

Figure 1. Absorption (—, room temperature) and corrected emission (---, 77 K) spectra of zinc(II) complexes in $\text{CHCl}_3/\text{EtOH}$ (1:19, v/v): (a) $\text{ZnCl}_2(\text{phen})$; (b) $\text{Zn}(\text{F}_3\text{PhS})_2(\text{phen})$, a time-resolved emission spectrum (···) at 77 K is included (0.5- μs delay, 0.25- μs window); (c) $\text{Zn}(4\text{-ClPhS})_2(\text{phen})$; (d) $\text{Zn}(4\text{-MeOPhS})_2(\text{phen})$.

and the spin multiplicity of the new excited state are still not definitively characterized.

Detailed spectroscopic studies between 77 and 4 K of these types of zinc(II) molecules and other (nd)¹⁰ ($n = 3, 4$) complexes containing various N-heterocyclic ligands and both mono and dithiol ligands will be published elsewhere.

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Product Translational Energy Distributions as a Probe of Organometallic Reaction Mechanisms: Dehydrogenation of Alkanes by Groups 8-10 Transition-Metal Ions

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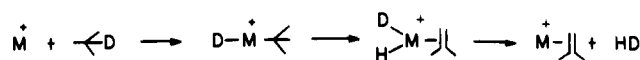
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The complex mechanisms by which carbon-hydrogen and carbon-carbon bonds are cleaved by gas-phase transition-metal ions remain highly speculative.³⁻⁶ In the present work we dem-

Scheme I



onstrate the use of product translational energy distributions to characterize potential energy surfaces for organometallic reactions, using alkane dehydrogenation as an example.

Dehydrogenation of isomeric butanes by first-row group 8-10 metal ions has been investigated extensively. All three metal ions induce HD elimination from 2-methylpropane-2- d_1 to yield a metal ion-2-methylpropene complex.^{6,7} A postulated mechanism for this 1,2-dehydrogenation is shown in Scheme I where $\text{M} = \text{Fe}^+$, Co^+ , or Ni^+ .

In contrast, the products of *n*-butane dehydrogenation are metal specific. Ion cyclotron resonance^{8,9} studies indicate Ni^+ forms exclusively a bis(ethylene) complex on dehydrogenation of *n*-butane, while Fe^+ and Co^+ form both bis(ethylene) complexes and M^+ -butene complexes. High-energy collision-induced dissociation studies¹⁰ also indicate two distinct dehydrogenation products in the reaction of Fe^+ with *n*-butane. Reaction of Ni^+ in a low-energy ion beam with *n*-butane-1,1,1,4,4,4- d_6 shows exclusive loss of D_2 .⁹ These results suggest Scheme II for formation of the bis(ethylene) complex. In similar experiments with Fe^+ and Co^+ , D_2 , HD and H_2 eliminations are observed in different proportions. The latter products suggest that either a 1,2-elimination to form a metal-butene complex in analogy with Scheme I is occurring or scrambling occurs in Scheme II before hydrogen elimination, or both.¹¹ Since the two pathways can be viewed as representing fundamentally different modes of initial interaction of a metal ion with a saturated hydrocarbon, it is of interest to determine the relative importance of 1,2- vs. 1,4-elimination.¹²

To complement the ICR and low-energy ion beam results, the product translational energy distributions for the metastable loss of hydrogen from nascent metal ion-butane complexes have been studied.¹³ In Figure 1, kinetic energy release distributions associated with the metastable loss of HD from nascent (2-methylpropane-2- d_1)cobalt(+) (1,2-elimination) and loss of D_2 from (butane-1,1,1,4,4,4- d_6)nickel(+) (1,4-elimination) are compared.¹⁴ The shape and average kinetic energy release¹⁴ (0.20 eV) for HD loss from (2-methylpropane-2- d_1)cobalt(+) (Figure 1a) is quite distinct from the D_2 loss from (butane-1,1,1,4,4,4- d_6)nickel(+) (Figure 1b), which occurs with an average energy release of 0.40 eV. The maximum energy release of 1.4 eV for the 1,4-process is close to the estimated ΔH for the reaction.¹⁵

(5) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

(6) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

(7) Hanratty, M. A.; Beauchamp, J. L., unpublished results.

(8) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (b) *J. Am. Chem. Soc.* **1983**, *105*, 736.

(9) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

(10) (a) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (b) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(11) This assumes that no scrambling occurs with 1,2-elimination from *n*-butane. (No scrambling is observed with 1,2-elimination from isobutane.)

(12) This methodology is complementary to other techniques that provide more direct product structural information, such as the determination of the relative amounts of mono- and bis(olefin) products in the dehydrogenation of alkanes.⁸⁻¹⁰

(13) Experiments were conducted at UCSB on a reverse-geometry double-focusing mass spectrometer previously described. See: Illies, A. J.; Bowers, M. T. *Chem. Phys.* **1982**, *65*, 281. Illies, A. J.; Jarrold, M. F.; Bass, L. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 5775. Metal ions were produced by 150-eV electron impact on $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Ni}(\text{CO})_4$. Metal butane adducts were formed in a high-pressure source operated typically at 10^{-4} torr of total pressure. Under these conditions metal-alkane clusters were formed and extracted from the source before undergoing subsequent collisions.

(14) For details on kinetic energy release distribution calculations, see: Jarrold, M. F.; Illies, A. J.; Kirchner, N. J.; Wagner-Redeker, W.; Bowers, M. T.; Mandich, M. L.; Beauchamp, J. L. *J. Phys. Chem.* **1983**, *87*, 2213 and references therein.

† The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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(3) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332.

(4) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.

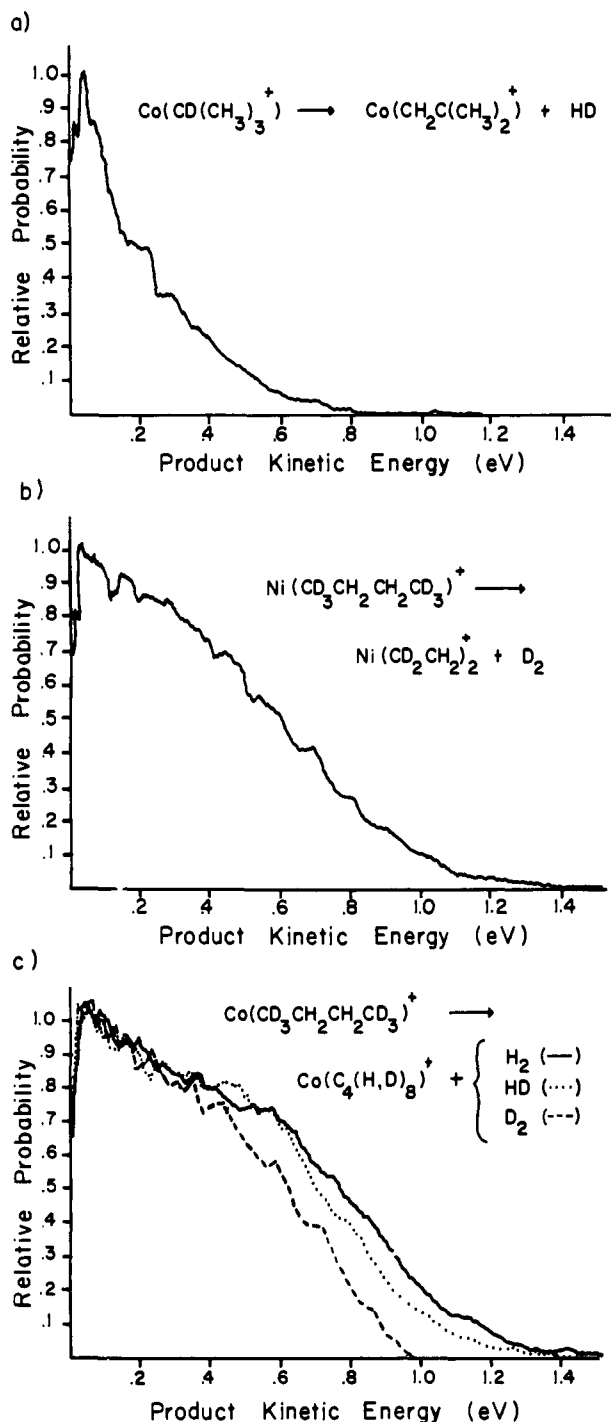


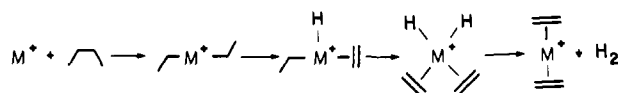
Figure 1. Product translational energy distributions for the metastable loss of (a) HD from (2-methylpropane-2-*d*₁)cobalt(+), (b) D₂ from (butane-1,1,1,4,4,4-*d*₆)nickel(+), and (c) H₂ (—), HD (---), and D₂ (---) from (butane-1,1,1,4,4,4-*d*₆)cobalt(+). In each case the maximum probability is set equal to unity.

The relatively narrow kinetic energy distribution peaked at low energy in Figure 1a suggests a less exothermic reaction for 1,2- than for 1,4-elimination.

Figure 1c gives the kinetic energy release distributions for metastable H₂, HD, and D₂ elimination from nascent (butane-

(15) Assuming $D[\text{Ni}(\text{C}_2\text{H}_4)^+ - \text{C}_2\text{H}_4] = 40$ kcal/mol, $D[\text{Ni}^+ - \text{C}_2\text{H}_4] = 50$ kcal/mol, and $D[\text{Ni}^+ - \text{C}_4\text{H}_8] = 50$ kcal/mol, formation of $\text{Ni}(\text{C}_2\text{H}_4)_2^+$ is calculated to be exothermic by 35 kcal/mol (1.5 eV), while formation of Ni^+ (butene) is 22 kcal/mol (0.95 eV) exothermic.⁸ Thermochemical information for hydrocarbons is taken from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

Scheme II



1,1,1,4,4,4-*d*₆)cobalt(+).¹⁶ The nearly identical distributions suggest that a single mechanism complicated by scrambling is dominant. The similarity of the distributions for Co⁺ shown in Figure 1c and the Ni⁺ results in Figure 1b suggests that the 1,4-dehydrogenation process is more prevalent than the 1,2-process for Co⁺ dehydrogenation of *n*-butane since the latter would be expected to have a narrow kinetic energy distribution resembling Figure 1a.

Reductive elimination of H₂ from the metal center is the last step in the postulated mechanisms for 1,2- and 1,4-dehydrogenation of butane. While the greater exothermicity of the latter process may be responsible for the larger average kinetic energy release, the somewhat different shapes of the distributions in Figure 1, parts a and b may reflect distinctly different potential-energy surfaces for the two reactions.¹⁷ An earlier study inferred that the dehydrogenation of cyclohexane by Co⁺ occurred via a 1,2-mechanism.¹⁸ The shape of the distribution in this system¹⁹ closely resembles the result for 2-methylpropane dehydrogenation given in Figure 1a, in support of the earlier suggestion.

The present results indicate that product translational energy distributions can be characteristic of, and used to identify, specific reaction mechanisms.¹² A comparison of kinetic energy release distributions for isotopic products can distinguish cases where specific reaction mechanisms are primarily responsible for distinct isotopic products from instances where a single mechanism that includes scrambling produces the observed isotopic product distribution. In addition, the maximum observed kinetic energy release is a lower limit on the reaction exothermicity and thus provides a method to confirm reaction thermochemistry. The substantial amount of energy released to product translation in the dehydrogenation reactions (especially the 1,4-elimination) suggests a significant barrier to the reverse reaction, oxidative addition of H₂ to the M⁺(olefin) complex. The general failure to observe D₂ addition to gas-phase ionic cobalt or nickel olefin complexes further supports this conclusion.²⁰ Barriers can have origins in specific electronic correlation of reactants, intermediates, and products.²¹ However, the similar behavior observed for the different groups 9 and 10 metal ions suggests a more general correlation of product translational energy distributions with mechanism. Reproducing the experimental distributions with theoretical models remains an interesting and challenging problem.

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(16) For these processes, the energy release distributions became narrower as the mass of the departing neutral increased. This was also found to be the case for H₂ and HD loss from (2-methylpropane)cobalt(+) and (2-methylpropane-2-*d*₁)cobalt(+), respectively. The origin of this isotope effect is under investigation.

(17) See, for example: Jarrold, M. F.; Bass, L. M.; Kemper, P. R.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *78*, 3756.

(18) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6628.

(19) Illies, A. J.; Bowers, M. T.; Hanratty, M. A.; Beauchamp, J. L., unpublished results.

(20) There are only a few reported examples of H/D exchange to nickel or cobalt olefin ionic complexes. See: Kappes, M. M. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, 1981. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492. A large class of olefins was examined and showed no evidence of D₂ addition. See: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

(21) See, for example: Blomberg, M. R. A.; Brandemark, U.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1983**, *105*, 5557. Blomberg, M. R. A.; Siegbahn, P. E. M.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *81*, 1373. Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 6928.