

Competition between C–C and C–H Insertion in Prototype Transition Metal–Hydrocarbon Reactions

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The oxidative insertion of transition metal centers into the C–H bonds of hydrocarbons, a key step in many catalytic reactions, is well documented.^{1,2} The analogous process involving insertion into C–C bonds is of great potential importance in more efficiently converting petroleum feedstocks into more useful forms. However, despite extensive experimental effort, C–C insertion has only been observed in select cases.^{3–5} Several fundamental factors lead to a strong preference for C–H insertion.^{6–8} Not only are C–H bonds more abundant than C–C bonds in hydrocarbons, metal–hydrogen bonds are usually stronger than metal–carbon bonds, making C–H insertion thermodynamically favored.³ Also, the spherical 1s orbital of the hydrogen atom favors multicenter bonding, leading to low-energy transition states for C–H insertion. In contrast, C–C bonds are highly directional, resulting in less favorable multicenter bonding and larger potential energy barriers for insertion.^{6–8}

To understand these effects more quantitatively, *ab initio* and density functional theory calculations have been employed, but electron correlation and relativistic effects make the determination of potential energy barrier heights (activation energies) for reactions of transition metal complexes difficult.^{6–10} Consequently, the most extensive series of calculations have focused on *model systems* involving transition metal atoms, without the complications of solvent or ligands.^{6–9} Because early transition metals have relatively few valence electrons, (e.g., 5s²4d¹ for Y), the simplest neutral metallic systems for which C–C and C–H insertion may compete involve second-row transition-metal atoms M (= Y, Zr, Nb and Mo*) reacting with cyclopropane. Siegbahn and co-workers have performed *ab initio* calculations to determine the energetics and geometries of important stationary points along the reaction coordinate.^{7,8} As illustrated in Figure 1, insertion of Y into a C–C bond of cyclopropane is predicted to form a four-member cyclic intermediate that may rearrange to form YCH₂ + C₂H₄.^{7,8} Insertion into a C–H bond, on the other hand, forms a different complex that may eliminate H₂, yielding either Y-allene or Y-propyne. These calculations, which used the PCI-80 method to correct correlation errors, are thought to be accurate to within 2–3 kcal/mol^{7,8} and have been used as benchmarks against which newer methods such as density functional theory are tested.¹⁰ However, there have been no direct experimental tests of their accuracies.

Except at temperatures near zero Kelvin, the internal and translational energy distributions of molecules are broad. However, when reactants are prepared in supersonic molecular beams, rotational and translational temperatures are reduced by adiabatic cooling.¹¹ Thus, in our experiment, the total energy of the reactants, which is nearly all translational, may be precisely controlled, facilitating studies of competing reaction pathways as a function of total energy.¹² Although competition between C–C and C–H insertion has been observed in reactions of transition-metal cations,^{13,14} because of the nature of the potential energy surfaces for those systems it was not possible to relate measured product branching ratios to calculated C–C and C–H insertion barrier

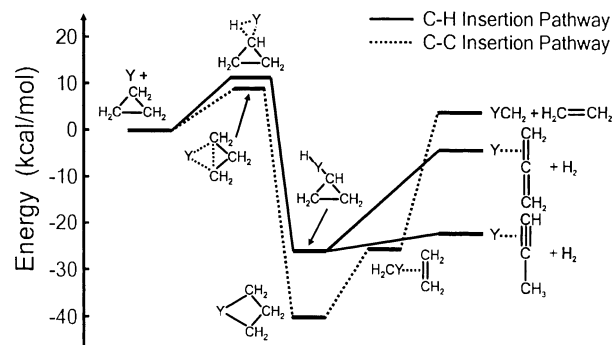


Figure 1. Schematic potential energy diagram for reactions of Y with cyclopropane.⁷ Dotted line indicates C–C insertion pathway leading to YCH₂ + C₂H₄, while solid line indicates C–H insertion pathway leading to YC₃H₄ + H₂.

heights.¹⁵ In reactions of *neutral* transition metal atoms with cyclopropane, the rate-limiting step is C–C or C–H bond insertion.^{7,8} Since there should be no interconversion between the C–C and C–H insertion intermediates, the product branching ratio, $\sigma_{\text{MCH}_2}/\sigma_{\text{MC}_3\text{H}_4}$ is a direct measure of the competition between C–C and C–H insertion.¹⁶ This quantity may be directly related to the heights of the corresponding potential energy barriers.

The reactions were studied using a rotatable source crossed molecular beams apparatus.¹⁷ The atomic metal beam was generated by laser vaporization in an inert carrier gas. Laser induced fluorescence and photodepletion experiments confirmed that products resulted from reactions of the ground electronic states of Y(*a*²D), Zr(*a*³F), and Nb(*a*⁶D), or for Mo, the first metastable electronically excited Mo*(*a*⁵S) state prepared by optical pumping.¹⁸

A molecular beam containing 5% or 10% cyclopropane in an inert carrier gas intersected the metal beam at 90°. Neutral products from single collisions drifted, without undergoing secondary collisions, to a detector 24.1 cm away, where they were photoionized at 157 nm, mass selected, and counted.¹⁷ Product time-of-flight (TOF) spectra were obtained by scanning the delay of the photoionization laser relative to time zero for reaction. By rotating the beams together with respect to the fixed detector, TOF spectra were recorded at various laboratory angles. The analysis involved a transformation to the center-of-mass reference frame using a forward convolution technique in which an input product flux distribution, $P(\nu, \theta)$, was iteratively varied to give optimal agreement between simulated and experimental data.

The potential energy barrier heights for C–C and C–H insertion by the four different second-row metal atoms, calculated by Siegbahn and co-workers,^{7,8} are summarized in Figure 2a.¹⁹ For Mo*, $E_{\text{CH}} - E_{\text{CC}}$ is a large positive quantity, implying that reaction should greatly favor C–C insertion, whereas for Y a small preference for this channel is anticipated. For Nb and Zr, on the other hand, because $E_{\text{CH}} - E_{\text{CC}}$ is negative, C–H insertion is predicted to be dominant. We have measured the product branching

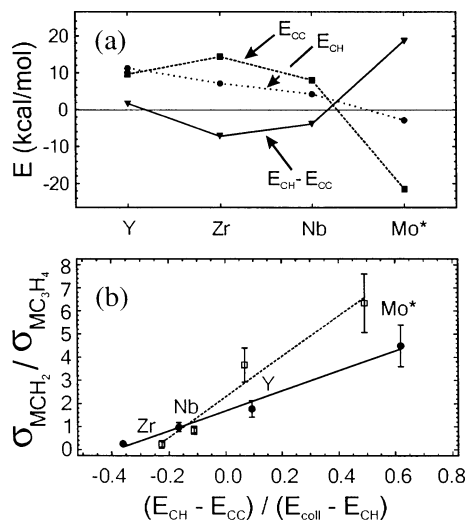


Figure 2. (a) Ab initio C–H and C–C insertion barrier heights for $M +$ cyclopropane and their difference, $(E_{CH} - E_{CC})^{7,8}$ (b) Plot of $\sigma_{MCH_2} / \sigma_{MC_3H_4}$ versus $(E_{CH} - E_{CC}) / (E_{coll} - E_{CH})$ at $E_{coll} \approx 27$ kcal/mol (circles) and 37 kcal/mol (squares).

ratio, $\sigma_{MCH_2} / \sigma_{MC_3H_4}$, for reactions of all four metals with cyclopropane at $E_{coll} = 27$ and 37 kcal/mol. As predicted by the calculated values for $E_{CH} - E_{CC}$, the product branching ratios decreased in the order $Mo^* \gg Y > Nb > Zr$ (Figure 2b).

The line-of-centers (or hard spheres) model is the energy analogue of the temperature-dependent Arrhenius equation. It predicts that reaction cross-sections (σ) increase with collision energy (E_{coll}) above threshold according to:²⁰

$$\sigma(E_{coll}) = \pi d^2 (1 - E_{th} / E_{coll}) \quad (1)$$

In eq 1, E_{th} is the threshold energy for reaction, which we take to be the calculated potential energy barrier heights for insertion, E_{CC} or E_{CH} , and d is the critical distance for reaction at which the kinetic energy along the line-of-centers must be greater than E_{th} . Using the above equation, the product branching ratio is predicted to be:

$$\frac{\sigma_{MCH_2}}{\sigma_{MC_3H_4}} = \frac{d_{CC}^2}{d_{CH}^2} \left[1 + \frac{E_{CH} - E_{CC}}{E_{coll} - E_{CH}} \right] \quad (2)$$

For a given collision energy above threshold, a plot of $\sigma_{MCH_2} / \sigma_{MC_3H_4}$ versus $(E_{CH} - E_{CC}) / (E_{coll} - E_{CH})$ should be linear. As shown in Figure 2b, the plots are linear at each collision energy, confirming a direct correlation to the relative barrier heights for C–C and C–H insertion. It is interesting to note that for Y and Mo^* , the importance of C–C insertion increased with E_{coll} , suggesting that the transition state for this process is looser than that for C–H insertion. For Zr and Nb, the opposite is true. Also, for a hypothetical metal atom with the same potential energy barrier heights for C–C and C–H insertion ($E_{CH} - E_{CC} = 0$), the branching ratio at these collision energies is predicted to be ~ 2 . Since cyclopropane contains three C–C and six C–H bonds, on a per bond basis, C–C insertion is preferred for such a metal by a factor of ~ 4 relative to C–H

insertion at these collision energies. Clearly, C–C insertion is strongly driven by the relief of ring strain in insertion reactions involving cyclopropane.

We have studied the competition between C–C and C–H insertion in reactions of four different metals with cyclopropane, and have correlated the branching ratios to the relative ab initio barrier heights. This agreement between experiment and theory confirms that theory is able to predict the relative ordering of potential energy barrier heights in transition-metal atom reactions. With the rapid increase in computational power, and the recent development of more powerful theoretical methods suitable for systems containing many electrons, the explicit inclusion of ligand and solvent effects may soon become feasible in calculations of transition state energies for reactions involving transition metals. Clearly, the synergy between experimental and theoretical chemistry will continue to play a key role in this field.

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Supporting Information Available: Time-of-flight spectra and laboratory angular distributions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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- (15) For cation reactions, at least two stable species are formed prior to the rate-limiting step; thus, product branching ratios are complex functions of several potential energy barrier heights along each reaction coordinate.
- (16) For $M +$ cyclopropane, the absence of wide-angle nonreactive scattering demonstrated that decay of insertion complexes back to reactants was negligible. Since $\sigma_{MCH_2} / \sigma_{MC_3H_4}$ was different for reactions of a given metal with cyclopropane and propene, and because C–C and C–H insertion barriers are larger than subsequent barriers, interconversion between C–C and C–H insertion complexes is insignificant.
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