ground states perhaps produced by significant contributions of nonisotropic exchange coupling.[17] Last, the existence of pure spin-quartet clusters is not an isolated phenomenon. We have also demonstrated this state in, e.g., $(Me_4N)_3[Fe_4Se_4(SPh)_4]$.

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Crossed-Beam Studies of Energy and Angular Distributions of Organometallic Reactions: Decarbonylation of Acetaldehyde by Fe^+ and Cr^+

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The energetics and dynamics of the reactions of gas-phase transition-metal ions with organic molecules are topics of active research and speculation at present.[3,4] In the present work, we report the first crossed-beam studies of gas-phase transition-metal ion chemistry, demonstrating that product kinetic energy and angular distributions probe the potential energy surface topology of simple carbon–carbon bond cleavage reactions. The studies yield information on the lifetimes and stabilities of key intermediates and assess the partitioning of energy in these species. We present results on the direct decarbonylation of acetaldehyde by Fe^+ and Cr^+.[5]

$$Fe^+ + CH_3CHO \rightarrow FeCO^+ + CH_4 \qquad \Delta H = -24 \text{ kcal mol}^{-1}$$

$$Cr^+ + CH_3CHO \rightarrow CrCO^+ + CH_4 \qquad \Delta H = -27 \text{ kcal mol}^{-1}$$

Gas-phase decarbonylations of aldehydes and ketones by cyclopentadienyl nickel cation, $CpNi^+$, as well as the bare Fe^+ and Co^+ cations have been demonstrated in ICR experiments by Beauchamp[6,7] and Freiser,[8] as well as ion beam experiments by Beauchamp and collaborators,[9] and Scheme I represents the mechanism which has been proposed for these systems.[9,10]

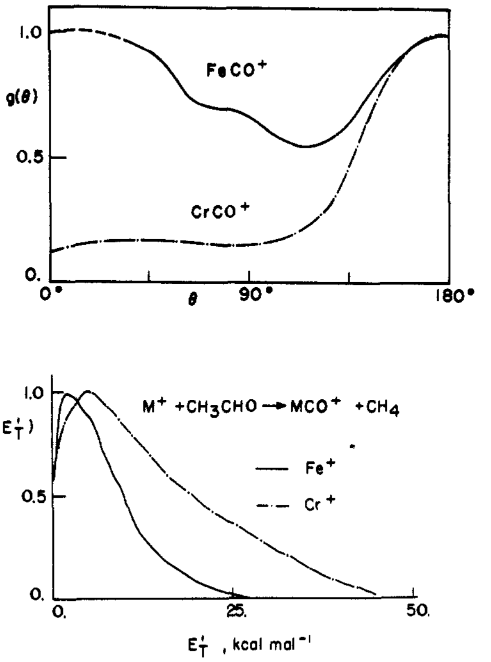


Figure 1. Product angular and kinetic energy distributions for $FeCO^+$ and $CrCO^+$ production. The dashed portion of the $FeCO^+$ angular distribution in the top panel corresponds to forward scattered products inaccessible to our detector, and therefore the curve is extrapolated.

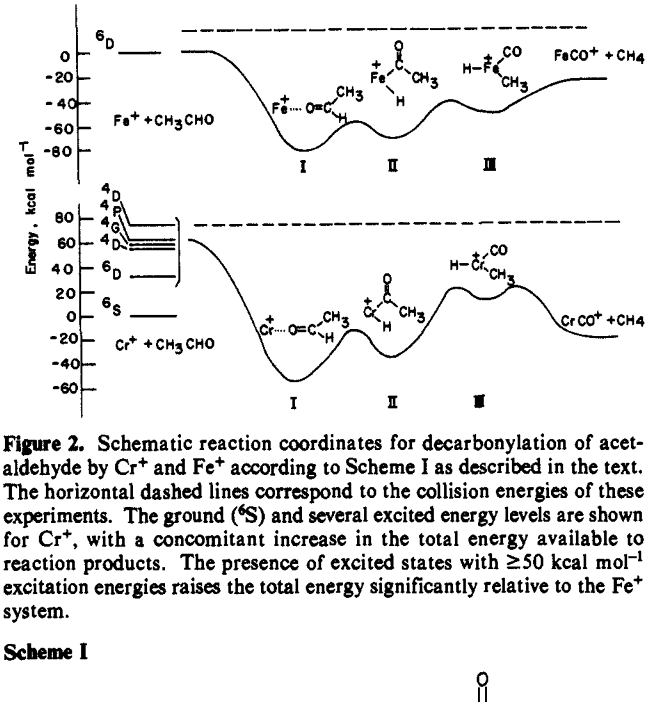
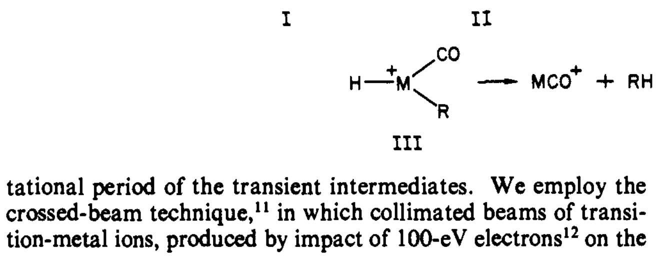


Figure 2. Schematic reaction coordinates for decarbonylation of acetaldehyde by Cr^+ and Fe^+ according to Scheme I as described in the text. The horizontal dashed lines correspond to the collision energies of these experiments. The ground (^6S) and several excited energy levels are shown for Cr^+, with a concomitant increase in the total energy available to reaction products. The presence of excited states with ≥50 kcal mol^{-1} excitation energies raises the total energy significantly relative to the Fe^+ system.

Scheme I



Our experiments address the nature of the intermediates along the Scheme I reaction coordinate by measuring product fluxes which contain dynamical information on the timescale of a rotational period of the transient intermediates. We employ the crossed-beam technique,[11] in which collimated beams of transition-metal ions, produced by impact of 100-eV electrons[12] on the

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metal carbonyl, intersect a molecular beam of the neutral, prepared by supersonic expansion of a 10% acetaldehyde/90% hydrogen mixture through a 100-μm nozzle. We detect reactively scattered products with an energy analyzer/quadrupole mass filter which rotates about the collision center.

Our initial experiments were performed at collision energies of 12.0 kcal mol^{-1} and 20.8 kcal mol^{-1} for Fe^+ and Cr^+, respectively. The measured fluxes are transformed to the center of mass collision system to yield product angular and kinetic distributions.[13,14] Figure 1 shows these distributions; the barycentric angular distribution for $FeCO^+$ formation shows clear symmetry about $\theta = 90°$, providing evidence that one or more intermediates in Scheme I live at least several rotational periods.[15] In contrast, $CrCO^+$ formation proceeds with an angular distribution that is quite broad but shows a significant peak at $\theta = 180°$. Although the collision energy for $CrCO^+$ formation is only 8.8 kcal mol^{-1} higher than for $FeCO^+$ formation, the reactive intermediate lives only a fraction of a rotational period,[16,17] or $\sim 10^{-13}$ s in the Cr^+ case.

The top panel of Figure 2 shows the reaction coordinate for Scheme I decarbonylation by Fe^+, indicating approximate energetics for the reaction of the ground-state cation. Although the energies of the various intermediates and the barriers separating them are unknown, the Fe^+–H and Fe^+–CH_3 bond strengths of 71 and 59 kcal mol^{-1}, respectively[18] allow us to make some estimates of the energies of intermediates I–III relative to the reaction products, as shown in Figure 2. The expected nonreactivity of the $3d^5$ Cr^+ ground-state configuration and the clear evidence for excited states in Cr^+ produced by electron impact[12] suggest strongly that excited states of this ion participate in the decarbonylation reaction. The larger available energy for the excited-state reaction, coupled with smaller Cr^+–H and Cr^+–CH_3 bond strengths[19] relative to the Fe^+ system, yields a potential energy profile shown in the bottom panel of Figure 2, where several low-lying quartet states of Cr^+ are included. Simple thermochemical arguments[20] suggest that intermediate III in the Cr^+ system may lie above the products, leading to an exit barrier to product formation. The additional electrons in Fe^+ lead to stabilization of the Fe^+ intermediates relative to their Cr^+ analogues, resulting in deeper potential energy wells. Coupled with a higher total energy in the Cr^+ system arising from excited electronic states in the metal ions, the reaction intermediates exhibit substantially shorter lifetimes.

The kinetic energy distributions shown in the lower panel of Figure 1 also illustrate the differences between these two systems: the narrow distribution for $FeCO^+$ production peaks near 2 kcal mol^{-1}, with the significantly broader $CrCO^+$ distribution peaking near 5 kcal mol^{-1}. These results are consistent with the larger total energy accessible to this product, the shorter lifetimes of the transient intermediates, and the possibility of an exit channel barrier[21] in the formation of $CrCO^+$. These and related questions of excited-state reactivity suggest that additional experiments over a range of collision energies and with ground-state ions, in conjunction with theoretical calculations of the requisite surfaces, will lead to an enhanced understanding of organometallic reaction dynamics in the gas phase.

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(12) Electron impact on metal carbonyls may generate significant excited-state populations. Reents et al. (Reents, W. D.; Strobel, F.; Freas, R. B.; Wronka, J.; Ridge, D. P. *J. Phys. Chem.* **1985**, *89*, 5666) have shown that Cr^+ produced by electron impact on $Cr(CO)_6$ is ~70% in excited states. Recent work by Halle et al. (Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962) provides kinetic evidence that some of these states are quartet states. There was no *kinetic* evidence for more than one Fe^+ electronic state produced by electron impact on $Fe(CO)_5$ in the work of Reents et al. Recent work by Elkind and Armentrout (Elkind, J. L.; Armentrout, P. B., unpublished results) suggests enhanced reactivity with D_2 for $Fe^+(^4F)$ relative to ground-state $Fe^+(^6D)$. This study also indicates that Fe^+ reactivity with larger molecules is relatively insensitive to the electronic state of Fe^+. Extant data thus suggest that excited electronic state reactivity may be greater for Cr^+ than for Fe^+.

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(20) A very crude estimate of the stability of intermediate III relative to the products can be computed from the C–H bond srength in CH_4, 103 kcal mol^{-1}, and the appropriate M^+–H and M^+–CH_3 bond energies. Thus $FeCO(CH_3)H^+$ lies ~27 kcal below the products, while $CrCO(CH_3)H^+$ lies ~31 kcal *above* the products. Comparable calculations for intermediate II using the C–C bond strength in acetone (80 kcal mol^{-1}) give stabilities shown in Figure 2. These calculations ignore the increase in the M^+–CO bond strength in the transformation from II and III to products and must be viewed as qualitative only.

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pH Dependence of the Electrochemical Behavior of Surfaces Modified with a Polymer Derived from a Monomer Consisting of Two Viologen Subunits Linked by a Quinone: Evidence for "Rectification" by Synthetic Molecular Materials

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We report results concerning use of the surface-derivatizing reagent I that demonstrates a kind of rectification that is important in systems such as the photosynthetic apparatus. The important finding is that an electrode-bound redox polymer formed via hydrolysis of the Si–OMe bonds of I, $(BV\text{–}Q\text{–}BV^{6+})_n$, undergoes a $4e^-/2H^+$ reduction, but below pH 5 only $2e^-$ can be electrochemically withdrawn from the reduced material. Reduction of quinone centers, Q, in the $(BV\text{–}Q\text{–}BV^{6+})_n$ polymer to their dihydroxy form, QH_2, is mediated by the viologen, $BV^{2+/+}$, redox system, but the process cannot be reversed at low pH because the QH_2 is thermodynamically incapable of delivering charge back to the BV^{2+} centers. Direct equilibration of the electrode with the Q/QH_2 centers in the $(BV\text{–}Q\text{–}BV^{6+})_n$ polymer does not occur.

Relevance of our new finding to systems like the photosynthetic apparatus rests in the fact that charge separation in the photosynthetic system is achieved by a kind of rectification: the charge transport process involves a series of effectively unidirectional e^- transfer events.[1] Such rectification in immobilized $(BV\text{-}Q\text{-}BV^{6+})_n$ occurs for a range of coverages: approximately a monolayer (1.8×10^{-10} mol/cm^2) to thick polymers ($>10^{-8}$ mol/cm^2). Recent demonstrations[2,3] of rectification using electrode-bound redox polymer bilayer assemblies provide evidence that an effectively unidirectional e^- transfer event can be observed between molecular materials having sufficiently different redox potentials. New

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