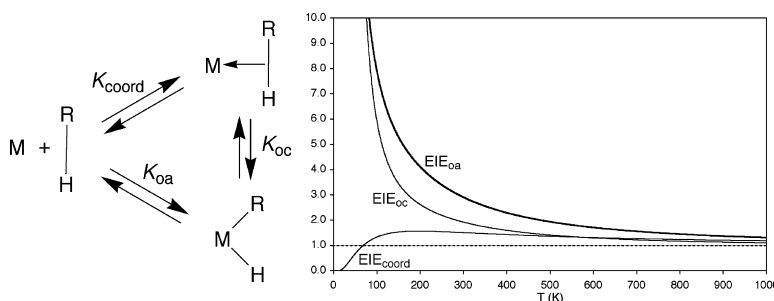## Communication

Temperature-Dependent Transitions between Normal and Inverse Equilibrium Isotope Effects for Coordination and Oxidative Addition of C−H and H−H Bonds to a Transition Metal Center

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Temperature-Dependent Transitions between Normal and Inverse Equilibrium Isotope Effects for Coordination and Oxidative Addition of C−H and H−H Bonds to a Transition Metal Center

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Equilibrium isotope effects (EIEs) provide invaluable information concerned with both molecular structure and the determination of reaction mechanisms. For example, the influence of partial deuterium substitution on the chemical shift of a fluxional transition metal methyl compound may be used to provide evidence as to whether or not there exists an agostic interaction.[1] Furthermore, knowledge of EIEs is essential for interpreting kinetic isotope effects associated with multistep reactions.[2] In this paper, we report EIE calculations pertaining to the interaction of H−H and C−H bonds with transition metal centers (Scheme 1). These calculations (i) demonstrate that the EIEs for coordination and oxidative addition of C−H bonds have fundamentally different EIE temperature profiles and (ii) provide a possible explanation for the previous experimental observations of both normal and inverse EIEs for coordination of alkanes.

Previous studies have demonstrated that the EIEs for both coordination and oxidative addition of H_2 to a transition metal center are invariably characterized by inverse EIEs (i.e., $K_H/K_D < 1$),[3] such that the corresponding interactions with D_2 are thermodynamically more favored than the interaction with H_2.[4] While there are fewer studies concerned with the EIEs for coordination and oxidative addition of C−H bonds, it is evident that there are interesting differences with the corresponding reactions of H−H bonds. Thus, whereas oxidative addition of the H−H bond is characterized by an inverse EIE, oxidative addition of a C−H bond is characterized by a *normal* EIE.[5,6] Even more unusual, both normal and inverse EIEs have been reported for *coordination* of a C−H bond. Specifically, Geftakis and Ball reported a normal EIE (1.33 at −93 °C) for coordination of cyclopentane to $[CpRe(CO)_2]$,[7] whereas Bergman and Moore reported substantially inverse EIEs for the coordination of cyclohexane (~0.1 at −100 °C) and neopentane (~0.07 at −108 °C) to $[Cp*Rh(CO)]$.[8] In view of these differing results, Bullock and Bender have pointed out that the issue of whether coordination of an alkane would be characterized by a normal or inverse EIE is not trivial.[2b] For this reason, we decided to analyze in detail the EIEs for both coordination and oxidative addition of methane to $\{[H_2Si(C_5H_4)_2]W\}$ using DFT (B3LYP) calculations.[9]

Equilibrium isotope effects are typically calculated by the expression EIE = K_H/K_D = SYM·MMI·EXC·ZPE, where SYM is the symmetry factor, MMI is the mass-moment of inertia term, EXC is the excitation term, and ZPE is the zero point energy term.[10] The EIE calculated for coordination of CH_4 and CD_4 to $\{[H_2Si(C_5H_4)_2]W\}$, as determined using the computed frequencies of the σ-complexes, $[H_2Si(C_5H_4)_2]W(\sigma\text{-}HCH_3)$ and $[H_2Si(C_5H_4)_2]W(\sigma\text{-}DCD_3)$,[11] is 1.45 at 100 °C. While the observation of a normal EIE is in accord with that reported for coordination of cyclopentane to $[CpRe(CO)_2]$,[7] it is not in accord with the inverse EIEs reported for coordination of cyclohexane and neopentane to $[Cp*Rh(CO)]$.[8] In an effort to reconcile the observation of both normal and inverse
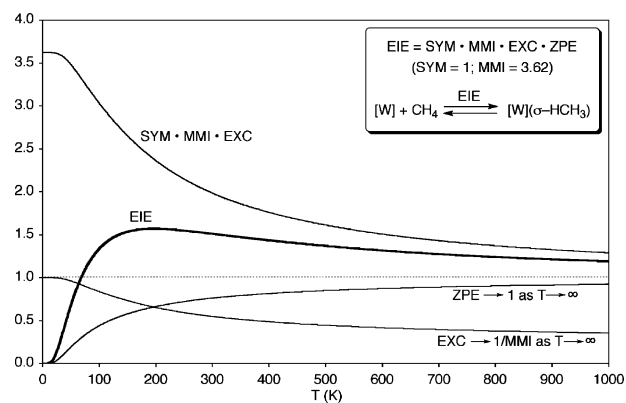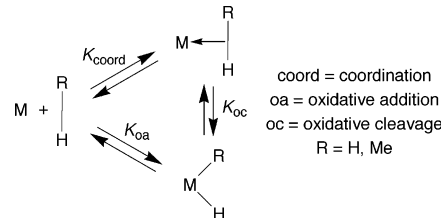

Figure 1. Calculated EIE as a function of temperature for coordination of CH_4 and CD_4 to $\{[H_2Si(C_5H_4)_2]W\}$. The temperature dependence of the individual EXC and ZPE components, as well as the combined [SYM·MMI·EXC] function, are also included.

Scheme 1

EIEs for coordination of a C−H bond, we postulated that the normal EIE for $\{[H_2Si(C_5H_4)_2]W\}$ could become inverse at low temperature, i.e., conditions under which the experimental measurements on $[Cp*Rh(CO)]$ were made.[8] However, rather than becoming inverse, the EIE for $\{[H_2Si(C_5H_4)_2]W\}$ at −100 °C (1.57) actually *increased* slightly from the value at 100 °C (1.45). This result was also counter to Bender's calculation that the EIE for coordination of methane to $OsCl_2(PH_3)_2$ decreases as the temperature is reduced.[12] To probe these differing results in more detail, the full temperature dependence of the EIE for coordination of methane to $\{[H_2Si(C_5H_4)_2]W\}$ was determined.

Interestingly, as illustrated in Figure 1, the EIE for coordination of methane to $\{[H_2Si(C_5H_4)_2]W\}$ does *not* vary with temperature in the simple monotonic manner predicted by the van't Hoff relationship, for which the EIE would be expected either to increase or decrease progressively with temperature. Rather, the temperature dependence of the EIE exhibits a maximum: the EIE is 0 at 0 K, increases to a maximum value of 1.57, and then decreases to unity at infinite temperature.[13] *Thus, depending upon the temperature, both normal (>69 K) and inverse (<69 K) EIEs may be obtained for coordination of a C−H bond in the same system.* The precise form of the temperature dependence of the EIE is determined by the magnitudes and temperature dependencies of the individual

SYM, MMI, EXC, and ZPE terms. Since the SYM (1.00) and MMI (3.62) terms are temperature independent,[14] the occurrence of a maximum is a result of the opposing temperature dependencies of the ZPE and EXC terms, as illustrated in Figure 1.[15] It is also worth noting that the ZPE and EXC terms are always ≤ 1 and thereby favor an inverse EIE at *all* temperatures. However, these terms are mitigated by the large MMI term (3.62), such that the EIE becomes normal at temperatures $\geq$ ca. -200 °C.

While both the ZPE and the EXC terms are ≤ 1, it is evident that it is the ZPE term (which is zero at 0 K) which is the dominant inverse component of the EIE at low temperatures. At high temperatures, the EXC term becomes the most inverse component, but because this approaches 1/MMI (and not zero) at infinite temperature,[15,16] it is incapable of causing the EIE to become inverse. In view of the relationship between EXC and MMI at high temperature, it is useful to analyze the temperature dependence of the EIE in terms of the combined [SYM·MMI·EXC] term (i.e., the dominant terms that influence entropy component of the EIE) and the ZPE term (i.e., the dominant term that influences the enthalpy component of the EIE). Since EXC is unity at 0 K and becomes 1/MMI in the limit of infinite temperature, the product MMI·EXC varies from MMI to unity over this temperature range. Thus, at all temperatures, the [SYM·MMI·EXC] entropy component is ≥ 1 and favors a normal EIE, while the ZPE enthalpy component favors an inverse EIE. At high temperatures, the [SYM·MMI·EXC] entropy component dominates, and the EIE is normal, while at low temperatures, the ZPE enthalpy component dominates, and the EIE is inverse.

If the EIEs for coordination of C−H bonds in other systems were to exhibit a profile similar to that for coordination of methane to $\{[H_2Si(C_5H_4)_2]W\}$, it provides a means to rationalize the literature reports of both normal[7] and inverse[8] EIEs for alkane coordination. However, it should be recognized that the exact form of the profile and whether or not a maximum exists will depend critically on (i) the nature of the σ-complex and its corresponding vibrational frequencies and (ii) the MMI component. The latter term is very sensitive to the size of the coordinating organic molecule; for example, the MMI term is greater for methane than for cyclohexane because methane is smaller and substitution by deuterium influences the mass and moment of inertia to a greater extent than that for cyclohexane. Thus, the [SYM·MMI·EXC] entropy term that favors a normal EIE would be expected to be less significant for coordination of cyclohexane. The ZPE term is quantitatively more difficult to evaluate in a general manner because it depends on the precise structure of the σ-complex. The existence of a maximum in the EIE profile, however, requires that the ZPE term is less than unity; correspondingly, if the ZPE term were to be greater than unity, a normal EIE would be observed at all temperatures because the ZPE term now reinforces the normal [SYM·MMI·EXC] component.

In addition to investigating the EIE for coordination of methane, we have also calculated the EIE for oxidative addition to $\{[H_2Si(C_5H_4)_2]W\}$ (Figure 2). The analysis reveals that the EIE for oxidative addition is normal at *all* temperatures and exponentially approaches infinity at 0 K. The dramatically different temperature dependencies of the EIEs for methane coordination and oxidative addition are specifically associated with the ZPE terms: the ZPE term for coordination of methane is inverse at all temperatures (and zero at 0 K), while the ZPE term for oxidative addition is normal at all temperatures and approaches infinity at 0 K.

The ZPE term for coordination of methane is inverse because association results in the creation of six additional isotope sensitive vibrations that are derived from rotational and translational degrees
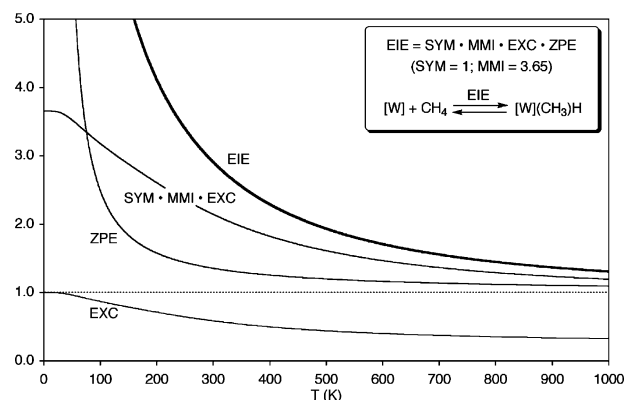

Figure 2. Calculated EIE as a function of temperature for oxidative addition of CH_4 and CD_4 to $\{[H_2Si(C_5H_4)_2]W\}$. Note that the EIE approaches infinity at low temperature, whereas that for coordination approaches zero.
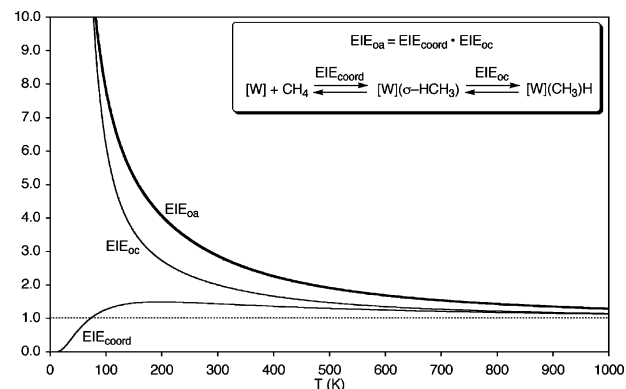

Figure 3. Markedly different temperature dependencies of the EIEs for coordination and oxidative addition of CH_4 and CD_4 to $\{[H_2Si(C_5H_4)_2]W\}$.

of freedom of methane.[17] The combined ZPE associated with these new isotopically sensitive vibrations is sufficient that it results in the ZPE change for $[H_2Si(C_5H_4)_2]W(\sigma\text{-HMe})$ upon isotopic substitution being greater than that for methane. In contrast, the isotopically sensitive vibrations associated with the W−H bond of the methyl hydride complex $[H_2Si(C_5H_4)_2]W(Me)H$, namely a W−H stretch and two bends, are of sufficiently low energy that they do not counter those associated with the C−H bond that has been broken. As a result, the ZPE term for oxidative addition of the C−H bond is ≥ 1. Since the [SYM·MMI·EXC] entropy term is also required to be ≥ 1 (vide supra), the EIE for oxidative addition is *normal* at all temperatures. Given that oxidative addition of methane involves the sequence of (i) coordination of methane followed by (ii) oxidative cleavage of $[H_2Si(C_5H_4)_2]W(\sigma\text{-HMe})$ to $[H_2Si(C_5H_4)_2]W(Me)H$ (Scheme 1), a corollary to the above discussion is that the EIE for the latter transformation is normal at all temperatures (Figure 3).

In contrast to the normal EIEs that have been reported for oxidative addition of a C−H bond,[5] oxidative addition of H_2 has so far only been characterized by inverse EIEs.[4] We were, therefore, interested in determining the temperature dependence of the EIE for oxidative addition of H_2 and D_2 to $\{[H_2Si(C_5H_4)_2]W\}$ in an effort to ascertain whether it is possible for the oxidative addition of H_2 to be characterized by a normal EIE. Significantly, the calculations indicate that while the EIE for oxidative addition of H_2 is inverse at low temperature, it does indeed become normal at higher temperature (358 K), as illustrated in Figure 4.[18]

The temperature profile for the EIE for oxidative addition of H_2 (Figure 4) is thus *very* different from that for oxidative addition of CH_4 (Figure 2). The origin of this difference is that the ZPE
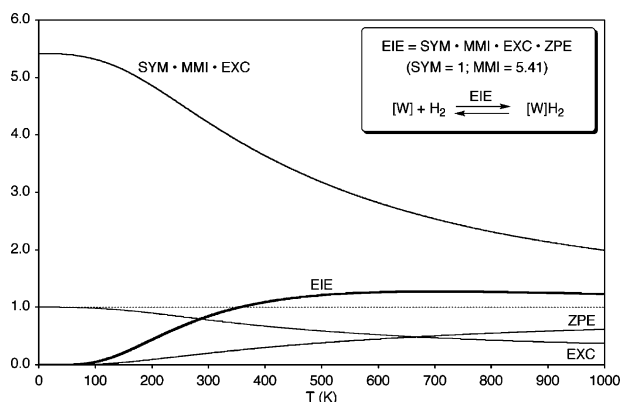
Figure 4. Calculated EIE as a function of temperature for oxidative addition of H₂ and D₂ to {[H₂Si(C₅H₄)₂]W}. The temperature dependence of the individual EXC and ZPE components, as well as the combined [SYM·MMI·EXC] function, are also included. Note that the EIE remains inverse at a higher temperature than that for coordination of CH₄ and CD₄.

component of the EIE for oxidative addition of CH₄ is ≥1, whereas that for oxidative addition of H₂ is ≤1. The difference in the ZPE terms results from the fact that oxidative addition of H₂ results in a greater number of significantly sensitive isotopic vibrations than does oxidative addition of CH₄. This is a consequence of H₂ being a linear molecule with a single isotopically sensitive vibration, while the dihydride [H₂Si(C₅H₄)₂]WH₂ has *six* isotopically sensitive vibrations (two stretches and four bends).

In summary, coordination of an X–H bond (X = Me, H) to a metal center (X = Me, H) results in an increase in the number of isotopically sensitive vibrations derived from translational and rotational degrees of freedom of the X–H molecule, regardless of the nature of X. The existence of these new vibrational modes causes the ZPE component of the EIE to be ≤1, with the result that the EIE is predicted to be inverse at low temperature and normal at high temperature. Similar behavior is also predicted for the temperature dependence of the EIE for oxidative addition of H₂, for which ZPE ≤ 1. However, the ZPE term for oxidative addition of C–H bonds is ≥1, and the EIE is predicted to be normal at all temperatures and increase in magnitude as the temperature is lowered.

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Supporting Information Available: Computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Examples of statistically corrected intramolecular EIEs for oxidative addition of CH₃D include: {[Tp^Me₂]Rh(CNCH₂Buᵗ)}, 2.1 (25 °C);ᵃ {[Me₃-tacn]Rh}, 2.2 (50 °C);ᵇ [Cp₂W], 1.6 (43 °C);ᶜ and {[Me₂Si(C₅Me₄)₂]W}, 1.3 (100 °C).ᵈ (a) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974–3983. (b) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647–1648. (c) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897–3908. (d) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403–1420.

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(12) Bender, B. R., unpublished results cited in ref 2b.

(13) In terms of ΔH and ΔS, a simple exponential variation of K as a function of temperature, according to K = exp(−ΔH/RT)exp(ΔS/R), merely requires that ΔH and ΔS do not vary significantly over the temperature range studied. The existence of a maximum and a transition between normal and inverse EIEs is a result of ΔS being temperature dependent.

(14) The combined [SYM·MMI] term is equivalent to the product of the translational and rotational partition function ratios of the products and reactants, that is, (Q_tr^P)(Q_rot^P)/(Q_tr^R)(Q_rot^R). This term is only strictly temperature independent when T ≫ Θ_rot, the rotational temperature. However, this variation has no effect on the actual low-temperature limit of the EIE.

(15) The ZPE term increases from zero to a limiting value of unity as the temperature is increased, while EXC decreases from unity to a limiting value of 1/MMI (i.e., 1/VP).

(16) For any given set of vibrational frequencies, the product VP·EXC approaches unity at infinite temperature. Since VP is mathematically equivalent to MMI, the product MMI·EXC likewise approaches unity (as also required for the EIE to approach SYM). However, in view of errors in computed frequencies (Schaad, L. J.; Bytautas, L.; Houk, K. N. *Can. J. Chem.* **1999**, *77*, 875–878), the calculated VP term may not be *exactly* equal to the MMI term. Thus, while VP·EXC approaches unity, MMI·EXC actually approaches the ratio MMI/VP. For coordination and oxidative addition of methane to {[H₂Si(C₅H₄)₂]W}, the MMI/VP ratios are 1.05 and 1.01, respectively. These discrepancies have little effect on the derived EIE.

(17) See ref 2b for a description of the six new vibrations. Note that, although there are six new vibrations, they do not contribute equally to the EIE.

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