

A normal equilibrium isotope effect for oxidative addition of H₂ to (η⁶-anthracene)Mo(PMe₃)₃†

Guang Zhu, Kevin E. Janak and Gerard Parkin*

Received (in Berkeley, CA, USA) 20th March 2006, Accepted 10th April 2006

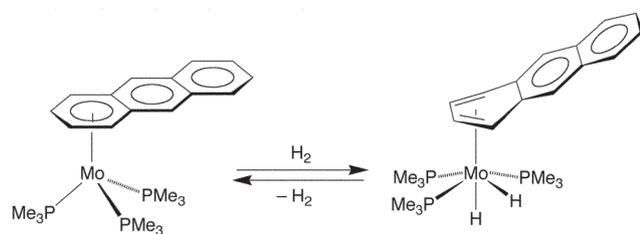
First published as an Advance Article on the web 5th May 2006

DOI: 10.1039/b604159k

Oxidative addition of H₂ and D₂ to the anthracene complex (η⁶-AnH)Mo(PMe₃)₃ giving (η⁴-AnH)Mo(PMe₃)₃X₂ (X = H, D) is characterized by a normal equilibrium isotope effect ($K_H/K_D > 1$) at temperatures close to ambient; calculations on (η⁴-AnH)Mo(PH₃)₃H₂ indicate that this is a consequence of relatively low energy Mo–H vibrational modes.

The influence of deuterium substitution on the spectroscopic properties and reactivity of a molecule provides a powerful means to establish details concerned with both molecular structures and reaction mechanisms. In particular, kinetic isotope effects are routinely used to afford insight into the nature of a transition state for the rate determining step of a reaction.¹ For multistep reactions, however, the kinetic isotope effect is a composite of the isotope effects for all forward and reverse steps up to, and including, the rate determining step. As a consequence, a knowledge of equilibrium isotope effects (EIEs) is essential for interpreting kinetic isotope effects associated with multistep reactions.² The oxidative addition of dihydrogen to a metal center plays an important role in many processes involving H₂ and is generally characterized by an inverse value,^{1,3,4} e.g. 0.43 at 25 °C for [Rh(bpy)₂]⁺.^{3c} Recently, however, we demonstrated that the EIE for oxidative addition of H₂ to Ir(PMe₂Ph)₂(CO)Cl exhibits an interesting transition from an inverse value to a normal value at high temperature (>90 °C).⁵ In this paper, we (i) report an example of oxidative addition of dihydrogen for which the EIE is normal at close to ambient temperature and (ii) explain why the normal/inverse EIE transition temperature is a sensitive function of the system.

We have recently reported that the anthracene complex (η⁶-AnH)Mo(PMe₃)₃ (AnH = anthracene) undergoes reversible oxidative addition of H₂ at room temperature to give (η⁴-AnH)Mo(PMe₃)₃H₂ (Scheme 1).⁶ This observation is noteworthy



Department of Chemistry, Columbia University, New York, NY 10027, USA. E-mail: parkin@columbia.edu

† Electronic supplementary information (ESI) available: Experimental and computational details. See DOI: 10.1039/b604159k

in view of the fact that the benzene and naphthalene counterparts are inert to H₂ under similar conditions.

Although the influence of substituents on the oxidative addition of dihydrogen has not been widely investigated, several studies point to the fact that substituents may exert interesting effects. For example, the exothermicity of oxidative addition of H₂ to *trans*-M(PMe₃)₄X₂ (M = Mo, W; X = F, Cl, Br, I) increases in the sequence I < Br < Cl < F,⁷ whereas that for *trans*-Ir(PPh₃)₂(CO)X exhibits the opposite trend.^{8,9} Correspondingly, since the exothermicity of the oxidative addition of H₂ is dictated by the strength of the M–H bonds that are formed, it is evident that the influence of a substituent on M–H bond dissociation energies (BDEs) is also critically dependent on the system. A knowledge of metal–hydrogen BDEs is central to understanding and predicting reaction pathways involving H₂, but such values are rather limited.^{10,11} For this reason, we sought to determine the Mo–H BDE for (η⁴-AnH)Mo(PMe₃)₃H₂ *via* the temperature dependence of the equilibrium constant (*K*) for oxidative addition of H₂ to (η⁶-AnH)Mo(PMe₃)₃ (Table 1). Thus, measurement of *K* over the temperature range 30–90 °C allows determination of Δ*H* = –13.9(2) kcal mol^{–1},¹² from which a value of 59.1 kcal mol^{–1} may be obtained for the average Mo–H BDE *via* the relationship Δ*H* = *D*(H–H) – 2*D*(Mo–H).¹³ Although an extensive series of Mo–H BDEs does not exist, the values that have been reported previously are in the range ≈60–70 kcal mol^{–1}.¹⁴ It is, therefore, evident that the average Mo–H BDE in (η⁴-AnH)Mo(PMe₃)₃H₂ is relatively low, a result that is in accord with the observation that reductive elimination of H₂ is facile.

In addition to measuring the Mo–H BDE, we have also determined the EIE for oxidative addition of H₂ and D₂ to (η⁶-AnH)Mo(PMe₃)₃. Most interestingly, and in contrast to previous reports pertaining to the EIE for oxidative addition of H₂ and D₂ to a single metal center,¹⁶ the EIE for oxidative addition of H₂ and D₂ to (η⁶-AnH)Mo(PMe₃)₃ is *normal* over virtually the entire temperature range (30–90 °C) measured (Table 1). Despite the prevalence of inverse EIEs for oxidative addition and coordination

Table 1 Equilibrium constant and EIE data for oxidative addition of H₂ and D₂ to (η⁶-AnH)Mo(PMe₃)₃¹⁵

Temperature/°C	K_H/M^{-1}	K_D/M^{-1}	EIE
30	$1.59(5) \times 10^4$	$1.60(6) \times 10^4$	0.99(1)
40	$8.2(4) \times 10^3$	$8.0(5) \times 10^3$	1.03(2)
50	$4.1(3) \times 10^3$	$3.8(3) \times 10^3$	1.07(3)
60	$2.2(2) \times 10^3$	$2.0(2) \times 10^3$	1.13(5)
70	$1.2(1) \times 10^3$	$1.0(1) \times 10^3$	1.20(4)
80	$6.5(9) \times 10^2$	$5.1(6) \times 10^2$	1.27(8)
90	$3.5(7) \times 10^2$	$2.8(7) \times 10^2$	1.25(9)

of H₂ and D₂, however, we have recently demonstrated that oxidative addition to Ir(PMe₂Ph)₂(CO)Cl exhibits a temperature dependent transition from inverse to normal at *ca.* 90 °C.⁵ A temperature dependent transition between inverse and normal EIEs is unexpected since it is normally considered that an EIE would exponentially approach unity as the temperature is increased.¹⁷ The unusual behavior for Ir(PMe₂Ph)₂(CO)Cl has, nevertheless, been rationalized by calculations on the simpler system Ir(PH₃)₂(CO)Cl, which demonstrate that the EIE does not vary monotonically with temperature, but exhibits a maximum: the EIE is 0 at 0 K, increases to a maximum value of 1.15 at 867 K, and then decreases to unity at infinite temperature.⁵ This unusual behavior is explained by competition between the enthalpy (ZPE) and entropy (SYM·MMI·EXC) components of the EIE.¹⁸ Thus, at low temperatures the ZPE enthalpy component dominates and the EIE is inverse,¹⁹ while at high temperatures the [SYM·MMI·EXC]²⁰ entropy component dominates and the EIE is normal.²¹ Despite this rationalization of a normal EIE for oxidative addition of dihydrogen, it is evident that the EIE for oxidative addition to (η⁶-AnH)Mo(PMe₃)₃ is unique in the sense that it is normal at temperatures close to ambient.

Since the form of the temperature dependence (*i.e.* a transition from inverse to normal with a maximum) predicted for Ir(PH₃)₂(CO)Cl is likely to be general, an important issue resides with the factors that influence the transition temperature, since this is critical for predicting whether a particular system will exhibit a normal or inverse EIE. Therefore, in an effort to establish the factors that influence the transition temperature, we have performed calculations on (η⁴-AnH)Mo(PH₃)₃H₂ (Fig. 1). Significantly, the calculated transition temperature for oxidative addition to (η⁶-AnH)Mo(PH₃)₃ is 223 K lower than that for Ir(PH₃)₂(CO)Cl, as illustrated in Fig. 2. This result is in accord with the experimental observation that the onset of a normal EIE for oxidative addition to (η⁶-AnH)Mo(PMe₃)₃ occurs at a significantly lower temperature than that for Ir(PMe₂Ph)₂(CO)Cl. For further comparison, the calculated temperature dependence of the EIE for oxidative addition of dihydrogen to several other molecules is also illustrated in Fig. 2, thereby indicating that the transition temperature spans a range of 377 K for these systems. Consideration of the temperature dependence of the ZPE and combined [SYM·MMI·EXC] components indicates that it is the ZPE term that exhibits the greater sensitivity and is the

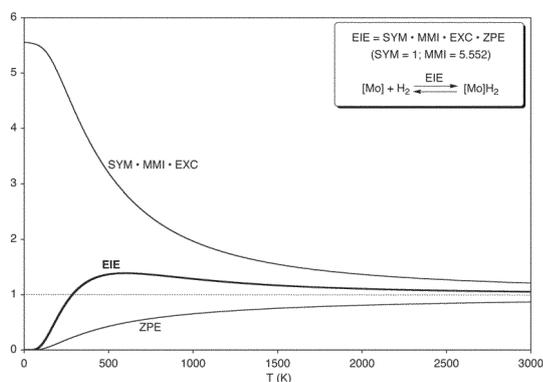


Fig. 1 Calculated overall EIE as a function of temperature for oxidative addition of H₂ and D₂ to (η⁶-AnH)Mo(PH₃)₃ expressed in terms of SYM, MMI, EXC, and ZPE components.

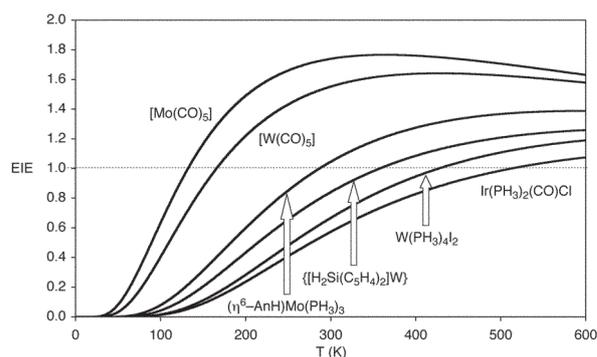


Fig. 2 Variation of the inverse-to-normal EIE transition temperature for oxidative addition of H₂ and D₂ to various metal centers.

major component in determining the variation in transition temperature. Since the ZPE term is an exponential function of the combined differences between vibrational frequencies (ν_H and ν_D) for each mode within the isotopologues, the transition temperature correlates with $\Sigma(\nu_H - \nu_D)$, as illustrated in Fig. 3. While this sum is for *all* vibrational frequencies, the two largest components are the M–H(D) stretches and thus the transition temperature is more likely to be reached at an experimentally accessible temperature for molecules with low M–H(D) stretching frequencies.²² In accord with this notion, the M–H stretches for (η⁴-AnH)Mo(PH₃)₃H₂ (1863 cm⁻¹ and 1755 cm⁻¹) are of significantly lower energy than those of Ir(PH₃)₂(CO)ClH₂ (2241 cm⁻¹ and 2043 cm⁻¹).²³

Primary isotope effects are often rationalized in terms of ZPE arguments using the concept that deuterium prefers to be located in the highest frequency oscillator.²⁴ In this regard, the normal isotope effect for oxidative addition of H₂ to (η⁶-AnH)Mo(PH₃)₃ could simply be interpreted to be a consequence of the sum of the two Mo–H stretching frequencies of (η⁴-AnH)Mo(PH₃)₃H₂ being lower than that of the H–H stretching frequency. Such an analysis, however, would be incorrect because the ZPE term actually favors an inverse EIE at *all* temperatures and the occurrence of a normal EIE is purely a consequence of the [SYM·MMI·EXC] (entropy) term. The important feature of (η⁴-AnH)Mo(PH₃)₃H₂ which results in a normal EIE at relatively low temperatures is that the M–H vibrational modes are of low energy and cause the ZPE term to have a relatively large exponent such that it approaches unity more quickly than for molecules with high energy modes.²³ Thus, the [SYM·MMI·EXC] term is able to dominate the EIE at a relatively low temperature, thereby resulting in a normal EIE.²⁵

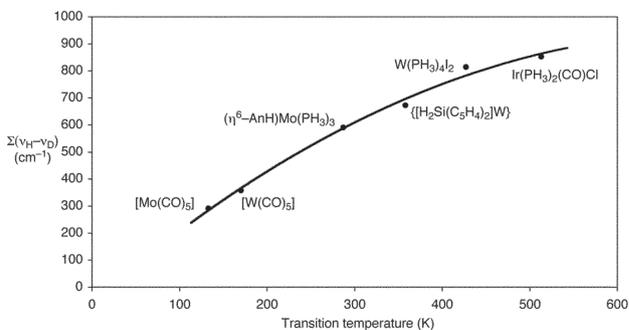


Fig. 3 Correlation of the inverse to normal EIE transition temperature with $\Sigma(\nu_H - \nu_D)$.

In summary, measurement of the temperature dependence of the equilibrium constant for the oxidative addition of H₂ to (η⁶-AnH)Mo(PMe₃)₃ has enabled the average Mo–H BDE of 59.1 kcal mol⁻¹ for (η⁴-AnH)Mo(PMe₃)₃H₂ to be determined. In contrast to the majority of related systems, the EIE for oxidative addition of H₂ and D₂ is normal at ambient temperature. As such, the study serves to emphasize that, for reactions involving small molecules such as H₂, the nature of an isotope effect (*i.e.* normal *versus* inverse) may be highly system and temperature dependent.

We thank the U. S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-93ER14339) for support of this research.

Notes and references

- (a) R. M. Bullock and B. R. Bender, Isotope methods in homogeneous catalysis, in *Encyclopedia of Catalysis*, ed. I. T. Horváth, 2003; (b) W. D. Jones, *Acc. Chem. Res.*, 2003, **36**, 140–146; (c) O. Matsson and K. C. Westaway, *Adv. Phys. Org. Chem.*, 1998, **31**, 143–248; (d) E. Rosenberg, *Polyhedron*, 1989, **8**, 383–405; (e) V. E. Anderson, *Curr. Opin. Struct. Biol.*, 1992, **2**, 757–764; (f) A. Kohen, *Prog. React. Kinet. Mech.*, 2003, **28**, 119–156; (g) R. M. Bullock, in *Transition Metal Hydrides*, ed. A. Dedieu, VCH, New York, 1992, pp. 263–307; (h) L. Melander and W. H. Saunders, *Reactions Rates of Isotopic Molecules*, Wiley, New York, 1980; (i) K. Laidler, *Chemical Kinetics*, Harper and Row, New York, 3rd edn, 1987; (j) T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1976; (k) *Isotope Effects in Chemical Reactions*, ed. C. J. Collins and N. S. Bowman, Van Nostrand, New York, 1970; (l) *Isotopes in Organic Chemistry*, ed. E. Buncl and C. C. Lee, Elsevier, Amsterdam, 1987.
- For some recent influential studies concerned with the computation of isotope effects in organometallic systems, see: (a) L. M. Slaughter, P. T. Wolczanski, T. R. Klinckman and T. R. Cundari, *J. Am. Chem. Soc.*, 2000, **122**, 7953–7975; (b) B. R. Bender, *J. Am. Chem. Soc.*, 1995, **117**, 11239–11246; (c) F. Abu-Hasanayn, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 1993, **115**, 8019–8023; (d) B. R. Bender, J. A. Kubas, L. H. Jones, B. I. Swanson, J. Eckert, K. B. Capps and C. D. Hoff, *J. Am. Chem. Soc.*, 1997, **119**, 9179–9190.
- See, for example: (a) D. Rabinovich and G. Parkin, *J. Am. Chem. Soc.*, 1993, **115**, 353–354; (b) T. Hascall, D. Rabinovich, V. J. Murphy, M. D. Beachy, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 1999, **121**, 11402–11417; (c) F. Abu-Hasanayn, K. Krogh-Jespersen and A. S. Goldman, *J. Am. Chem. Soc.*, 1993, **115**, 8019–8023; (d) J. H. Shin and G. Parkin, *J. Am. Chem. Soc.*, 2002, **124**, 7652–7653; (e) S. G. Yan, B. S. Brunschwig, C. Creutz, E. Fujita and N. Sutin, *J. Am. Chem. Soc.*, 1998, **120**, 10553–10554.
- Inverse EIEs have also been observed for coordination of H₂ to give dihydrogen complexes, [M(η²-H₂)]. See, for example, ref. 2d and: (a) D. G. Gusev, V. I. Bakhmutov, V. V. Grushin and M. E. Vol'pin, *Inorg. Chim. Acta*, 1990, **177**, 115–120; (b) B. E. Hauger, D. Gusev and K. G. Caulton, *J. Am. Chem. Soc.*, 1994, **116**, 208–214; (c) V. I. Bakhmutov, J. Bertrán, M. A. Esteruelas, A. Lledós, F. Maseras, J. Modrego, L. A. Oro and E. Sola, *Chem.–Eur. J.*, 1996, **2**, 815–825.
- K. E. Janak and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 13219–13224.
- G. Zhu, K. E. Janak, J. S. Figueroa and G. Parkin, *J. Am. Chem. Soc.*, 2006, **128**, 5452–5461.
- (a) D. Rabinovich and G. Parkin, *J. Am. Chem. Soc.*, 1993, **115**, 353–354; (b) T. Hascall, D. Rabinovich, V. J. Murphy, M. D. Beachy, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 1999, **121**, 11402–11417.
- L. Vaska and M. F. Werneke, *Ann. N. Y. Acad. Sci.*, 1971, **172**, 546–562.
- For a computational analysis on oxidative addition of H₂ to *trans*-Ir(PH₃)₂(CO)X, see: (a) F. Abu-Hasanayn, K. Krogh-Jespersen and A. S. Goldman, *Inorg. Chem.*, 1993, **32**, 495–496; (b) F. Abu-Hasanayn, A. S. Goldman and K. Krogh-Jespersen, *Inorg. Chem.*, 1994, **33**, 5122–5130.
- (a) Bonding Energetics in Organometallic Compounds, ed. T. J. Marks, *ACS Symp. Ser.*, 1990, **428**; (b) J. A. Martinho Simões and J. L. Beauchamp, *Chem. Rev.*, 1990, **90**, 629–688; (c) D. C. Eisenberg and J. R. Norton, *Isr. J. Chem.*, 1991, **31**, 55–66.
- (a) H. A. Skinner and J. A. Connor, *Pure Appl. Chem.*, 1985, **57**, 79–88; (b) J. A. Connor, *Top. Curr. Chem.*, 1977, **71**, 71–110; (c) G. Pilcher and H. A. Skinner, in *The Chemistry of the Metal–Carbon Bond*, ed. F. R. Hartley and S. Patai, Wiley, New York, 1982, vol. 1, ch. 2, pp. 43–90; (d) J. A. Labinger and J. E. Bercaw, *Organometallics*, 1988, **7**, 926–928; (e) J. U. Mondal and D. M. Blake, *Coord. Chem. Rev.*, 1982, **47**, 205–238.
- ΔS = –26.5(6) e.u.
- For dihydrogen, D(H–H) = 104.2 kcal mol⁻¹ and D(D–D) = 106.0 kcal mol⁻¹. *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, CRC Press, Boca Raton, Florida, 70th edn, 1989–1990, p. F-199.
- D. Wang and R. J. Angelici, *J. Am. Chem. Soc.*, 1996, **118**, 935–942 and references therein.
- To minimize systematic errors, the deuterium equilibrium isotope effect was determined at each temperature by evaluating the ratio K_H/K_D for each pair of samples prepared with the same initial partial pressures of H₂ and D₂, rather than comparing the average values of K_H and K_D.
- The addition of H₂ across the Cr–Cr bond in the dinuclear fulvalene complex (μ-η⁵,η⁵-C₁₀H₈)[Cr(CO)₃]₂ to give dinuclear (μ-η⁵,η⁵-C₁₀H₈)[Cr(CO)₃H]₂ is characterized by a normal EIE of 1.45(10) at 55 °C. See: K. P. C. Vollhardt, J. K. Cammack, A. J. Matzger, A. Bauer, K. B. Capps and C. D. Hoff, *Inorg. Chem.*, 1999, **38**, 2624–2631.
- More generally, the EIE approaches the ratio of the symmetry numbers.
- The EIE is conventionally determined 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. The ZPE term corresponds closely to the enthalpy component (*i.e.* ZPE ≈ [exp(–ΔΔH/RT)]), whereas the combined [SYM·MMI·EXC] term may be viewed as corresponding closely to the entropy component (*i.e.* [SYM·MMI·EXC] ≈ [exp(ΔΔS/R)]). See ref. 21 and references therein.
- The ZPE term is inverse (<1) because the [MH₂] fragment has a greater number of isotopically sensitive vibrations than that of the single stretch in H₂ and the energies of these vibrations are sufficient that they cause the total zero point stabilization of [MD₂] *versus* [MH₂] to be greater than that for D₂ *versus* H₂.
- The combined [SYM·MMI·EXC] term is >1 because it corresponds largely to the difference in entropy of H₂ (34.0 e.u. at 300 K) and D₂ (39.0 e.u. at 300 K). See: H. W. Wooley, R. B. Scott and F. G. Brickwedde, *J. Res. Natl. Bur. Stand. (U. S.)*, 1948, **41**, 379–475.
- Temperature dependent transitions between inverse and normal EIEs have also been predicted for the coordination of dihydrogen and methane. See, for example: (a) K. E. Janak and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 6889–6891; (b) K. E. Janak and G. Parkin, *Organometallics*, 2003, **22**, 4378–4380.
- Note that this statement is only an approximation because of coupling of the motion of the hydride ligands to other vibrational modes and the fact that the contribution from the bends is not insignificant.
- Furthermore, the sum of the six principal isotopically sensitive modes for (η⁴-AnH)Mo(PH₃)₃H₂ (6687 cm⁻¹) is considerably less than that for Ir(PH₃)₂(CO)ClH₂ (7596 cm⁻¹).
- See, for example: M. Wolfsberg, *Acc. Chem. Res.*, 1972, **5**, 225–233.
- In this regard, the normal EIE observed for oxidative addition to dinuclear (μ-η⁵,η⁵-C₁₀H₈)[Cr(CO)₃]₂ (ref. 16) is also most likely a consequence of the Cr–H vibrations being of low energy so that the transition temperature is relatively low.