J|A|C|S
ARTICLES

Experimental Evidence for a Temperature Dependent Transition between Normal and Inverse Equilibrium Isotope Effects for Oxidative Addition of H_2 to $Ir(PMe_2Ph)_2(CO)Cl$

Kevin E. Janak and Gerard Parkin*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027

Received May 21, 2003; E-mail: parkin@chem.columbia.edu

Abstract: The equilibrium isotope effect (EIE) for oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ has been measured over a large temperature range, thereby demonstrating that the inverse (<1) EIE previously observed at ambient temperature becomes normal (>1) at high temperature (>90 °C). The temperature dependence of the EIE for oxidative addition of H_2 and D_2 to $Ir(PH_3)_2(CO)Cl$ has been calculated using the geometry and vibrational frequencies obtained from DFT (B3LYP) calculations on $Ir(PH_3)_2(CO)ClH_2$ and $Ir(PH_3)_2(CO)ClD_2$, and is in accord with the experimentally observed transition from an inverse to normal EIE for oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$: the EIE is calculated to be inverse between 0 and 510 K, reach a maximum value of 1.15 at 867 K and then slowly decrease to unity as the temperature approaches infinity. This deviation from simple van't Hoff behavior, and the occurrence of a maximum in the EIE, is the result of the entropy term being temperature dependent. At low temperature, the enthalpy term dominates and the EIE is inverse, whereas at high temperatures the entropy term dominates and the EIE is normal. The observation of both normal and inverse EIEs for the same system indicate that inferences pertaining to the magnitude of an isotope effect at a single temperature may require more detailed consideration than previously realized.

Introduction

The oxidative addition of dihydrogen to a metal center is one of the most fundamental reactions in transition metal chemistry and plays a role in many important processes, such as metal catalyzed olefin hydrogenation. We have previously studied the equilibrium isotope effect (EIE) for this transformation and in 1993 reported that the EIE for the oxidative addition of H_2 and D_2 to $W(PMe_3)_4I_2$ is inverse (i.e., $K_H/K_D < 1$), such that the cleavage of the stronger D−D bond is thermodynamically more favored than that of the weaker H−H bond.[1] While this observation may at first appear counterintuitive, and indeed counter to the commonly held notion that deuterium prefers to be located in the stronger bond to a greater extent than does hydrogen,[2] it is readily rationalized by the fact that the $[MH_2]$ fragment has a substantially greater number of isotopically sensitive vibrations (i.e., two stretches and four bends) than that of the single stretch in H_2; the additional vibrations of the $[MH_2]$ unit are derived from the rotational and translational degrees of freedom of H_2 molecule, as illustrated in Figure 1. Although each of the vibrations of the $[MH_2]$ fragment are lower in energy than that of the H_2 stretch, the combination causes the total zero point stabilization of $[MD_2]$ versus $[MH_2]$ to be greater than that for D_2 versus H_2. Inverse EIEs have not only been reported for other examples of oxidative addition of H_2 to a metal center,[3] but have also been observed for coordination of H_2 to give dihydrogen complexes, $[M(\eta^2\text{-}H_2)]$.[4,5,6] In this paper, we report

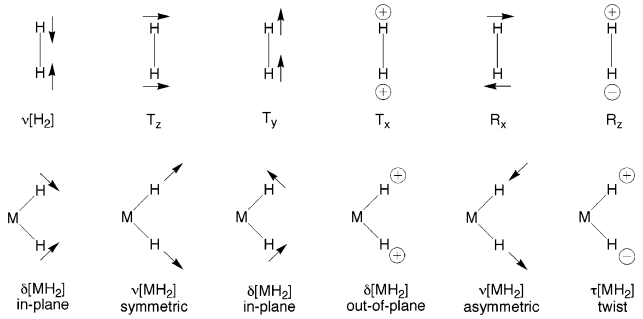


Figure 1. Vibrational modes associated with a C_2-symmetric $[MH_2]$ fragment and the vibrational, translational, and rotational modes of H_2 from which they are derived.

---

[1] (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353−354. (b) Hascall, T.; Rabinovich, D.; Murphy, V. J.; Beachy, M. D.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 11 402−11 417.

[2] Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225−233.

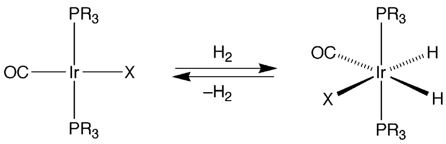
[3] See, for example: (a) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019−8023. (b) Shin, J. H.; Parkin, G. *J. Am. Chem. Soc.* **2002**, *124*, 7652−7653. (c) Yan, S. G.; Brunschwig, B. S.; Creutz, C.; Fujita, E.; Sutin, N. *J. Am. Chem. Soc.* **1998**, *120*, 10 553−10 554.

[4] See, for example: (a) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179−9190. (b) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *177*, 115−120. (c) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208−214. (d) Bakhmutov, V. I.; Bertrán, J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Modrego, J.; Oro, L. A.; Sola, E. *Chem. Eur. J.* **1996**, *2*, 815−825.

[5] For some isotope effects in binary metal hydrides, see: (a) Wiswall, R. H., Jr.; Reilly, J. J. *Inorg. Chem.* **1972**, *11*, 1691−1696. (b) Luo, W.; Clewley, J. D.; Flanagan, T. B. *J. Chem. Phys.* **1990**, *93*, 6710−6722.

10.1021/ja0362611 CCC: $25.00 © 2003 American Chemical Society

Scheme 1



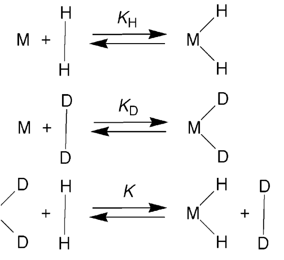
experimental evidence for the interesting observation that the EIE for oxidative addition of H_2 to a metal center may undergo a transition from an inverse to a normal value upon raising the temperature.

Results and Discussion

EIEs (and equilibrium constants in general) are typically expected to vary in an exponential manner as the temperature is raised. Recently, however, we reported calculations which predict that the temperature dependence of the EIE for oxidative addition of H_2 to the 16-electron tungstenocene species $\{[H_2Si(C_5H_4)_2]W\}$ would *not* exhibit such behavior. Thus, rather than vary monotonically with temperature, the EIE for oxidative addition of hydrogen to $\{[H_2Si(C_5H_4)_2]W\}$ is predicted to exhibit 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.[7,8] Prompted by this result, we sought to obtain experimental evidence that the EIE for oxidative addition of H_2 to a transition metal center could undergo a temperature-dependent transition from an inverse to a normal value. Since we anticipated that high temperatures would be required to observe this effect, we elected to study oxidative addition of H_2 in a system that is thermally robust. For this reason, we chose to investigate the Vaska system because previous studies have demonstrated that the interconversion of $Ir(PR_3)_2(CO)X$ and $Ir(PR_3)_2(CO)XH_2$ is well-characterized for a wide range of substituents (Scheme 1).[3,9,10,11]

1. Computational Evaluation of the Temperature Dependence of the EIE for Oxidative Addition of H_2 and D_2 to $Ir(PH_3)_2(CO)Cl$. Previous experimental and computational studies have demonstrated that the oxidative addition of H_2 to $Ir(PR_3)_2(CO)Cl$ complexes is characterized by an inverse EIE at ambient temperature.[3a,b] Prior to experimentally determining whether the EIE for oxidative addition of H_2 to $Ir(PR_3)_2(CO)Cl$ would exhibit a temperature-dependent transition from inverse to normal, akin to that predicted for $\{[H_2Si(C_5H_4)_2]W\}$,[7] we first performed calculations on the simplified $Ir(PH_3)_2(CO)ClH_2$ system.

Scheme 2



$$\mathrm{EIE} = K = K_H/K_D$$

Scheme 3

$$\mathrm{EIE} = K_H/K_D = \mathrm{SYM} \cdot \mathrm{MMI} \cdot \mathrm{EXC} \cdot \mathrm{ZPE}$$

$$\mathrm{SYM} = \frac{\{(\sigma n)^R{}_H/(\sigma n)^R{}_D\}}{\{(\sigma n)^P{}_H/(\sigma n)^P{}_D\}} \qquad \mathrm{MMI} = \frac{(M^P{}_H/M^R{}_H)^{3/2}(I^P{}_H/I^R{}_H)^{1/2}}{(M^P{}_D/M^R{}_D)^{3/2}(I^P{}_D/I^R{}_D)^{1/2}}$$

$$\mathrm{EXC} = \frac{\Pi\,\{[1-\exp(-u^R{}_{iH})]/[1-\exp(-u^R{}_{iD})]\}}{\Pi\,\{[1-\exp(-u^P{}_{iH})]/[1-\exp(-u^P{}_{iD})]\}} \qquad \mathrm{ZPE} = \frac{\exp\{\Sigma\,(u^R{}_{iH}-u^R{}_{iD})/2\}}{\exp\{\Sigma\,(u^P{}_{iH}-u^P{}_{iD})/2\}}$$

where $u_{iX} = h\nu_{iX}/k_BT$, $R = X_2$, and $P = Ir(PH_3)_2(CO)ClX_2$ $(X = H, D)$

Although the equilibrium isotope effect for oxidative addition of H_2 is defined as the ratio K_H/K_D, it is evident that the EIE is identical to the equilibrium constant for the isodesmic exchange reaction (Scheme 2). An advantage of viewing the EIE in this way is that its evaluation does not require any information concerned with $Ir(PH_3)_2(CO)Cl$, but only requires thermodynamic data on $Ir(PH_3)_2(CO)ClH_2$, $Ir(PH_3)_2(CO)ClD_2$, H_2 and D_2. In this regard, it is conventional to determine the EIE by the expression $\mathrm{EIE} = K_H/K_D = \mathrm{SYM} \cdot \mathrm{MMI} \cdot \mathrm{EXC} \cdot \mathrm{ZPE}$, where SYM is the symmetry factor,[12] MMI is the mass-moment of inertia term, EXC is the excitation term, and ZPE is the zero point energy term (Scheme 3).[13,14] The SYM term is determined by the symmetry number ratio of the species involved and is unity for oxidative addition of H_2/D_2 to $Ir(PH_3)_2(CO)Cl$; the MMI term is determined by their structures (i.e. their masses and moments of inertia);[15] and the EXC and ZPE terms are determined by their vibrational frequencies. The required structural and vibrational data were obtained by DFT calculations using the B3LYP functional and the 6-31G**/LACVP** basis sets. The geometry optimized structure of $Ir(PH_3)_2(CO)Cl$ (Figure 2) corresponds closely to that of previous calculations[3a] and the principal vibrations that are isotopically sensitive are summarized in Table 1. It should be noted that the six normal modes associated with the $[IrH_2]$ moiety mix with other vibrational modes, as illustrated by the isotopic sensitivity of

---

(6) Bullock, R. M.; Bender, B. R. Isotope Methods in Homogeneous Catalysis. In *Encyclopedia of Catalysis*; Horváth, I. T., Ed.; 2002.

(7) Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 6889−6891.

(8) For other examples of situations in which there is a temperature-dependent transition between a normal and inverse EIE, see ref 2.

(9) (a) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. (A)* **1969**, 1128−1134. (b) Hyde, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1975**, 765−767.

(10) (a) Vaska, L.; Werneke, M. F. *Ann. N. Y. Acad. Sci.* **1971**, *172*, 546−562. (b) Zhou, P.; Vitale, A. A.; San Filippo, J., Jr.; Saunders: W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8049−8054. (c) Kunin, A. J.; Johnson, C. E.; Maguire, J. A.; Jones, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1987**, *109*, 2963−2968. (d) Kunin, A. J.; Farid, R.; Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 5315−5317.

(11) It should be noted that although oxidative addition of H_2 to $Ir(PR_3)_2(CO)X$ gives $Ir(PR_3)_2(CO)XH_2$ in which the H_2 has added parallel to the OC−Ir-*X* axis, unstable isomers derived from addition parallel to the P−Ir−P axis have also been detected by parahydrogen induced polarization. See: (a) Hasnip, S. K.; Colebrook, S. A.; Sleigh, C. J.; Duckett, S. B.; Taylor, D. R.; Barlow, G. K.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **2002**, 743−751. (b) Hasnip, S. K.; Duckett, S. B.; Sleigh, C. J.; Taylor, D. R.; Barlow, G. K.; Taylor, M. J. *J. Chem. Soc., Chem. Commun.* **1999**, 1717−1718.

(12) The symmetry factor includes both external (σ) and internal (n) symmetry numbers. See: Bailey, W. F.; Monahan, A. S. *J. Chem. Educ.* **1978**, *55*, 489−493.

(13) (a) Wolfsberg, M.; Stern, M. J. *Pure Appl. Chem.* **1964**, *8*, 225−242. (b) Melander, L.; Saunders: W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York 1980. (c) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*, Wiley-Interscience: New York 1984. (d) Ishida, T. *J. Nucl. Sci. Technol.* **2002**, *39*, 407−412. (e) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261−267.

(14) For some recent influential studies concerned with the computation of isotope effects in organometallic systems, see: (a) Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953−7975. (b) Bender, B. R. *J. Am. Chem. Soc.* **1995**, *117*, 11 239−11 246. (c) ref 3a and 4a.

(15) Application of the Teller−Redlich product rule permits the MMI term to be replaced by the vibrational product (VP) derived from the vibrational frequencies. See ref 13.

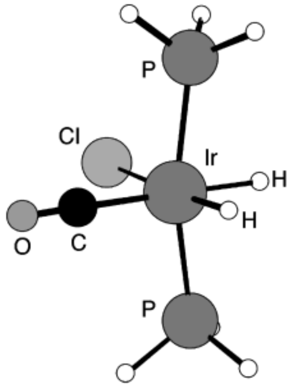


Figure 2. Geometry optimized structure of $Ir(PH_3)_2(CO)ClH_2$. Selected bond lengths (Å): Ir−P 2.317 and 2.318, Ir−$H_{(trans\ \mathrm{to\ Cl})}$ 1.588, Ir−$H_{(trans\ \mathrm{to\ CO})}$ 1.632, Ir−Cl 2.529, Ir−CO 1.951.

Table 1. Principal Isotopically Sensitive Vibrations in $Ir(PH_3)_2(CO)ClH_2$ and $Ir(PH_3)_2(CO)ClD_2$

assignment	$Ir(PH_3)_2(CO)ClH_2$ (cm^{-1})	$Ir(PH_3)_2(CO)ClD_2$ (cm^{-1})
$\nu_{1\ \mathrm{stretch;\ trans\ to\ Cl}}$	2240.6	1588.6
ν_{CO}	2153.3	2121.6
$\nu_{2\ \mathrm{stretch;\ trans\ to\ CO}}$	2042.7	1470.3
$\delta_{1\ \mathrm{out\ of\ plane}}$	903.7	688.6
$\delta_{2\ \mathrm{out\ of\ plane}}$	814.1	611.9
$\delta_{1\ \mathrm{in\ plane}}$	845.1	644.1
$\delta_{2\ \mathrm{in\ plane}}$	750.2	586.2

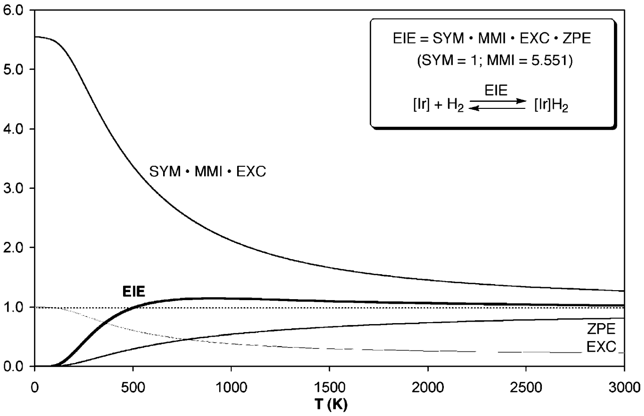


Figure 3. Calculated EIE as a function of temperature for oxidative addition of H_2 and D_2 to $Ir(PH_3)_2(CO)Cl$ expressed in terms of SYM, MMI, EXC, and ZPE components.

the ν(CO) stretch in $Ir(PH_3)_2(CO)ClH_2$ and $Ir(PH_3)_2(CO)ClD_2$. Therefore, the EIE calculation was performed using *all* frequencies.

The temperature dependence of the individual terms and the EIE for oxidative addition of H_2/D_2 to $Ir(PH_3)_2(CO)Cl$ is illustrated in Figure 3.[16] Significantly, the EIE for oxidative addition of H_2 to $Ir(PH_3)_2(CO)Cl$ exhibits a similar temperature dependence to that for $\{[H_2Si(C_5H_4)_2]W\}$; that is, the EIE is inverse between 0 and 510 K, reaches a maximum value of 1.15 at 867 K and then slowly decreases to unity as the temperature approaches infinity. Since the SYM and MMI terms are temperature independent,[17] the occurrence of a maximum is a result of the ZPE and EXC terms opposing each other. Thus, the ZPE term increases from zero to a limiting value of unity as the temperature is increased, whereas EXC decreases from unity to a limiting value of 1/MMI.[13a] In view of the latter relationship between EXC and MMI, it is convenient to analyze the temperature dependence of the EIE in terms of the combined [SYM · MMI · EXC] term and the ZPE term. In this regard, the [SYM · MMI · EXC] term may be viewed to correspond closely to the entropy component, whereas the ZPE term corresponds closely to the enthalpy component,[18] as illustrated by comparison of Figures 3 and 4.

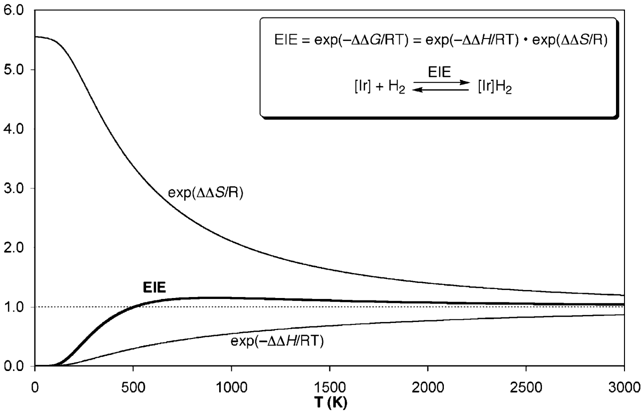


Figure 4. Calculated EIE as a function of temperature for oxidative addition of H_2 and D_2 to $Ir(PH_3)_2(CO)Cl$, expressed in terms of $\exp(-\Delta\Delta H/RT)$ and $\exp(\Delta\Delta S/R)$.

In terms of enthalpy and entropy considerations, deviation from the simple exponential relationship according to $K = \exp(-\Delta\Delta H/RT)\exp(\Delta\Delta S/R)$ occurs if either $\Delta\Delta H$ or $\Delta\Delta S$ are not constant over the temperature range studied (where $\Delta\Delta H = \Delta H_H - \Delta H_D$ and $\Delta\Delta S = \Delta S_H - \Delta S_D$). Examination of $\Delta\Delta H$ and $\Delta\Delta S$ as a function of temperature (Figure 5) indicates that it is the variation of $\Delta\Delta S$ that is primarily responsible for the deviation from van't Hoff behavior and the occurrence of a maximum in the EIE: thus, over the temperature range 0−1000 K, $\Delta\Delta S$ varies from 3.41 to 1.48 e.u. (i.e., a reduction of 56.6%), whereas $\Delta\Delta H$ only varies from 1.22 to 1.20 kcal mol^{-1} (i.e., a reduction of 1.6%).

As illustrated in Figures 3 and 4, the [SYM · MMI · EXC] (entropy) component favors a normal EIE, varying from the value of [SYM · MMI][19] = 5.55 at 0 K to unity at infinite temperature, whereas the ZPE (enthalpy) component favors an inverse EIE. The ZPE term is < 1 because the $[MH_2]$ fragment has a greater number of isotopically sensitive vibrations than that of the single stretch in H_2 and the energies of these vibrations are sufficient that they cause the total zero point

---

[16] The EIE at 300 K is 0.57 in good agreement to the value of 0.46 calculated by Krogh-Jespersen and Goldman (ref 3a).

[17] The combined [SYM · MMI] term is equivalent to the product of the translational and rotational partition function ratios of the products and reactants, i.e., $(Q_{tr}^{P})(Q_{rot}^{P})/(Q_{tr}^{R})(Q_{rot}^{R})$. This term is only strictly temperature independent when $T \gg \Theta_{rot}$, the rotational temperature. The EIE data presented here are obtained by treating the rotational and nuclear partition functions classically. Consideration of quantum effects serves to modify the [SYM · MMI · EXC] (entropy) term at low temperature, but has no effect on the low-temperature limit of the EIE which is dominated by the ZPE (enthalpy) term.

[18] It should be noted that the ZPE and enthalpy $[\exp(-\Delta\Delta H/RT)]$ terms are not identical because the thermal population of vibrationally excited states also provides a contribution to the enthalpy term. Correspondingly, the [SYM · MMI · EXC] and entropy $[\exp(\Delta\Delta S/R)]$ terms are not identical, but differ by a similar component to that relating ZPE and enthalpy. However, these differences are small such that ZPE ≈ $[\exp(-\Delta\Delta H/RT)]$ and [SYM · MMI · EXC] ≈ $[\exp(\Delta\Delta S/R)]$ are good approximations. For example, at 100 K, ZPE = 0.002 and $[\exp(-\Delta\Delta H/RT)] = 0.002$, whereas SYM · MMI · EXC = 5.48, and $\exp(\Delta\Delta S/R) = 5.48$; at 1000 K, ZPE = 0.542 and $[\exp(-\Delta\Delta H/RT)] = 0.547$, whereas SYM · MMI · EXC = 2.12, and $\exp(\Delta\Delta S/R) = 2.11$.

[19] EXC is unity at 0 K, and so [SYM · MMI · EXC] = [SYM · MMI]

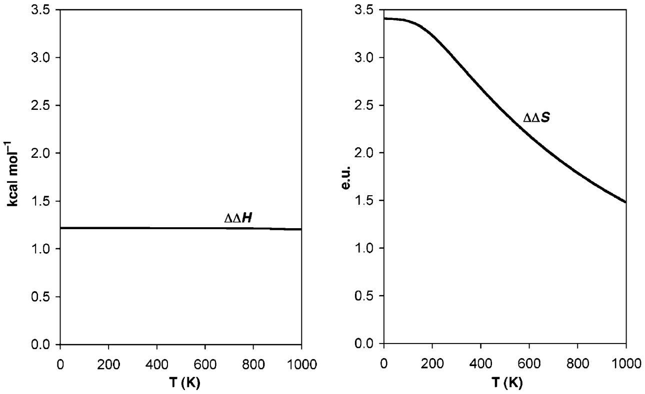


Figure 5. Calculated temperature dependence of $\Delta\Delta H = \Delta H_H - \Delta H_D$ and $\Delta\Delta S = \Delta S_H - \Delta S_D$. $\Delta\Delta H$ varies from 1.22 to 1.20 kcal mol^{-1} from 0 to 1000 K, whereas $\Delta\Delta S$ varies from 3.41 to 1.48 e.u.

stabilization of [MD_2] versus [MH_2] to be greater than that for D_2 versus H_2. Although EXC < 1, the combined [SYM · MMI · EXC] term is >1 because it is dominated by the [SYM · MMI] component (5.55). The combined [SYM · MMI] term is equivalent to the product of the translational and rotational partition function ratios of the products and reactants, i.e., $(Q_{tr}^{P})(Q_{rot}^{P})/(Q_{tr}^{R})(Q_{rot}^{R})$[17] and the dominant component is associated with the large difference in entropy between H_2 and D_2 as compared to that between [MH_2] and [MD_2]. Specifically, translational entropy of D_2 is greater than that of H_2 because of a mass effect,[20] whereas the rotational entropy of D_2 is greater than that of H_2 because (i) the rotational levels of D_2 are more closely spaced than those of H_2 due to a mass effect via the moment of inertia,[21] and (ii) the degeneracy of the rotational levels for D_2 are greater than those for H_2.[22]

The calculations thus predict that the EIE for oxidative addition of dihydrogen to $Ir(PH_3)_2(CO)Cl$ would exhibit a transition from an inverse to normal value due to competition between the ZPE (enthalpy) and [SYM · MMI · EXC] (entropy) terms. At low temperatures, the ZPE enthalpy component dominates and the EIE is inverse, whereas at high temperatures the [SYM · MMI · EXC] entropy component dominates and causes a transition from an inverse to normal EIE. Experimental evidence for this transition was, therefore, sought.

2. Experimental Evidence for a Transition from Inverse to Normal EIE for Oxidative Addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$. For the experimental study, we chose to investigate oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$[23] due to (i) the favorable ^1H NMR spectroscopic properties associated with the PMe_2Ph versus PPh_3 ligand, and (ii) the fact that the reaction with H_2 to give $Ir(PMe_2Ph)_2(CO)ClH_2$ is facile.[9] The equilibrium constants for the oxidative addition of H_2 and D_2 in benzene and toluene were determined by ^1H NMR spectroscopy, from which the EIE at each temperature was determined (Tables 2 and 3). Most interestingly, the data support the theoretical prediction that the EIE undergoes a transition from inverse to normal as the temperature is raised. Thus, while K_H is less than K_D at 25 °C, K_D decreases more rapidly than does K_H upon raising the temperature, such that they become equal at ca. 90 °C; above this temperature, K_H becomes greater than K_D (Figure 6). Hence, in accord with the calculations on $Ir(PH_3)_2(CO)ClH_2$ and $Ir(PH_3)_2(CO)ClD_2$, the strongly inverse EIE [0.41(4)] observed for oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ at 25 °C in benzene becomes normal at

Table 2. Equilibrium Constant and Equilibrium Isotope Effect Data for Oxidative Addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ in Benzene (errors are reported at the 95% confidence level)

T (°C)	K_H (M^{-1})	K_D (M^{-1})	EIE = K_H/K_D
25	$2.5(2) \times 10^4$	$6.0(5) \times 10^4$	0.41(4)
30	$2.03(9) \times 10^4$	$4.1(1) \times 10^4$	0.49(3)
35	$1.5(2) \times 10^4$	$2.79(9) \times 10^4$	0.52(6)
45	$6.3(3) \times 10^3$	$1.03(5) \times 10^4$	0.62(4)
55	$3.4(3) \times 10^3$	$5.15(5) \times 10^3$	0.65(5)
70	$1.97(8) \times 10^3$	$2.7(3) \times 10^3$	0.74(8)
85	$8.9(3) \times 10^2$	$9.7(4) \times 10^2$	0.92(5)
100	$3.8(3) \times 10^2$	$3.6(2) \times 10^2$	1.05(9)
110	$3.12(4) \times 10^2$	$2.53(4) \times 10^2$	1.23(3)
120	$2.0(1) \times 10^2$	$1.60(3) \times 10^2$	1.23(8)
130	$1.36(3) \times 10^2$	$9.7(3) \times 10^1$	1.41(6)
140	$1.8(1) \times 10^1$	$1.65(3) \times 10^1$	1.13(10)
158	$1.21(7) \times 10^1$	9.8(4)	1.24(9)
185	7.4(3)	6.2(2)	1.19(6)

Table 3. Equilibrium Constant and Equilibrium Isotope Effect Data for Oxidative Addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ in Toluene (errors are reported at the 95% confidence level)

T (°C)	K_H (M–^{1})	K_D (M–^{1})	EIE = K_H/K_D
45	$1.05(3) \times 10^4$	$1.72(3) \times 10^4$	0.61(2)
55	$5.5(3) \times 10^3$	$8.0(5) \times 10^3$	0.69(6)
70	$2.4(1) \times 10^3$	$3.19(5) \times 10^3$	0.76(4)
85	$1.45(9) \times 10^3$	$1.68(7) \times 10^3$	0.87(7)
100	$6.8(4) \times 10^2$	$7.1(3) \times 10^2$	0.95(8)
110	$4.8(1) \times 10^2$	$4.69(8) \times 10^2$	1.02(3)
115	$4.03(5) \times 10^2$	$3.7(1) \times 10^2$	1.10(4)
120	$2.51(6) \times 10^2$	$1.9(1) \times 10^2$	1.36(10)
130	$1.77(5) \times 10^2$	$1.22(6) \times 10^2$	1.45(8)
158	10.4(1)	8.1(3)	1.29(14)

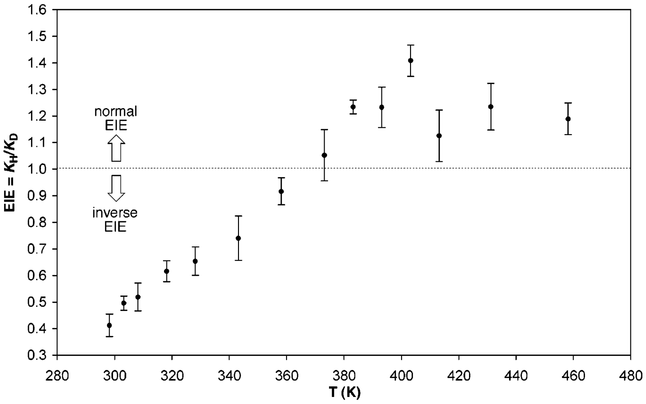


Figure 6. Temperature dependence of the EIE for oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ in benzene.

---

(20) $\Delta S_{trans}[D_2 - H_2] = (3/2)R\ln[M(D_2)/M(H_2)] = 2.04$ e.u.

(21) The energy of the rotational levels is given by $\epsilon_J = (h^2/8\pi^2 I)J(J + 1)$ where I is the moment of inertia. Since $I(D_2) > I(H_2)$, the rotational levels are more closely spaced for D_2. At high temperature, $\Delta S_{rot}[D_2 - H_2] = R\ln[I(D_2)/I(H_2)] = 1.36$ e.u.

(22) Homonuclear diatomic molecules with nuclei of integer spin require odd J rotational levels to be coupled with $I(2I + 1)$ antisymmetric nuclear spin functions (i.e., para), whereas even J rotational levels are coupled with the $(I + 1)(2I + 1)$ symmetric nuclear spin functions (i.e., ortho). For nuclei with half-integer spins, the situation is reversed and odd J rotational levels are coupled with $(I + 1)(2I + 1)$ symmetric nuclear spin functions and even J rotational levels are coupled with $I(2I + 1)$ antisymmetric nuclear spin functions. Thus, while both H_2 ($I = 1/2$) and D_2 ($I = 1$) have triply degenerate odd J levels, even J levels for D_2 and H_2 are 6-fold and singly degenerate, respectively. At high temperature, the entropy associated with the different nuclear spin state degeneracies is $\Delta S_{nuc}[D_2 - H_2] = R\ln\{[(2I_D + 1)^2/(2I_H + 1)^2] = R\ln(9/4) = 1.61$. See: (a) McQuarrie, D. A. “Statistical Mechanics”, Harper and Row: New York 1976. (b) Herzberg, G. *Molecular Spectra and Molecular Structure. II Infrared and Raman Spectra of Polyatomic Molecules*, van Nostrand: New York 1959 pp 508−509.

(23) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. (A)* **1968**, 1887−1889.

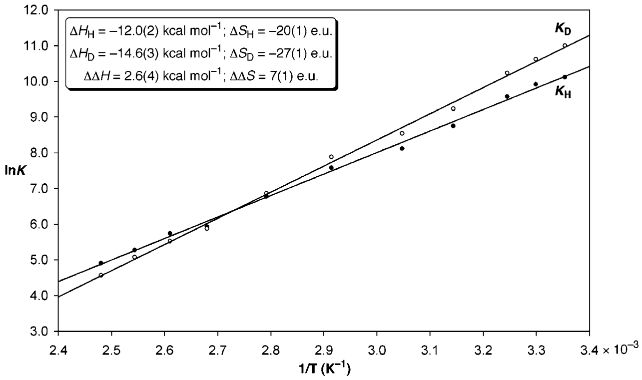


Figure 7. van't Hoff plot for oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ in benzene over the range 25−130 °C.

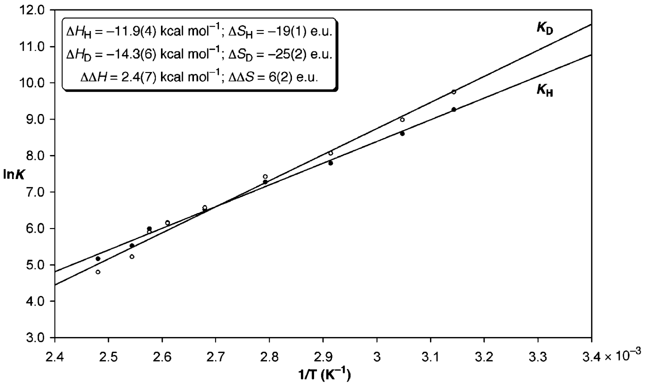


Figure 8. van't Hoff plot for oxidative addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ in toluene over the range 25−130 °C.

temperatures greater than ca. 90 °C, and reaches a maximum value of 1.41(6) at 130 °C (Figure 6). It should, however, be noted that despite the qualitatively similar form of the experimental temperature dependence of the EIE for oxidative addition of H_2 to $Ir(PMe_2Ph)_2(CO)Cl$ to the computed value for $Ir(PH_3)_2(CO)Cl$, there are quantitative differences. For example, the experimental transition from inverse to normal EIE for $Ir(PMe_2Ph)_2(CO)Cl$ occurs at ca. 370 K (benzene), whereas that computed for $Ir(PH_3)_2(CO)Cl$ occurs at 510 K. Such discrepancy is understandable on the basis that the experimental and computational systems feature different PR_3 ligands, i.e., PMe_2Ph versus PH_3, the latter being employed for computational expediency. In addition, anharmonicity, which is not taken into account in the computational study, will also influence the temperature at which the transition from inverse to normal EIE occurs. Specifically, introduction of anharmonicity to the vibrational potential energy surface would result in the vibrational energy levels becoming more closely spaced, thereby affecting both the ZPE and EXC terms; however, the most significant effect has been reported to be on the ZPE term.[24] Anharmonic effects generate a *less* inverse ZPE term and thereby result in both (i) a *lower* temperature for the transition from inverse to normal and (ii) a *larger maximum* value for the observed EIE.

Although the calculated temperature dependence of the EIE does not follow van't Hoff behavior over the full temperature range (Figures 2 and 3), a linear dependence between ln*K* and 1/*T* is observed for the experimental data over a significant portion of the temperature range of the study for the individual reactions of H_2 and D_2 (Figures 7 and 8). The enthalpies and entropies determined from these plots (Table 4) indicate that both ΔH and ΔS are more positive for addition of H_2 than for addition of D_2: for benzene solution $\Delta\Delta H = \Delta H_H - \Delta H_D$ = 2.6(4) kcal mol^{-1} and $\Delta\Delta S = \Delta S_H - \Delta S_D$ = 7(1) e.u. As noted above, an important component of the $\Delta\Delta S$ term is the difference in entropies of H_2 (34.0 e.u. at 300 K) and D_2 (39.0 e.u. at 300 K).[25,26]

The positive $\Delta\Delta H$ and $\Delta\Delta S$ values obtained from the experimental study support the computational study which indicates that $\Delta\Delta H$ (ZPE) favors oxidative addition of D_2 versus H_2 (i.e., an inverse EIE), whereas $\Delta\Delta S$ (SYM · MMI · EXC) favors oxidative addition of H_2 versus D_2 (i.e., a normal EIE). By comparison to the $\Delta\Delta H$ term, the $\Delta\Delta S$ component is small [7(1) e.u.] so that a normal EIE is only obtained at high temperatures when the $T\Delta\Delta S$ term competes with $\Delta\Delta H$.

Table 4. Enthalpy and Entropy Data for Oxidative Addition of H_2 and D_2 to $Ir(PMe_2Ph)_2(CO)Cl$ in Benzene and Toluene Determined from van't Hoff Plots (errors are one standard deviation)

	benzene[a]	toluene[b]
ΔH_H (kcal mol^{-1})	−12.0(2)	−11.9(4)
ΔH_D (kcal mol^{-1})	−14.6(3)	−14.3(6)
$\Delta\Delta H = \Delta H_H - \Delta H_D$ (kcal mol^{-1})	2.6(4)	2.4(7)
ΔS_H (e.u.)	−20(1)	−19(1)
ΔS_D (e.u.)	−27(1)	−25(2)
$\Delta\Delta S = \Delta S_H - \Delta S_D$ (e.u.)	7(1)	6(2)

[a] Temperature range 25−130 °C. [b] Temperature range 45−130 °C.

The nature of an isotope effect (i.e., normal versus inverse) is often invoked to infer details of the reaction coordinate and structural changes of the molecules involved. However, since both normal and inverse equilibrium isotope effects have now been obtained in the same system, it is apparent that conclusions derived from the magnitude of an isotope effect at a single temperature may be more unreliable than previously considered. For example, on the basis of the typical explanation for the nature of an equilibrium isotope effect, i.e., deuterium prefers to be located in the highest frequency oscillator,[2] the observation of a normal EIE for oxidative addition of H_2 at elevated temperatures could have been interpreted as being due to a zero point energy effect resulting from the H_2 (D_2) molecule having a stronger bond than the combined Ir−H(D) bonds. However, the zero point energy term is actually inverse and the origin of the normal EIE at elevated temperature is purely due to entropy effects dominating.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon or dinitrogen atmosphere. Solvents were purified and degassed by standard procedures. $Ir(PMe_2Ph)_2(CO)Cl$ was prepared by a literature method for related derivatives.[27] Benzene-d_6 and toluene-d_8 were obtained from Cambridge Isotopes and dried over 4Å molecular sieves prior to use. ^{1}H NMR spectra were measured on Bruker 300 DRX and Bruker Avance 500 DMX spectrometers.

---

[24] Torres, L.; Gelabert, R.; Moreno, M.; lluch, J. M. *J. Phys. Chem. A* **2000**, *104*, 7898.

[25] Wooley, H. W.; Scott, R. B.; Brickwedde, F. G. *J. Res. Natl. Bur. Standards* **1948**, *41*, 379−475.

[26] Note that the entropy difference between H_2 and D_2 in the absence of contributions from nuclear spin statistics is 3.4 e.u. See ref 18 and *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton 1991; p 5−35.

[27] Shin, J. H.; Bridgewater, B. M.; Churchill, D. G.; Parkin, G. *Inorg. Chem.* **2001**, *40*, 5626−5635.

Determination of the EIE for Oxidative Addition of H_2 and D_2 to Ir($PMe_2Ph)_2$(CO)Cl. In a typical experiment, a solution of Ir($PMe_2Ph)_2$(CO)Cl in C_6D_6 (0.5 mL of 15 mM) in a gastight NMR tube was saturated with H_2 (1 atm at 24 °C). The sample was placed in a constant-temperature bath (±1 °C), and removed periodically to monitor (by ^{1}H NMR spectroscopy) the conversion to the equilibrium mixture with Ir($PMe_2Ph)_2$(CO)ClH_2. The molar ratio of Ir($PMe_2Ph)_2$(CO)Cl to Ir($PMe_2Ph)_2$(CO)ClH_2 was determined directly from the ^{1}H NMR spectra, whereas the molar concentration of dihydrogen in solution at equilibrium was determined by a method similar to that described previously,[28] using a combination of Henry's law with the mole fraction solubility of H_2 obtained from the literature data. The calculation of equilibrium constant requires knowledge of the total amount of H_2 initially present in the closed system, which is the sum of that in the gas phase above the solution and that in solution. The number of moles of H_2 in the gas phase is determined using the ideal gas law and knowledge of the partial pressure of H_2[29] and the volume of the headspace above the solution. The number of moles of H_2 initially in solution is calculated from the solubility expressions given by Clever.[30] At equilibrium, the concentration of H_2 is determined from the total number of moles of H_2 present at equilibrium.[31] Specifically, the concentration of H_2 in solution is obtained by solving the two simultaneous equations that relate (i) the number of moles of H_2 in the gas phase to the partial pressure of H_2 in the gas phase via the ideal gas law, and (ii) the number of moles of H_2 in solution to the partial pressure of H_2 in the gas phase.[30]

The equilibrium constant (K_H) was measured as a function of temperature (Table 2) and ΔH and ΔS were determined from a van't Hoff plot over the temperature range 25−130 °C.[32] An analogous procedure was used to determine K_D as a function of temperature for the corresponding reaction between Ir($PMe_2Ph)_2$(CO)Cl and D_2,[33] from which the EIE in benzene was determined. The equilibrium constants for oxidative addition of H_2 and D_2 were measured in $C_6D_5CD_3$ using a similar protocol.[34,35]

Computational Details

All calculations were carried out using DFT as implemented in the Jaguar 4.1 suite of ab initio quantum chemistry programs.[36] Geometry optimizations and frequency calculations were performed with the B3LYP[37] functional and the 6-31G** (C, H, O, P, and Cl) and LACVP** (Ir) basis sets. The Cartesian coordinates for the derived geometries of Ir($PH_3)_2$(CO)ClH_2 and H_2, together with the vibrational frequencies for Ir($PH_3)_2$(CO)ClH_2, Ir($PH_3)_2$(CO)ClD_2, H_2, and D_2 are listed in the Supporting Information. The MMI term was determined from the geometries of Ir($PH_3)_2$(CO)ClX_2 and X_2 (X = H, D), whereas the EXC and ZPE terms at the temperature of interest were determined from the vibrational frequencies (see Scheme 2). The EIE was determined at 1 degree intervals over the range 0−3000 K.

Conclusions

In summary, an experimental investigation of the oxidative addition of hydrogen to Ir($PMe_2Ph)_2$(CO)Cl provides support for the theoretical prediction that the EIE for this reaction exhibits a temperature-dependent transition from an inverse value to a normal value upon increasing the temperature. Since the EIE for oxidative addition of hydrogen to $\{[H_2Si(C_5H_4)_2]W\}$ also exhibits this transition, it will be of interest to determine how general is this phenomenon and whether it also applies to the coordination of hydrogen to give dihydrogen complexes. The observation of both normal and inverse EIEs for the same system indicate that inferences pertaining to the magnitude of an isotope effect at a single temperature may require more detailed consideration than previously realized.

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

Supporting Information Available: Computational details (5 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0362611

---

(28) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219.

(29) In a system under 1 atm of pressure, the partial pressure of H_2 in the gas phase is 1 atm minus the partial pressure of solvent: for benzene, $\log p_{\text{benzene}} = -1784.8/T + 7.9622$, where T is the temperature at which the sample is prepared; for toluene, $\log p_{\text{toluene}} = -2047.3/T + 8.330$. See: *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton 1991; p 6−84.

(30) Mole fraction solubility of H_2 in benzene: $\ln x = -5.6949 - 765.47/(T/K)$. See: Clever, H. L. In *Solubility Data Series*; Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Volume 5/6: Hydrogen and Deuterium, p 164.

(31) The total number of moles of H_2 (D_2) present at equilibrium is determined by the relative integration of Ir($PMe_2Ph)_2$(CO)Cl and Ir($PMe_2Ph)_2$(CO)ClX_2 (X = H, D) which indicates how much of the originally present H_2 (D_2) has reacted.

(32) The van't Hoff plot does not include the high-temperature data due to the deviation from ideal behavior at high temperature (see text).

(33) Mole fraction solubility of D_2 in benzene: $\ln x = -5.7399 - 743.44/(T/K)$. See: Clever, H. L. In *Solubility Data Series*; Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Volume 5/6: Hydrogen and Deuterium, p 287.

(34) Mole fraction solubility of H_2 in toluene: $\ln x = -6.0373 - 603.07/(T/K)$. See: Clever, H. L. In *Solubility Data Series*; Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Volume 5/6: Hydrogen and Deuterium, p 169.

(35) Mole fraction solubility of D_2 in toluene: $\ln x = -6.0781 - 580.52/(T/K)$. See: Clever, H. L. In *Solubility Data Series*; Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Volume 5/6: Hydrogen and Deuterium, p 288.

(36) Jaguar 4.1 Schrödinger, Inc., Portland, Oregon, 2001.

(37) (a) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974. (b) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211. (c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (d) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (e) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.