-1} larger in Mo. Stronger spin–orbit coupling in the 4d series increases the repulsion between diabatic curves of different spin, which decreases the adiabatic barrier height.

Transition Metal Cations, M$^+$. Eller and Schwarz[3a] have recently reviewed the gas-phase chemistry of M$^+$. Our goal here is to illustrate how the same kinds of chemical reasoning that helped us systematize neutral metal atom reactivity are useful for M$^+$ as well. We focus on a proposed mechanism by which certain 3d-series metals dehydrogenate or demethanate small alkanes. Two well-studied reactions are

$$V^+ + C_3H_8 \rightarrow VC_3H_6^+ + H_2 \tag{1}$$

$$Fe^+ + C_3H_8 \rightarrow FeC_3H_6^+ + H_2 \tag{2a}$$

$$\rightarrow FeC_2H_4^+ + CH_4 \tag{2b}$$

We can see why certain metals activate alkanes efficiently while others do not. It is less clear why Sc$^+$, Ti$^+$, and V$^+$ preferentially attack C–H bonds and Fe$^+$, Co$^+$, and Ni$^+$ attack both C–H and C–C bonds. In the well-studied Co$^+$ + C_3H_8 reaction,[25] kinetic isotope effects and statistical modeling indicate that the initial chemical step is Co$^+$ insertion into a terminal C–H bond, presumably followed by migration of a β-hydrogen or the β-methyl group to the metal and elimination of H_2 or CH_4. In other systems, direct insertion of M$^+$ into C–C bonds may occur.

For V$^+$ + alkane reactions, we have an appealing picture of how electronic factors control chemical reactivity.[26,27] The model is supported by electronic-state-specific reactivity measurements. In the most informative experiments, we cross a beam of V$^+$ with a beam of hydrocarbon at well-defined kinetic energy. Using resonant two-photon ionization (R2PI) we can vary the initial V$^+$ state distribution and extract *state-specific reaction cross sections* (probabilities) and product branching ratios. We found that the low-lying *quintet* terms $3d^34s(^5F)$ and $3d^4(^5D)$ are quite inert (Figure 3). The *triplet* term $3d^34s(^3F)$, which has 25 kcal mol^{-1} of electronic energy, reacts at least 80 times more efficiently than quintets to eliminate H_2. The triplet's absolute reaction efficiency is 41% with C_3H_8 at 0.2-eV collision energy. The same 25 kcal mol^{-1} placed in reactant *kinetic energy* is ineffective.[27] From these results, we infer the importance of electron spin conservation in determining the pattern of state-specific reactivity.

If the rate-limiting step is M$^+$ insertion into a C–H or C–C bond of the alkane, then electron spin conservation restricts which M$^+$ + C_3H_8 reactant states provide low-energy paths to the bond-insertion intermediate, e.g., H–M$^+$–C_3H_7. In the more highly symmetric case of M$^+$ + H_2 collisions, orbital correlations are also important.[28] The data are not yet incisive on the role of orbital symmetry in M$^+$ + alkane collisions. In Figure 3, the coordinate is the approach of V$^+$ to a C–H bond of the alkane. All states of V$^+$ form electrostatically bound complexes at long range. Since bare V$^+$ has four unpaired electrons, a σ-bonded C–H insertion complex H–V$^+$–C_3H_7 has two unpaired electrons. Low-lying triplet states of the complex correlate diabatically to the excited $3d^34s(^3F)$ atomic asymptote. Here we use diabatic in the more limited sense of *conserving electron spin*. The lower energy quintet states cannot form two covalent bonds, and thus they produce only repulsive diabatic surfaces at short range. Weakly avoided crossings between *attractive, triplet* diabatic potentials and *repulsive, quintet* diabatic potentials create barriers on the lowest energy adiabatic surfaces from quintet reactants, explaining their relative inertness. Triplet reactants apparently remain on the attractive, triplet surfaces, find the bond-insertion intermediate, and eventually react.

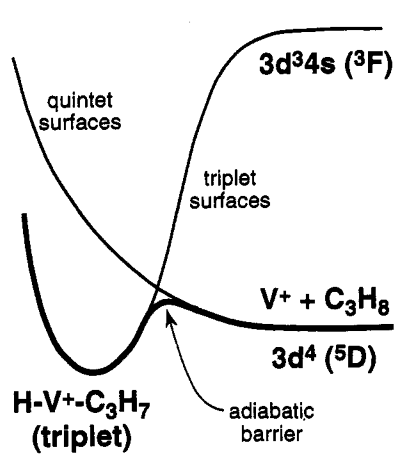

Figure 3. Schematic potential energy curves for V$^+$ + C_3H_8. The bold line is the lowest energy adiabatic curve.

More generally, spin conservation during M$^+$ insertion into a C–H or C–C bond can explain which ground-state, 3d-series M$^+$ cations react with alkanes in low-energy collisions and which do not (Figure 4).[18] The chemically active M$^+$ cations have either a ground state that can conserve spin during insertion (Co$^+$ and Ni$^+$) or a low-lying excited state that can do so (Sc$^+$, Ti$^+$, and the less reactive V$^+$ and Fe$^+$). Many inert M$^+$ have promotion energies to states of proper spin that are too large (≥1.3 eV for Cr$^+$ and Mn$^+$). Cu$^+$ must promote to a singlet $3d^94s^1$ state (3.2 eV) to form two σ bonds, and Zn$^+$ presumably must promote to a doublet $3d^94s4p$ state at 14 eV to make two σ bonds.

Dipositive Transition Metal Cations, M^{2+}. The second ionization potentials of transition metal atoms lie in the range 11–20 eV, which is larger than the first ionization potential of all alkanes except CH_4. Dipositive metal cations should be extraordinarily strong oxidizing agents capable of removing an electron even from alkanes. In fact, M^{2+} ions are indeed highly reactive, but the chemistry is often remarkably *gentle*. In the fast flow reactor at 0.4 Torr of He, Ti^{2+} is formed

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[25] 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; **1990**, *112*, 5663.

[26] Sanders, L.; Sappey, A. D.; Weisshaar, J. C. *J. Chem. Phys.* **1986**, *85*, 6952. Sanders, L.; Hanton, S. D.; Weisshaar, J. C. *J. Chem. Phys.* **1990**, *92*, 3485.

[27] Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 1806.

[28] Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 2037.

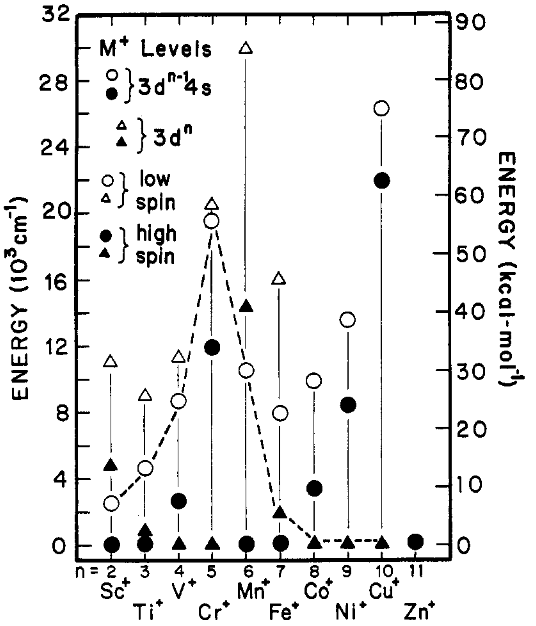

Figure 4. Energies of selected electronic terms for the 3d-series M^+. Configurations are indicated. "High" and "low" spin refer to the two common spin multiplicites within each configuration type. The dashed line connects the lowest energy states that can conserve spin while inserting into a C–H or C–C bond of an alkane.

by laser vaporization of a rotating Ti disk. We observed these *selective* reactions:[29]

$$Ti^{2+} + nCH_4 \rightarrow Ti(CH_4)_n{}^{2+}, \quad n = 1\text{-}4 \qquad \text{(adduct stabilization)} \quad (3)$$

$$Ti^{2+} + C_2H_6 \rightarrow TiH^+ + C_2H_5{}^+ \qquad \text{(hydride anion transfer)} \quad (4)$$

$$Ti^{2+} + C_3H_8 \rightarrow Ti^+ + C_3H_8{}^+ \qquad \text{(electron transfer)} \quad (5)$$

All three reactions are fast; efficiencies are ~0.1 for CH_4 and ~1 for C_2H_6 and C_3H_8. Each reaction is surprisingly selective. The products shown dominate the chemistry, even though both e^- and H^- transfer are exothermic in all three cases.

A simple one-dimensional curve-crossing model (Figure 5) explains the specificity of these reactions. At long range, reactants Ti^{2+} + RH follow the *physical* ion-induced dipole potential $V_1(r) = -2\alpha e^2/r^4$, where α is the RH polarizability and $+2e$ is the cation charge. The Ti^{2+}·RH complex may lie below the ion-pair asymptotes. Bimolecular ion-pair products $Ti^+ + RH^+$ and $TiH^+ + R^+$ follow repulsive Coulomb potentials $V_2(r) = +e^2/r$ at long range, crossing the Ti^{2+} + RH curve at a radius that depends sensitively on exothermicity.

The different alkanes CH_4, C_2H_6, and C_3H_8 in effect tune the radii of the crossing points r* and r′ between reactants and the two ion-pair product channels, thus controlling product branching. The calculated electron-transfer curve crossing occurs at 14.4 Å for $Ti^{2+} + CH_4$, 7.0 Å for C_2H_6, and 6.1 Å for C_3H_8. Apparently the electron will not jump 14.4 or 7.0 Å, but it jumps efficiently at 6.1 Å. The calculated hydride-transfer curve crossing occurs at 9.1 Å for CH_4, 4.6 Å for C_2H_6, and 4.5 Å for C_3H_8. $Ti^{2+} + C_2H_6$ reactants survive the electron-transfer crossing at 7.0 Å and reach 4.6 Å, where H^- transfer occurs and products separate. It seems sensible that the range of H^- transfer would be shorter than that of e^- transfer; the exponential tail of the quantum mechanical wave function is less extensive for H^- than for e^-. $Ti^{2+} + CH_4$ survives both the electron- and hydride-transfer crossings, reaching the adduct ion well at short range. About 10% of the adducts are collisionally stabilized before dissociation back to Ti^{2+} + CH_4.

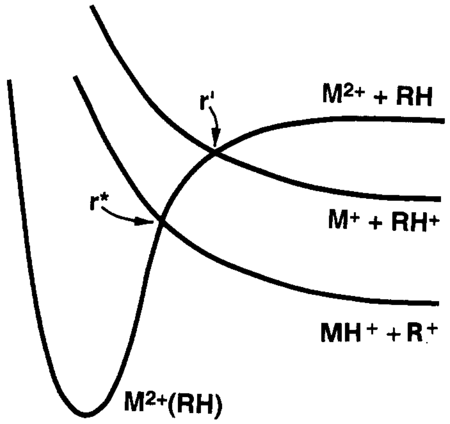

Figure 5. Schematic one-dimensional potential energy curves for M^{2+} + alkane. Crossing points for electron transfer (r′) and hydride transfer (r*) control the outcome of collisions.

Recently Freiser and co-workers[3b,5] discovered many new M^{2+} + alkane reactions that produce H_2 and CH_4 elimination products similar to those of M^+:

$$M^{2+} + C_2H_6 \rightarrow M^+ + C_2H_6{}^+ \quad (6a)$$

$$\rightarrow MH^+ + C_2H_5{}^+ \quad (6b)$$

$$\rightarrow MC_2H_4{}^{2+} + H_2 \quad (6c)$$

$$\rightarrow MC_2H_2{}^{2+} + 2\,H_2 \quad (6d)$$

$$\rightarrow MCH_2{}^{2+} + CH_4 \quad (6e)$$

Nb^{2+} undergoes reactions 6a,b,d; Ta^{2+} undergoes only reaction 6a; and Zr^{2+} undergoes reactions 6b–e.

All of the data suggest the following picture. As M^{2+} approaches alkane, it encounters the e^--transfer curve crossing first. The efficiency of e^- transfer rises sharply for crossing radii below 7 Å. Those M^{2+} + alkane pairs that survive the e^--transfer crossing may encounter an H^--transfer crossing at 4–6 Å; if so, H^- transfer is efficient. But if the H^- transfer radius is smaller than about 4 Å, H^- transfer does *not* occur. Other rearrangement channels leading to H_2 or CH_4 elimination then dominate the products. Apparently the chemical forces become too strong at short range to allow M^{2+} to escape with H^-. In a sense, both e^- and H^- transfer are *physical reactions* controlled by the exothermicities of the two product channels and the long-range ion-induced dipole and ion–ion potentials, which have the *same shape* for all M^{2+} + hydrocarbon reactions.

Summary

At a certain level, we are beginning to understand how the electronic structure of gas-phase transition

[29] Tonkyn, R.; Weisshaar, J. C. *J. Am. Chem. Soc.* 1986, *108*, 7128.

metal atoms determines their chemical reactivity. Each of the charge states M, M^+, and M^{2+} finds unique reaction paths, yet we can see common themes. The "physical reactions" of electron and hydride transfer are unique to M^{2+}. However, many M^{2+} and M^+ are rather similar chemicals that digest hydrocarbons whenever the metal atom can approach the alkane or alkene to short range. The cations are highly reactive partly because the chemically active $d^{x-1}s$ and d^x configurations lie low in energy and partly because the attractive ion-induced dipole potential counteracts intrinsic chemical barriers at long range. The inertness of neutral M further highlights the importance of the long-range potential in determining the outcome of gas-phase collisions.

A recurring theme in all the gas-phase work is the importance of intersections between different kinds of diabatic potential energy surfaces arising from different low-lying atomic asymptotes. It is really the overall *pattern* of low-lying states that determines reactivity. Even for M^+ and M^{2+}, the ground state itself often has the wrong spin or electron configuration to form chemical bonds. Perhaps the neutral atoms would be highly active chemicals if only they were able to penetrate long-range potential barriers to bond insertion. To examine this possibility, we hope to devise experiments that prepare specific $d^{x-1}s$ excited states of neutral M and study their reactivity.

While long-range forces and simple bonding concepts based on spin and configuration may explain which atoms react and which do not, we have only begun to probe the subtle chemical questions. We do not know the geometries and energetics of all of the key intermediate potential wells and saddle points for *any* of the reactions discussed here, although progress is being made. We do not begin to understand how orbital sizes and energies dictate the *chemical branching* between H_2 and CH_4 elimination and its variation from metal to metal. Here is where ab initio quantum chemistry will make a major contribution in the next five years.

Finally, we ask whether gas-phase work has anything at all to do with solution-phase organometallic chemistry. The gas phase differs from the solution phase in many important ways. Bond energies such as $D_0(M-CH_3)$ and $D_0(M-H)$ change substantially from gas phase to solution phase due to differential solvation effects. A nominal +2 oxidation state of a ligated metal in solution does not indicate a genuine 2+ charge on the metal; the charge is attenuated by ligands. There are no steric effects in bare metal atom chemistry; there are no ligands! Hybridization of a bare metal can occur without regard for the presence of ligands to the rear of the metal. In a sense, hybridization has already occurred in ligated metal species. In single-collision conditions in the gas phase, internal energy in the complex remains available for overcoming barriers and ejecting product molecules. There is no solvent robbing energy from the reaction coordinate.

Closer parallels between gas-phase and solution-phase chemistry will eventually emerge, especially as we begin to explore the gas-phase chemistry of ligated and solvated metal cations.[30] The unique charm of bare metal atom chemistry remains the ability to select a specific reactant electronic state and kinetic energy and study the chemical outcome of individual bimolecular collisions.

I want to thank all my graduate students for their insight and hard work over the past 10 years in Madison. The National Science Foundation, the donors of the Petroleum Research Fund, and the Wisconsin Alumni Research Foundation have generously supported this work.

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(30) For a review of ligated metal cation chemistry, see: Buckner, J. S.; Freiser, B. S. *Polyhedron* 1988, *7*, 1583.