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# An Analysis of the Deuterium Equilibrium Isotope Effect for the Binding of Ethylene to a Transition-Metal Complex

**Bruce R. Bender**

*Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523*

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**Abstract:** The secondary deuterium equilibrium isotope effect (EIE) for the reversible binding of $C_2H_4$ to $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (**1**) and $C_2D_4$ to $(\mu\text{-}\eta^1,\eta^1\text{-}C_2D_4)Os_2(CO)_8$ (**1**-$d_4$) has been measured in dodecane solvent. The measured EIE is "inverse" ($C_2D_4$ binds better than $C_2H_4$) and has a value of $K_H/K_D = 0.7(1)$ at 313 K (40 °C) where $K_H/K_D = [C_2D_4]_{(s)}[\mathbf{1}]/[C_2H_4]_{(s)}[\mathbf{1}\text{-}d_4]$. Previously published vibrational assignments for **1** and **1**-$d_4$ and literature values for $C_2H_4$ and $C_2D_4$ allowed the calculation of the same EIE using 16 isotopically sensitive vibrational modes for both **1** and **1**-$d_4$ and all 12 vibrational modes for both $C_2H_4$ and $C_2D_4$. The calculated EIE is also "inverse" and has a value of 0.7110 at 313 K (40 °C). The EIE calculated from vibrational frequencies may be resolved into a mass and moment of inertia factor (MMI = 2.272), a vibrational excitation factor (EXC = 0.8820), and a zero-point energy factor (ZPE = 0.3548), where EIE = MMI × EXC × ZPE. Using symmetry correlation rules, contributions to the EXC and ZPE factors from changes in ethylene vibrational modes for individual modes may be determined. The MMI component may be further resolved into translation and rotational contributions with the help of moments of inertia calculated from a previously determined single-crystal neutron diffraction structure of **1**. The analysis reveals that, contrary to expectation, most of the EIE is not due to changes in vibrational frequencies common to free and complexed ethylene upon coordination but is instead primarily due to a zero-point energy factor from a vibrational mode (a $b_2$-symmetry twist) for **1** and **1**-$d_4$ which is not present in free ethylene. This interpretation of the observed "inverse" EIE appears to be general for alkene complexation and may underlie other recently observed "inverse" secondary deuterium equilibrium isotope effects for the coordination of small molecules (including alkanes and dihydrogen) to transition-metal complexes.

## Introduction

Transition-metal complexes have long been known to bind alkenes reversibly[1] (eqs 1 and 2) and several reports of secondary deuterium equilibrium isotope effects (EIE's) for various ethylene complexes have appeared.[2]

$$C_2H_4 + \text{“}ML_n\text{”} \overset{K_H}{\rightleftharpoons} (\eta^2\text{-}C_2H_4)ML_n \qquad (1)$$

$$C_2D_4 + \text{“}ML_n\text{”} \overset{K_D}{\rightleftharpoons} (\eta^2\text{-}C_2D_4)ML_n \qquad (2)$$

Secondary deuterium EIE's for alkene complexation are usually "inverse", i.e., $K_H < K_D$ (deuterated ethylenes bind better), and supporting theoretical treatments[2b,e] have implicated changes in zero-point vibrational energies as the ethylene carbons rehybridize from $sp^2$ toward $sp^3$ as the underlying cause of the observed "inverse" effect, although "steric" and "electronic" secondary deuterium isotope effects for alkene complexation have also been invoked.[3]

Our interest in isotope effects for alkenes binding to transition metals arose from our mechanistic studies of ethylene dissociation from the diosmacyclobutane complex, $(\mu\text{-}\eta^1,\eta^1\text{-}C_2H_4)Os_2(CO)_8$ (**1**). The measured secondary kinetic isotope effect (KIE) for the dissociation of **1** and **1**-$d_4$ showed that $C_2H_4$ was replaced faster than was $C_2D_4$ ($k_H/k_D = 1.29(1)$ at 39 °C),[4] a result consistent with ethylene carbon hybridization changing from $sp^3$ to nearly $sp^2$ in the transition state[5] (our neutron diffraction study of **1** showed that its ethylene carbons were essentially rehybridized to $sp^3$).[6] Because kinetic and thermodynamic secondary deuterium isotope effects are usually related,[7] we wanted the corresponding thermodynamic EIE for the binding of $C_2H_4$ vs $C_2D_4$ to "$Os_2(CO)_8$"[8] for comparison to the KIE observed for the dissocation of those alkenes.

Diosmacyclobutane **1** reversibly dissociates ethylene at ambient temperature and exchanges its $C_2H_4$ ligand for $C_2D_4$ without isotope scrambling.[9] In the presence of excess ethylene, olefin exchange may be followed for many half-lives of dissociation

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[8] $Os_2(CO)_8$ has been observed in: (a) Low-temperature matrices: Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383,* 497. (b) Solution by flash-photolysis studies: Grevels, F.-W.; Klotzbücher, W. E.; Seils, F.; Schaffner, K.; Takats, J. *J. Am. Chem. Soc.* **1990**, *112,* 1995. (c) The gas phase: Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1990**, *112,* 639.

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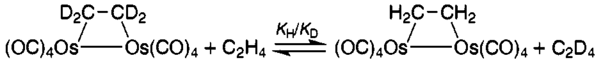
without decomposition.[9a] Those results suggested the possibility of monitoring an exchange reaction (eq 3) to determine $K_H/K_D$ directly.



$$(OC)_4Os(CD_2CD_2)Os(CO)_4 + C_2H_4 \underset{}{\overset{K_H/K_D}{\rightleftharpoons}} (OC)_4Os(CH_2CH_2)Os(CO)_4 + C_2D_4 \quad (3)$$

1-$d_4$ 1

Urey and Rittenberg first suggested the possibility of calculating equilibrium isotope effects for chemical equilibria from vibrational data alone.[10] Subsequently, quantum mechanical treatments of both equilibrium[11] and kinetic[12] isotope effects were developed in the late 1940's by Bigeleisen and Mayer. Within the Born-Oppenheimer approximation, the electronic potential energy surfaces for isotopic molecules are identical and the only sources of equilibrium isotope effects are mass related, i.e., from molecular translational, rotational, and vibrational partition function ratios. The harmonic approximation to molecular vibrations is a rather good one and the Bigeleisen–Mayer theory for the calculation of equilibrium isotope effects was developed within that approximation. Small corrections to equilibrium isotope effects due to the anharmonicity of molecular vibrations have been treated by Wolfsberg.[13]

A rigorous calculation of an equilibrium isotope effect from vibrational data using the Bigeleisen–Mayer formalism requires a detailed knowledge of all isotopically sensitive vibrational frequencies for both reactant and product and their isotopologues. Some time ago, we and our collaborators published vibrational assignments for the isotope sensitive normal modes of **1** and **1**-$d_4$.[14] Vibrational frequencies for ethylene and ethylene-$d_4$ have been measured and remeasured over the years and the best set of values appears to be those of Duncan and Hamilton.[15] Thus a complete set of isotopically sensitive vibrational frequencies for the four species shown in eq 3 existed and allowed a calculation of the EIE using the Bigeleisen–Mayer treatment.

We report here our analysis of the secondary deuterium equilibrium isotope effect for the complexation of $C_2H_4$ and $C_2D_4$ to **1** and **1**-$d_4$. We have experimentally determined $K_H/K_D$ for eq 3 and have calculated the same using published vibrational frequencies for **1**, **1**-$d_4$, and ethylene and ethylene-$d_4$. Our results have allowed us to analyze the equilibrium isotope effect for eq 3 in detail and to comment in general on the origin of such deuterium isotope effects for the complexation of alkenes and other small molecules to transition-metal complexes.

## Experimental Section

Ethylene (CP grade, Matheson) and ethylene-$d_4$ (99.7 atom %), Cambridge Isotopes) were used as received but were freeze–pump–thaw degassed to remove noncondensable impurities before use. The diosmacyclobutanes **1** and **1**-$d_4$ were prepared as previously reported.[4a,6]

The three principal moments of inertia for **1** were calculated[16] from its neutron diffraction determined structure.[6] The corresponding moments of inertia for **1**-$d_4$ were calculated by replacing the hydrogen atoms of **1** by deuterium atoms.

**Measured Equilibrium Isotope Effect.** Assuming equal Henry's law coefficients, $C_H$ and $C_D$, for the solubilities of $C_2H_4$ and $C_2D_4$ in dodecane,[17] the equilibrium expression, eq 3, may be expressed as concentrations of **1** and **1**-$d_4$ and the partial pressures of $C_2H_4$ and $C_2D_4$ gases (eq 4).

$$\frac{K_H}{K_D} = \frac{[\mathbf{1}] \times C_D \times P_{C_2D_4}}{[\mathbf{1}\text{-}d_4] \times C_H \times P_{C_2H_4}} = \frac{[\mathbf{1}]P_{C_2D_4}}{[\mathbf{1}\text{-}d_4] \times P_{C_2H_4}} \quad (4)$$

(at equilibrium)

As a consequence of the ideal gas law and equal Henry's law coefficients, the molar solution ratio of $C_2H_4$ and $C_2D_4$ is the same as the gas-phase molar ratio of $C_2H_4$ and $C_2D_4$ (eq 5). The quantities $n_{C_2D_4}$ and $n_{C_2H_4}$ are the moles of dissolved gases in solution.

$$\frac{K_H}{K_D} = \frac{[\mathbf{1}]}{[\mathbf{1}\text{-}d_4]} \times \frac{n_{C_2D_4}}{n_{C_2H_4}} \quad (5)$$

(at equilibrium)

If the concentrations [**1**] and [**1**-$d_4$] are now expressed as moles of each species per unit volume of solution, the solution volumes will cancel to give eq 6.

$$\frac{K_H}{K_D} = \frac{\text{mol of }\mathbf{1}/\text{vol}_{sol}}{\text{mol of }\mathbf{1}\text{-}d_4/\text{vol}_{sol}} \times \frac{n_{C_2D_4}}{n_{C_2H_4}}$$

$$\frac{K_H}{K_D} = \frac{\text{mol of }\mathbf{1}}{\text{mol of }\mathbf{1}\text{-}d_4} \times \frac{n_{C_2D_4}}{n_{C_2H_4}} \quad (6)$$

(at equilibrium)

Let $m_H$ equal a known initial amount of **1** that then equilibrates with known amounts of $C_2H_4$ and $C_2D_4$. The total moles of **1** at equilibrium will then equal $m_H - x$, where $x$ is the change in the number of moles of **1**. The moles of **1**-$d_4$ must then equal $x$, assuming no decomposition of **1** or **1**-$d_4$ (eq 7).

$$\frac{K_H}{K_D} = \frac{(m_H - x)}{x} \times \frac{n_{C_2D_4}}{n_{C_2H_4}} \quad (7)$$

Now let $N_H$ equal the total moles of $C_2H_4$ originally present in solution and in the gas phase, and let $N_D$ equal the total moles of $C_2D_4$ originally in solution and in the gas phase. At equilibrium, the total moles of $C_2H_4$ and $C_2D_4$, $N_{H_{eq}}$ and $N_{D_{eq}}$ are related to the changes in moles of **1** and **1**-$d_4$ by eq 8.

$$N_{H_{eq}} = N_H + x$$

$$N_{D_{eq}} = N_D - x \quad (8)$$

The ratio of total moles of free $C_2H_4$ to total moles of free $C_2D_4$ is then equal to the ratio of $C_2H_4/C_2D_4$ in solution and in the gas phase (eq 9).

$$\frac{(n_{C_2D_4})_{\text{gas phase}}}{(n_{C_2H_4})_{\text{gas phase}}} = \frac{N_D - x}{N_H + x} \quad (9)$$

At equilibrium, the gas-phase $C_2D_4/C_2H_4$ ratio and the solution-phase **1**/**1**-$d_4$ ratio are related by the same equilibrium constant, $K_H/K_D$. If a known amount of pure **1** is introduced into a closed system containing both $C_2H_4$ and $C_2D_4$, then at equilibrium the $C_2H_4$ and $C_2D_4$ will

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(9) (a) Hembre, R. T.; Ramage, D. L.; Scott, C. P.; Norton, J. R. *Organometallics* **1994**, *13*, 2995. (b) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3468.

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(11) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261.

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(15) Duncan, J. L.; Hamilton, E. *J. Mol. Struct.* **1981**, *76*, 65. These assignments were supported by extensive isotopic data and normal-coordinate calculations.

(16) Calculated using the program "Thermo" Rappé, A. K.

(17) See ref 2a. Stoutland and Bergman have measured the relative solubilities of $C_2H_4$ and $C_2D_4$ in cyclohexane and conclude that there is a negligible solubility difference ($C_2D_4$ is approximately 2–4% more soluble than $C_2H_4$ in cyclohexane).

**Table 1.** Absorbance and Molar Ratio Data for Gas Phase $C_2H_4$ and $C_2D_4$

| $C_2H_4/C_2D_4$ | $A_{(at949.1cm^{11})}$/ $A_{(at719.8cm^{-1})}$ | $C_2H_4/C_2D_4$ | $A_{(at949.1cm^{-1})}$/ $A_{(at719.8cm^{-1})}$ |
|---|---|---|---|
| 1.59(1) | 1.55(2) | 1.00(1) | 1.16(2) |
| 1.40(1) | 1.42(2) | 0.80(1) | 1.02(2) |
| 1.20(1) | 1.31(2) | 0.60(1) | 0.85(2) |

partition unequally into the diosmacyclobutane according to eq 10.

$$\frac{K_H}{K_D} = \frac{(m_H - x)}{x} \times \frac{N_D - x}{N_H + x} \tag{10}$$

(at equilibrium)

With known initial amounts of $C_2D_4$ and $C_2H_4$, the amount of exchange at equilibrium can be measured directly from the gas-phase $C_2D_4$ and $C_2D_4$ absorbances (eq 11).

$$R = \frac{N_H + x}{N_D - x} = \frac{(C_2H_4)_{gas}}{(C_2D_4)_{gas}} \tag{11}$$

The observed absorbance ratio $R$ may be related directly to actual molar ratios by comparison to a calibration curve constructed from equilibrating known ratios of $C_2H_4$ and $C_2D_4$ under controlled conditions. This also avoids having to measure absolute amounts of gas-phase ethylenes from extinction coefficients. For ethylene and ethylene-$d_4$, the out-of-plane wags at 949 $cm^{-1}$ ($C_2H_4$) and 720 $cm^{-1}$ ($C_2D_4$) were most conveniently measured because both bands were relatively intense and did not overlap with each other or with other IR bands present.

A gas-phase IR cell equipped with a side arm leading to a small vacuum bulb containing **1** and **1**-$d_4$ in dodecane solvent was constructed. A stopcock between the bulb and the cell allowed the removal of the bulb from the IR cell and allowed it to be immersed in a constant temperature bath for equilibration. When equilibration was reached, exchange was quenched (ice bath) and the bulb was reattached to the IR cell side arm. The cell was evacuated through the O-ring connection, and that stopcock was then closed. The stopcock to the vacuum bulb was then opened, and the ethylene was expanded into the evacuated IR cell for measurement (the solution was maintained at 0 °C to prevent further exchange). After each measurement, ethylenes were recondensed into the side arm bulb and detached from the cell and the process was repeated as often as necessary to reach full equilibration.

Because determination of absolute concentrations of gas phase ethylenes from extinction coefficients is fraught with difficulties,[18] a calibration curve for several molar ratios $C_2H_4/C_2D_4$ vs IR absorbance ratios was constructed and the results have been placed in Table 1. In order to ensure that the calibrated absorbance ratios would approximate the experimental conditions as closely as possible, all ratios were determined at a constant total ethylene pressure; the amounts of each gas were adjusted to give a total pressure of 29 Torr during each measurement. Pressure broadening was not employed since this has been shown to be effective (for ethylene) only at pressures approaching 100 psi,[19] which are well outside the range of this apparatus.[20] The calibration samples were prepared on a vacuum line Hg manometer. Small, accurately measured volumes and relatively high manometer pressure (200–800 Torr of each gas) were used to minimize errors in manometer readings.

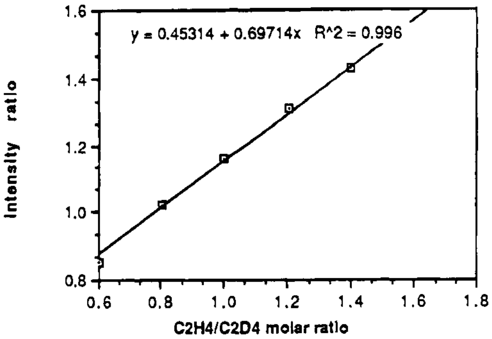

**Figure 1.** Plot of absorbance ratio vs molar ratio of $C_2H_4/C_2D_4$.

**Table 2.** Gas Phase $C_2H_4/C_2D_4$ Ratios for $K_H/K_D$ Determination

| time (h) | ratio: $C_2H_4/C_2D_4$ | ratio, corrected |
|---|---|---|
| 13 | 1.14(1) | 0.99 |
| 20 | 1.15(2) | 1.00 |
| 23 | 1.17(1) | 1.03 |
| 31 | 1.16(2) | 1.01 |

The data from Table 1 are plotted in Figure 1. The "curve" is approximately linear over the region of interest, but the non-zero intercept reflects a non-linear correlation for extrapolated values outside this range.

A solution of **1** (21.0 mg, 3.32 × $10^{-5}$ mol in 5 mL of dodecane) was equilibrated with approximately 4 equiv of $C_2H_4$ (1.33 × $10^{-4}$ mol) and 5 equiv of $C_2D_4$ (1.67 × $10^{-4}$ mol). An excess amount of total ethylenes was necessary to prevent decomposition and side reactions of **1** and **1**-$d_4$ at 40 °C. The gas-phase absorbance ratio of $C_2H_4/C_2D_4$ was checked periodically and was found to remain constant after approximately 24 h. The measured absorbance ratios after various times have been placed in Table 2, along with the corrected molar ratio values from the data of Table 1.

The molar ratios in Table 2 are related to the changes in $N_H$ and $N_D$ at equilibrium. The value of $x$ can determined from eq 11 and the equation in Figure 1, and it can then be used to determine $K_H/K_D$ from eq 10.

## Results

**Measured Equilibrium Isotope Effect.** It was not possible to measure directly the independent equilibrium constants (eqs 1 and 2) for the binding of ethylene and ethylene-$d_4$ to $Os_2(CO)_8$. However, division of eq 1 by eq 2 (with $ML_n = Os_2(CO)_8$) yields eq 3, and hence yields the ratio $K_H/K_D$, which is a direct measure of the EIE, and which *is* experimentally measurable.

At equilibrium, only the four species in eq 3 were present and their relative amounts were determined by monitoring changes in the gas-phase $C_2H_4$ and $C_2D_4$ intensity ratios by gas-phase IR. The measured value for the equilibrium isotope effect (eq 3) is $K_H/K_D = 0.7(1)$, showing that $Os_2(CO)_8$ binds $C_2D_4$ slightly better than $C_2H_4$. The rather large uncertainty (determined from the last three entries in Table 2) was a consequence of measuring small changes in relatively large amounts of free ethylene and ethylene-$d_4$.

**Calculated Equilibrium Isotope Effect.** The equilibrium isotope effect for eq 3 was calculated from 16 isotopically sensitive normal modes[14] for both **1** and **1**-$d_4$ and from literature values[15] for all 12 normal modes for both $C_2H_4$ and $C_2D_4$. The Bigeleisen equation (shown in abbreviated form below in eq 12) was used as presented by McLennan.[21]

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[18] (a) Overend, J. *Vibrational Intensities in Infrared and Raman Spectroscopy*; Person, W. B., Zerbi, G., Eds.; Elsevier: Amsterdam, 1982; Chapter 2. (b) Rochkind, M. M. *Anal. Chem.* **1968**, *40*, 762.

[19] Golike, R. C.; Mills, I. M.; Person, W. B.; Crawford, B., Jr. *J. Chem. Phys.* **1956**, *25*, 1266.

[20] In a separate experiment, samples of *cis*- and *trans*-1,2-dideuterioethylene were prepared at partial pressures of 10 Torr each; similar samples were prepared with added $N_2$ gas to give a total pressure of 650 Torr. Rotational fine structure was observed for all bands regardless of the total pressure and showed no broadening.

[21] McLennan, D. J. In *Isotopes in Organic Chemistry*; Buncel, E., Lee, E., Eds.; Elsevier: New York, 1987; Vol. 7, Chapter 6, p 395.

$$\mathrm{EIE} = \frac{K_\mathrm{H}}{K_\mathrm{D}} = \mathrm{MMI} \times \mathrm{EXC} \times \mathrm{ZPE} \qquad (12)$$

The calculated EIE is the product of three factors: a rotational and translational factor (abbreviated MMI, eq 13) containing the reduced (classical) rotational and translational partition function ratios of the reactants (A) and products (B) and their deuterium isotopologues (A* and B*); a factor (abbreviated EXC, eq 14) accounting for contributions from excitations of vibrational energy levels (such EXC factors only deviate from unity at high temperatures or low vibrational frequencies); and a factor (abbreviated ZPE, eq 15) comprising the much discussed, and important, zero-point energy contributions.

$$\mathrm{MMI} = \left(\frac{Q_\mathrm{tr}^{\mathrm{A}*}Q_\mathrm{rot}^{\mathrm{A}*}}{Q_\mathrm{tr}^{\mathrm{A}}Q_\mathrm{rot}^{\mathrm{A}}}\right)\left(\frac{Q_\mathrm{tr}^{\mathrm{B}}Q_\mathrm{rot}^{\mathrm{B}}}{Q_\mathrm{tr}^{\mathrm{B}*}Q_\mathrm{rot}^{\mathrm{B}*}}\right) \qquad (13)$$

$$\mathrm{EXC} = \frac{\displaystyle\prod_i^{3N_\mathrm{r}-6} \frac{1 - e^{-(h\nu_i^\mathrm{A}/kT)}}{1 - e^{-(h\nu_i^{\mathrm{A}*}/kT)}}}{\displaystyle\prod_j^{3N_\mathrm{p}-6} \frac{1 - e^{-(h\nu_j^\mathrm{B}/kT)}}{1 - e^{-(h\nu_j^{\mathrm{B}*}/kT)}}} \qquad (14)$$

$$\mathrm{ZPE} = \frac{\displaystyle\prod_i^{3N_\mathrm{r}-6} \frac{e^{(h\nu_i^\mathrm{A}/2kT)}}{e^{(h\nu_i^{\mathrm{A}*}/2kT)}}}{\displaystyle\prod_j^{3N_\mathrm{p}-6} \frac{e^{(h\nu_j^\mathrm{B}/2kT)}}{e^{(h\nu_j^{\mathrm{B}*}/2kT)}}} \qquad (15)$$

For the calculation of the EIE from vibrational data alone, the MMI factor (eq 13) may be re-expressed using the Teller–Redlich product rule.[21,22] This important theorem (shown in its most concise form in eq 16) allows the ratios of molecular masses and moments of inertia of isotopically related species to be expressed as a product of atomic masses and vibrational frequencies. In eq 16, $I_\mathrm{A}$, $I_\mathrm{B}$, and $I_\mathrm{C}$ are the principal molecular moments of inertia, $M$ and $M^*$ are molecular masses, and $m_\mathrm{j}$ and $m_\mathrm{j}^*$ are atomic masses.

$$\left(\frac{M^*}{M}\right)^{3/2}\left(\frac{I_\mathrm{A}^*I_\mathrm{B}^*I_\mathrm{C}^*}{I_\mathrm{A}I_\mathrm{B}I_\mathrm{C}}\right)^{1/2} = \prod_j^N \left(\frac{m_j^*}{m_j}\right)^{3/2} \prod_i^{3N-6} \frac{\nu_i^*}{\nu_i} \qquad (16)$$

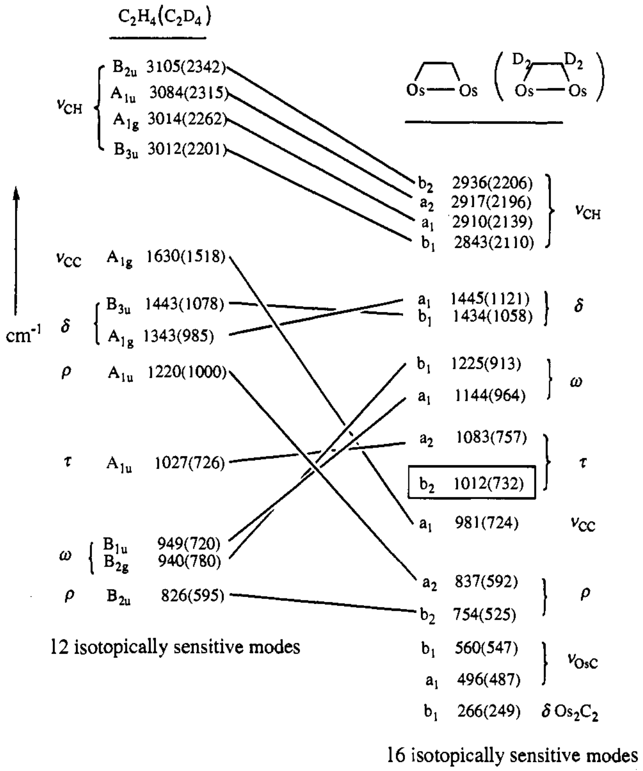
Division of eq 16 for isotopic ethylenes (A and A*) by the corresponding eq 16 for **1** and **1**-$d_4$ (B and B*) yields eq 17 (the products of *atomic* masses on both sides of eq 3 are the same and therefore are eliminated), therefore the MMI factor (eq 3) may be replaced with the vibrational product (VP) factor (eq 17), which accounts for the mass and moment of inertia ratios needed to calculate the EIE.[21]

$$\mathrm{VP} = \frac{\displaystyle\prod_i^{3N_\mathrm{r}-6} (\nu_i^{\mathrm{A}*}/\nu_i^\mathrm{A})}{\displaystyle\prod_j^{3N_\mathrm{p}-6} (\nu_j^{\mathrm{B}*}/\nu_j^\mathrm{B})} = \left(\frac{Q_\mathrm{tr}^{\mathrm{A}*}Q_\mathrm{rot}^{\mathrm{A}*}}{Q_\mathrm{tr}^{\mathrm{A}}Q_\mathrm{rot}^{\mathrm{A}}}\right)\left(\frac{Q_\mathrm{tr}^{\mathrm{B}}Q_\mathrm{rot}^{\mathrm{B}}}{Q_\mathrm{tr}^{\mathrm{B}*}Q_\mathrm{rot}^{\mathrm{B}*}}\right) \qquad (17)$$

**Table 3.** Correlation of Symmetry Point Groups

| $D_{2h}$ | $C_{2v}$ | $C_2$ |
|---|---|---|
| $A_g$, $B_{1u}$ | $A_1$ | A |
| $A_{1u}$, $B_{1g}$ | $A_2$ | A |
| $B_{2g}$, $B_{3u}$ | $B_1$ | B |
| $B_{3g}$, $B_{2u}$ | $B_2$ | B |

**Scheme 1.** Correlation of Normal Modes for $C_2H_4$, $C_2D_4$, **1**, and **1**-$d_4$



The calculated EIE for the complexation of ethylene to $Os_2(CO)_8$ is 0.7110 at 313 K (40 °C).[23] The calculated EIE agrees well with the experimentally measured value, 0.7(1), and is in remarkably good agreement with the EIE (0.73) predicted by "rule of thumb" estimates based on four deuterium–carbon bonds changing from $sp^2$ to $sp^3$ hybridization.[24]

**Analysis of the Calculated Equlibrium Isotope Effect.** A comparison of the symmetry properties of free ethylene and coordinated ethylene (as in **1**) provides a basis for the correlation of vibrational modes between ethylene and **1**. In the formation of **1** from free ethylene, symmetry elements are lost as the ethylene molecule transforms from $D_{2h}$ through $C_{2v}$ to $C_2$ symmetry (Table 3).[25]

Using the relations in Table 3, changes in the vibrational frequencies between free ethylene and ethylene coordinated as in **1** may be correlated. These normal mode correlations are shown below in Scheme 1 (deuterated modes are in parentheses). The $C_{2v}$ symmetry labels for the vibrational assignments **1** and **1**-$d_4$ were used.[14]

The EXC and ZPE factors for each individual mode were calculated and the results are presented in Table 4. The products

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[22] Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; p 20.

[23] The corresponding *dissociative* EIE ($1/K_\mathrm{H}/K_\mathrm{D}$ in eq 3) may be calculated by interchanging the A and B labels for the four species (i.e., transposing eq 3). This value (1.406 at 40 °C) is more insightful for comparison to the ethylene dissociation KIE = 1.29(1) at 39 °C (ref 4b).

[24] The usual "rule-of-thumb" calculations predict an EIE of 0.9235 *per deuterium* for carbon hybridization changing from $sp^2$ to $sp^3$: Hartshorn, S. R.; Shiner, V. J. *J. Am. Chem. Soc.* **1972**, *94*, 9002. See also ref 7. Taking the fourth power of that value, $(0.9235)^4$, predicts an overall EIE of 0.7276 for an equilibrium like that in eq 3.

[25] Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*; McGraw-Hill: New York, 1955; App. X, pp 334–336.

**Table 4.** Individual Mode Contributions to EXC and ZPE[a]

| mode/sym | $C_2H_4$ ($C_2D_4$) | $Os_2C_2H_4$ ($C_2D_4$) | EXC | ZPE |
|---|---|---|---|---|
| $\nu_{CH}$ (stretch) | | | | |
| $B_{2u}/b_2$ | 3105 (2342) | 2936 (2206) | 1.000 | 1.079 |
| $A_u/a_2$ | 3084 (2315) | 2917 (2196) | 1.000 | 1.117 |
| $A_{1g}/a_1$ | 3014 (2262) | 2910 (2139) | 1.000 | 0.9573 |
| $B_{3u}/b_1$ | 3012 (2201) | 2843 (2110) | 1.000 | 1.196 |
| $\delta$ (bend) | | | | |
| $A_{1g}/a_1$ | 1344 (985) | 1445 (1121) | 1.004 | 1.081 |
| $B_{3u}/b_1$ | 1444 (1078) | 1434 (1058) | 0.9994 | 0.9773 |
| $\omega$ (wag) | | | | |
| $B_{2g}/b_1$ | 940 (780) | 1225 (913) | 1.003 | 0.7051 |
| $B_{1u}/a_1$ | 949 (720) | 1144 (964) | 1.018 | 1.119 |
| $\tau$ (twist) | | | | |
| $A_{1u}/a_2$ | 1027 (726) | 1083 (757) | 1.003 | 0.9442 |
| $-/b_2$ | – | 1012 (732) | 0.9747 | $\underline{0.5254}$ |
| $\nu_{CC}$ (stretch) | | | | |
| $A_{1g}/a_1$ | 1630 (1518) | 981 (724) | 0.9752 | 0.7166 |
| $\rho$ (rock) | | | | |
| $A_{1u}/a_2$ | 1220 (1000) | 837 (592) | 0.9608 | 0.9442 |
| $B_{2u}/b_2$ | 826 (595) | 754 (525) | 0.9825 | 1.005 |
| $\nu_{OsC}$ (stretch) | | | | |
| $-/b_1$ | – | 560 (547) | 0.9949 | 0.9706 |
| $-/a_1$ | – | 496 (487) | 0.9952 | 0.9795 |
| $\delta Os_2C_2$ | | | | |
| (ring deformation) | – | 266 (249) | 0.9661 | 0.9617 |

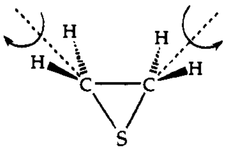
[a] VP = 2.272; $\Pi$ EXC = 0.8820; $\Pi$ ZPE = 0.3548; VP × $\Pi$ EXC × $\Pi$ ZPE = EIE = 0.7110.

of all contributions have been placed at the bottom of Table 4. It should be pointed out that the overall calculated EIE is independent of individual mode assignments for **1**, **1**-$d_4$, $C_2H_4$, and $C_2D_4$. Because the factors comprising the product terms in eqs 14, 15, and 17 all commute for a given species, the calculated EIE is independent of the correlations shown in Scheme 1 and in Table 4.[26] Symmetry labels, however, are useful for interpreting the "origin" of the EIE in terms of changes in particular vibrational frequencies,[27] thus each assignment is shown with its individual contributions to the EXC and ZPE factors. These results give unique insight into the origin of the calculated EIE for the complexation of ethylene to $Os_2(CO)_8$.

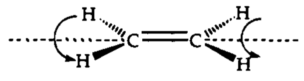
Scheme 1 and Table 4 show that all ethylene vibrational modes increase or decrease and therefore lead to opposing contributions to the overall EIE. A mode-by-mode comparison of vibrational frequencies reveals insightful changes in ethylene normal modes (and hence force constants) upon coordination. In the following analysis, a "normal" effect will mean that a particular mode contributes a factor greater than 1 to the total EIE; an "inverse" effect will mean that that particular mode contributes a factor less than 1 to the total EIE.

All four $\nu_{CH}$ stretching frequencies (hence force constants) decrease on going from ethylene to **1** as expected ($sp^2$ to $sp^3$ hybridization); the product of zero-point energy contributions from changes in CH stretching frequencies contributes a normal effect of 1.380 to the overall EIE. Because the overall EIE is inverse, other factors must determine the observed and calculated EIE.

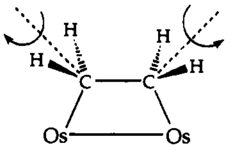
The normal modes of $a_1$ symmetry for **1** and **1**-$d_4$ in the region 1450 to 700 cm$^{-1}$ (and indeed those of $A_{1g}$ symmetry for ethylene itself) are strongly coupled (mixed), and thus modes of that symmetry should only be considered together for a given species. For example, because the $A_{1g}/a_1$-symmetry deformation mode ($\delta_{CH_2}$) increases slightly in frequency on going from $C_2H_4$ to **1**, an inverse contribution is expected. However, the change is greater for the deuterated species (a consequence of different coupling of $\delta_{CH(D)_2}$ modes to $\nu_{CC}$ for the $C_2H_4$ and $C_2D_4$ species) and the actual ZPE contribution from this mode is normal (1.081). For the $\nu_{CC}$ mode a large normal contributon might be expected because the frequency change is so large. The change is slightly greater for **1**-$d_4$ though, and the calculated ZPE contribution is inverse (0.7166). Finally, for the $B_{1u}/a_1$ wagging mode, $\omega_{CH_2}$, a normal ZPE contribution (1.119) is calculated. Overall, the strongly coupled $\delta_{CH_2}/\nu_{CC}/\omega_{CH_2}$ contributions oppose each other, and when all three are considered together, their product contributes an inverse effect (0.8668) to the total change in ZPE.



$b_2$ twist mode



free rotation



$b_2$ twist mode

**Figure 2.** Rotational and twisting modes for ethylene and ethylene complexes.

The change in the $B_{2g}/b_1$ wag (this mode is related to the out-of-plane deformation mode first identified by Streitwieser as the main source of secondary KIE's for $sp^2$ to $sp^3$ hybridization changes)[28] contributes a substantial inverse ZPE factor of 0.7051 to the EIE. This "inverse" factor is a direct consequence of the increase of this mode from 940 cm$^{-1}$ in free ethylene to 1225 cm$^{-1}$ in **1**.

The ZPE contribution from the $b_2$-symmetry twisting mode of **1** (underlined in Table 4) is large and inverse (0.5255). For diosmacyclobutane **1**, this mode corresponds to a rotation of the $CH_2$ planes about the bisectors of their respective H−C−H angles (Figure 2).

For ethylene, the bisector of the $CH_2$ angle coincides with the CC bond and therefore that $CH_2$ motion corresponds to a pure rotational mode. The $b_2$-symmetry twist mode for **1** therefore has no *vibrational* counterpart in ethylene. The quotient of reactant and product ratios (i.e., the zerò-point vibrational energy contribution, eq 15) therefore contains more denominator factors than numerator factors (i.e., $j > i$). Because zero-point energies for **1**-$d_4$ are intrinsically lower in energy than the corresponding modes for **1**, ZPE contributions from vibrational modes of **1** which are not present in free ethylene are "inverse".[23]

For the $A_u/a_2$ $\tau$(twist) mode, the changes in ZPE are small between coordinated and free ethylene and this mode contributes a small inverse factor of 0.9442. Of the remaining modes

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[26] Reassigning individual modes in Scheme 1 and Table 4 leads to compensating changes in contributions from individual modes but the EIE remains unchanged because the EIE is a thermodynamic equation of state.

[27] In our case, only the assignment for the $b_2$-symmetry $CH_2$ twist was crucial.

[28] Streitwieser, A.; Jagow, R. H.; Fehey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.

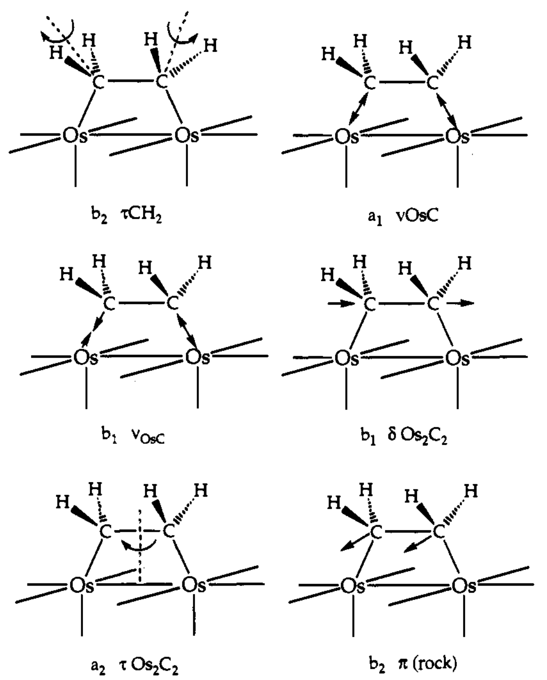

**Figure 3.** "New" vibrational modes for $(C_2H_4)Os_2(CO)_8$.

common to both **1** and ethylene, only the $A_u/a_2$ and $B_{2u}/b_2$ methylene rocking motions are important; they contribute an inverse effect and a normal effect, respectively.

Three substantial ZPE contributions which approach the calculated inverse EIE have been identified (last column in Table 4): the $B_{2g}/b_1$ out-of-plane wag (0.7052), the $b_2$ twist (0.5254), and the $a_1$ $\nu_{CC}$ (0.7166). However, each of these three modes also contributes its own VP (eq 17) and EXC (eq 14) factors. Accounting for these contributions, the total contribution to the EIE from the out-of-plane wage mode (VP × EXC × ZPE) is $1.113 \times 1.003 \times 0.7052 = 0.7875$; the total contribution to the EIE from the $b_2$-symmetry twisting mode is $1.383 \times 0.9747 \times 0.5254 = 0.7080$, and the total contribution to the EIE for the CC stretch is $1.262 \times 0.9752 \times 0.7166 = 0.8820$. Either of these three modes might be labeled as the "cause" of the observed inverse EIE; however, Table 4 clearly shows that the ZPE contribution from the $b_2$ twist mode (missing for free ethylene) is the most significant inverse factor contributing to the EIE.

Five other vibrational modes for **1** that are not present in free ethylene are illustrated in Figure 3 along with the $b_2$ twist already considered. These six vibrational modes correspond to the six translational and rotational degrees of freedom which are "lost" when ethylene and $Os_2(CO)_8$ combine to form the diosmacyclobutane. Four of the six modes (the $b_2$ twist, two OsC stretches, and the $b_1$-symmetry $Os_2C_2$ skeletal deformation mode) have been included in the calculation of the EIE. Except for the $b_2$-twist mode, they contribute small inverse effects to the total EIE (Table 4).

Two vibrational modes for **1** shown in Figure 3 have been neglected in our calculation because definite vibrational assignments for those modes are not known. The two neglected vibrations are a mode of $a_2$ symmetry that corresponds to a twist of the two ethylene carbons parallel to the two osmium atoms about the pseudo-$C_2$ axis[29] and a mode of $b_2$ symmetry that corresponds to an out-of-plane rock. Another neglected mode is the $\nu_{OsOs}$ stretch (not shown) that is one of the set of 18 expected normal modes for the "dimetallacyclobutane core". The $b_2$ out-of-plane rock is not part of that set, but it is included in Figure 3 because it corresponds to one of the "lost" translational modes.

**Table 5.** Moments of Inertia and Molecular Masses for **1**, **1**-$d_4$, $C_2H_4$, and $C_2D_4$[a]

| | moments of inertia, amu Å$^2$ | | | molecular mass, amu |
|---|---|---|---|---|
| $C_2H_4$ | 3.46 | 16.84 | 20.35 | 28.02 |
| $C_2D_4$ | 6.95 | 22.89 | 29.91 | 32.02 |
| **1** | 378.5 | 528.9 | 581.0 | 632.4 |
| **1**-$d_4$ | 387.4 | 537.9 | 583.5 | 636.4 |

[a] Moments of inertia for $C_2H_4$ and $C_2D_4$ and taken from: Mitchell, S. A. *Inter. J. Chem. Kinet.* **1994**, *26*, 97.

Of the three neglected modes, the $a_1$-symmetry $\nu_{OsOs}$ stretch (observed for **1** at 146 cm$^{-1}$)[14] is not expected to be deuterium sensitive and would therefore not contribute to the calculated EIE. Both low-frequency skeletal modes, the $a_2$ twist and the $b_2$ rock, involve mainly $Os_2C_2$ motion and are not formally deuterium sensitive and are too low in frequency to couple substantially with deuterium-sensitive modes of the same symmetry; they therefore are not expected to be substantially isotope sensitive in the present calculation. Indeed, neglecting both low-frequency modes leads to an omission of a factor of *ca.* 0.995 in the calculated EIE.[29]

**Rotational and Translational Contributions to the Calculated EIE.** The VP quotient (the isotopic ratio of reactant and product vibrational frequencies in eq 17) is 2.275 and represents rotational and translational contributions to the calculated EIE.[22] Rotational and translational effects thus appear to oppose the overall "inverse" EIE. We may more explicitly calculate the rotational and translational contributions to the EIE using eq 13 and expressions 18 and 19 which come from the classical rotational and translational partition function ratios. In eq 18, $M_H$ and $M_D$ are molecular masses, and in eq 19, $I_A$, $I_B$, and $I_C$ are the three principal molecular moments of inertia.

$$\frac{Q^{H}_{tr}}{Q^{D}_{tr}} = \left(\frac{M_H}{M_D}\right)^{3/2} \tag{18}$$

$$\frac{Q^{H}_{rot}}{Q^{D}_{rot}} = \left(\frac{I^H_A I^H_B I^H_C}{I^D_A I^D_B I^D_C}\right)^{1/2} \tag{19}$$

Our neutron diffraction results[6] for **1** have allowed us to calculate the moments of inertia for **1** and for **1**-$d_4$ by replacing hydrogen atoms with deuterium atoms. The results of these calculations along with literature values[31] for ethylene and ethylene-$d_4$ are collected in Table 5.

The contributions to the EIE from rotational and translational partition function ratios calculated from moments of inertia and molecular masses (eqs 13 and 18–19) are 2.003 and 1.221, respectively. The product of these factors (MMI) is 2.446, in good agreement with the VP factor (2.275) independently calculated from vibrational frequencies alone.

## Discussion

Cvetanovic and co-workers determined the equilibrium isotope effect (EIE) for $C_2H_4/C_2D_4$ complexation to Ag(I) from

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(29) A weak band in the Raman spectrum of **1** was observed at 235 cm$^{-1}$ which may be the neglected $a_2$ twist mode (C. E. Anson, personal communication to the author). Isotope ratios of 1.04 and 1.07 for the neglected $a_2$ twist and $b_2$ out-of-plane rock modes (both skeletal modes are not formally deuterium sensitive) may be expected: these isotope ratios are similar to those observed for the corresponding modes in the osmacyclopropane complexes, $(\eta^2\text{-}C_2H_4)Os(CO)_4$ and $(\eta^2\text{-}C_2D_4)Os(CO)_4$ (ref 30). Isotope ratios of this magnitude and estimated frequencies of 235 (225) and 110 (103) cm$^{-1}$ for the $a_2$ and $b_2$ modes predict only a small neglected factor (ca. 0.995) for the calculated EIE.

(30) Anson, C. E.; Sheppard, N.; Powell, D. B.; Bender, B. R.; Norton, J. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1449.

(31) Mitchell, S. A. *Int. J. Chem. Kinet.* **1994**, *26*, 97.

measured retention times of those gases passed through ethylene glycol solutions of $AgNO_3$ on a stationary support.[2f,g] Their results established that complexation is favored for $C_2D_4$ (e.g., $K_H/K_D = 0.888$ as defined in eqs 1 and 2). Those authors attributed the observed "inverse" EIE to an increase in the out-of-plane bending force constant upon complexation, a conclusion that paralleled the usual explanation of the origin of secondary deuterium isotope effects for organic systems.[5,7]

Jung and co-workers attempted to quantify the vibrational origin of the observed inverse EIE for ethylene binding to Ag(I) complexes by carrying out normal coordinate vibrational analyses of $Ag^+(C_2H_4)$ and $Ag^+(C_2H_3D)$ complexes.[2e] They also measured the EIE for ethylene and monodeuterated ethylene passing through Ag(I) impregnated GC columns and compared the experimental value to the EIE calculated from the Bigeleisen equation. They concluded that the EIE arose from ZPE changes for several modes, some of which contributed factors less than 1 and some of which contributed factors greater than 1. However, *no single dominant contribution was identified.*

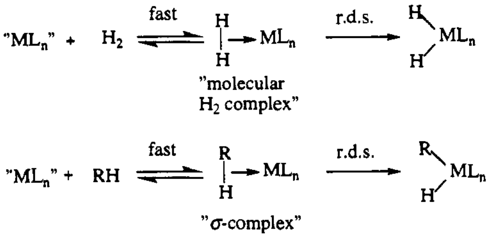
More recently, Jung and co-workers examined the EIE for the complexation of $C_2H_4$ and $C_2H_3D$ to Rh(I) complexes bound to a stationary GC chromatography support.[2b] The experimentally observed EIE was compared to the EIE calculated from vibrational frequencies obtained from normal coordinate analyses of $Rh(C_2H_4)$ and $Rh(C_2H_3D)$ complexes.[32] While good agreement was found between calculated and experimental EIE's, again, no single vibrational mode could be implicated, and those authors concluded that the inverse EIE was attributable to olefin rehybridization as in Ag(I) ethylene complexes.

Strausz has criticized[33] the idea that all secondary deuterium isotope effects arise from changes in out-of-plane bending motions (i.e., rehybridization), an idea which has widespread currency in organic chemistry.[5,7] Those workers measured the secondary deuterium KIE for the addition of ground state sulfur atoms $S(^3P)$ to a 50/50 mixture of $C_2H_4$ and $C_2D_4$ to give thiirane and thiirane-$d_4$. Analysis of $C_2H_4S$ and $C_2D_4S$ product ratios gave an "inverse" KIE of 0.877—a result consistent with the general notion that deuterium "prefers" $sp^3$ hybridization in the transition state. Strausz and co-workers compared the experimental KIE to that calculated from the full Bigeleisen equation using various transition-state vibrational models. The authors argued that the observed KIE arose not from force constant changes from any particular mode, but rather from an *increase* in the number of isotopically sensitive normal modes when ethylene encounters sulfur in the transition state. This analysis by Strausz and co-workers of a related secondary deuterium KIE is an important precedent for our interpretation of the secondary deuterium EIE for ethylene complexation to metal complexes.

Other possible causes of equilibrium isotope effects for alkene complexation may be steric and electronic.[3] Because the mean vibrational amplitude of a CD bond is less than that for a CH bond, deuterium is a "smaller" carbon substituent. While the mean vibrational amplitudes for the CH bonds are no doubt greater for **1** than are those for the CD bonds of **1**-$d_4$, our neutron diffraction study of **1** clearly showed that its CH bonds are not sterically encumbered by the carbonyl ligands.[6]

A carbon atom bonded to deuterium has been considered to be more electropositive than a carbon bonded to protium.[3a] But because electron-donating alkene carbon substituents destabilize alkene complexes related to **1**, we would thus expect **1**-$d_4$ to be less stable than **1**. This is *not* what is observed both kinetically[4b] and thermodynamically and thus we rule out electronic isotope effects as the cause of the observed EIE.

**Scheme 2.** Molecular $H_2$ and Alkane $\sigma$-Complexes and their Roles in Oxidative Addition to Transition-Metal Complexes



**Equilibrium Isotope Effects for the Binding of Other Small Molecules to Transition-Metal Complexes.** Several reports of unusual deuterium isotope effects for the activation of alkanes and dihydrogen ($H_2$) by transition-metal complexes have appeared recently.[34] Those studies have mostly reported kinetic isotope effects (KIE's) observed for the addition or elimination of alkanes or $H_2$ to or from various transition-metal complexes. Such KIE's are thought to give insight into transition states (early or late)[35] for isotopically sensitive CH and HH bond-forming and bond-breaking reactions (Scheme 2).

Molecular dihydrogen complexes are structurally and spectroscopically well-characterized,[36] and both theory and experiment now acknowledge the existence of analogous alkane $\sigma$-complexes.[37] But because molecular dihydrogen complexes and alkane $\sigma$-complexes are plausible intermediates *before* subsequent dihydrogen or alkane oxidative addition, a mechanistic subtlety encroaches: an observed KIE may be a composite of a rapid secondary[38] pre-equilibrium (thermodynamic) isotope effect and a slower primary (kinetic) isotope effect. A thorough understanding of such equilibrium and kinetic isotope effects is therefore necessary to deconvolute observed isotope effects and thus to distinguish stepwise from single-step oxidative addition and reductive elimination mechanisms.[39]

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(32) Some doubt must be cast on the reliability of the calculated frequencies in ref 2b. The normal mode analysis was fitted to only 7 of the 15 theoretical modes, and more importantly, the $b_2$ twisting mode was neglected.

(33) (a) Strausz, O. P.; Safarik, I.; O'Callaghan, W. B.; Gunning, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 1828. (b) Strausz, O. P.; Safarik, I. *J. Phys. Chem.* **1972**, *76*, 3613. (c) See also ref 5a, p 240, footnote 156.

(34) (a) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647. (b) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369. (c) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585. (d) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7629. (e) Bullock, R. M.; Headford, C. E. L.; Hennessy, K.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897. (f) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172. (g) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502.

(35) Bullock, R. M. *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1991; pp 263–307.

(36) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(37) (a) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Cundari, T. R. *J. Am. Chem. Soc.* **1994**, *116*, 340. (c) Song, J.; Hall, M. B. *Organometallics* **1993**, *12*, 3118. (d) Ziegler, T.; Tschike, C.; Fan, L.; Becke, A. D. *J. Am. Chem. Soc.* **1989**, *111*, 9177. (e) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 8321. (f) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

(38) We shall keep the definition that a secondary effect involves only bonds not broken in the transition state along the reaction coordinate. In a strict sense, the HH bond in a molecular dihydrogen complex and the CH bond of a $\sigma$-complex are weakened upon complexation but are not broken.

(39) A reviewer has argued that "the existence or non-existence of an alkane $\sigma$-complex intermediate prior to the rate determining step...cannot affect the observed KIE." The author maintains that a fast, reversible pre-equilibrium between the free and complexed dihydrogen or alkane (as in the $\sigma$-complex) *will* affect the observed KIE; there will be different pre-equilibrium concentrations of the $\sigma$-complex available for the subsequent and rate determining "oxidative addition".

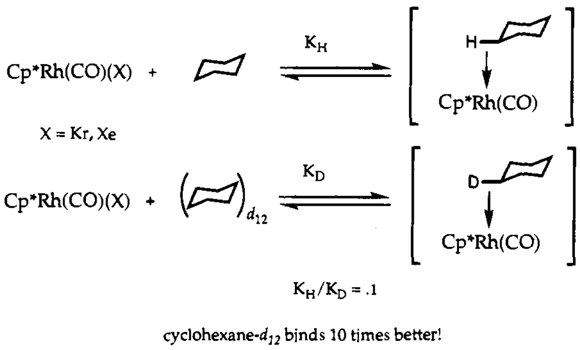

**Figure 4.** Equilibrium isotope effects for the formation of an alkane $\sigma$-complex.

Bergman and co-workers recently reported substantial inverse deuterium equilibrium isotope effects (at 165 K)[40] for the complexation of cyclohexane[34b] and neopentane[34c] and their deuterated isotopologues to the rhodium complex, Cp*Rh(CO), in noble-gas solvents. Those alkanes are thought to form alkane $\sigma$-complex intermediates before subsequent oxidative addition to the metal complex (Figure 4).

The observed inverse effect (deuterated alkane was bound an order of magnitude better than perprotiated alkane) was unusual and was the opposite of what one would have predicted from simple changes in CH-stretching frequencies alone; presumably, a CH(D) force constant is weakened in the $\sigma$-complex and thus deuterium should favor the stronger force constant, i.e., deuterated alkane should "prefer" to remain uncomplexed when compared with perprotioalkane. Bergman and co-workers rationalized the observed "inverse" effect by explaining that the alkane $\sigma$-complex gains additional isotope-sensitive vibrational modes upon complexation and that the zero-point energy for the deuterated alkane $\sigma$-complex is therefore lower.[40] This conclusion is supported by our results reported here.

Rabinovich and Parkin recently reported an inverse deuterium EIE for the addition of $H_2$ vs $D_2$ to the tungsten complex, $W(PMe_3)_4I_2$, to form $W(H)_2(PMe_3)_4I_2$ and $W(D)_2(PMe_3)_4I_2$, respectively.[41] This unusual result was not the one predicted from changes in WH(D) and HH(DD) stretching force constants alone, and the authors reasoned that ZPE contributions from additional isotope bending modes present in the dihydride and dideuteride complexes must explain why $D_2$ binds better than $H_2$. The conclusions of Rabinovich and Parkin have been supported theoretically by Goldman and co-workers;[42] the latter study emphasized the importance of both changes in ZPE (from new vibrational modes) and rotational energy contributions to EIE's when dihydrogen and alkanes form dihydride and alkyl hydride complexes, respectively.

## Conclusions

Most of the equilibrium isotope effect for alkene complexation comes from new isotope sensitive vibrational modes, rather than from changes in frequency between reactants and products. When two molecules combine to form one as in eqs 1 and 2, three rotational degrees and three translational degrees of freedom are lost. Several new vibrational modes appear in the formation of the complex because, in general, $3(n + m) - 6$ is greater than the sum $(3n + 3m - 12)$ of the vibrational modes from the two original molecules (where $n$ and $m$ are the number of atoms in the alkene and metal fragment). The appearance of new isotopically sensitive vibrational modes as in the formation of an alkene complex (or $H_2$ and alkane $\sigma$-complexes) will always contribute an "inverse" effect (a molecular separative effect)[11] to the observed EIE because the zero-point energy for the new deuterium sensitive mode(s) is intrinsically lower.

Rotational and translational isotope effects for the complexation of small alkenes (or other small molecules) will oppose the "inverse" zero-point energy factor because deuterium substitution will have a greater effect on the mass and moments of inertia of the smaller, free ligand. In other words, deuterium "prefers" the smaller molecule because of its greater effect on relative inertial energies. Indeed, deuterium substitution significantly changes the rotational energies of small hydrocarbons and may profoundly influence observed KIE's for alkane oxidative addition.[43] Of course, *changes* in particular vibrational frequencies present in both the hydrocarbon and the hydrocarbon complex will also contribute to the observed EIE; however, our analysis (Scheme 1 and Table 4) shows that such changes are compensated by other opposing changes.

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[40] The EIE for the diosmacyclobutane is also temperature dependent. The EIE calculated for eq 3 at 165 K is 0.309 and is thus substantially more "inverse" at that low temperature. The change again comes mainly from one "missing mode". This result implies (1) that Bergman's observed EIE would be substantially less "inverse" at higher temperatures and (2) that an inverse effect of 0.1 could be caused by the appearance of only 2–3 new isotope sensitive modes for the alkane $\sigma$-complex formation *at 165 K.*

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