Equilibrium Isotope Effect for the $W(CO)_3(PCy_3)_2(H)_2/W(Co)_3(PCy_3)_2(\eta^2\text{-}H_2)$ Tautomeric Equilibrium: A Nuclear Dynamics Variable Representation Study

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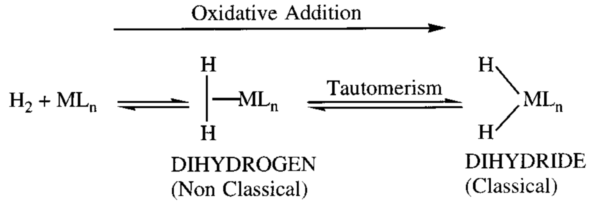
Experimental determination of the equilibrium isotope effect for the dihydride/dihydrogen tautomerism (EIE_T) in the Kubas complex $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ has not yet been achieved because of the lack of vibrational frequencies for the dihydride form. Even so, Bender, Kubas, Hoff, and co-workers[3] have estimated a normal EIE_T, which predicts that deuterium favors the classical site at 300 K. In this work, EIE_T for the Kubas complex tautomerism is theoretically studied by using two levels of calculation. First, the standard harmonic oscilator approach is used to obtain the harmonic partition functions and the corresponding harmonic EIE_T, which turns out to be inverse (0.485 at 300 K). Next, anharmonicity is included in some normal modes in order to obtain an improved EIE_T. Following a new scheme developed by our group in a previous work,[5] DVR nuclear calculations over bidimensional potential energy surfaces are employed to obtain the associated anharmonic partition functions and the corresponding anharmonic EIE_T, which turns out to be also inverse (0.534 at 300 K). So, theoretical corrected EIE_T predicts that deuterium favors the nonclassical site at 300 K.

Introduction

Due to its important role in catalytic hydrogenation processes, the coordination of H_2 to a transition metal has been one of the most studied phenomena in the recent organometallic chemistry.[1] Depending on the nature of this interaction, two basic types of compounds have been found: those where molecular H_2 coordinates as a two-electron ligand (nonclassical dihydrogen complexes) and those where the H−H bond has been broken to give two one-electron ligands (classical dihydride complexes). Dihydrogen complexes are often thought as intermediates of an oxidative addition of the H_2 to the metal , but today it is accepted that in certain cases a tautomeric equilibrium can exist between the dihydride and the dihydrogen forms (see Scheme 1).

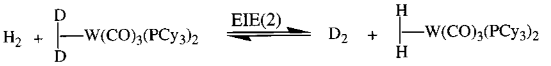
SCHEME 1



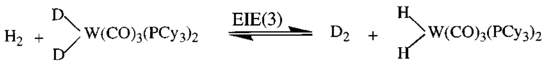
Equilibrium isotope effects (EIE's) for that tautomerism (eq 1) have been reported,[2] but the conclusions diverge to such an extent that, at the moment, no general rule exists concerning whether deuterium favors the classical versus the nonclassical site. Determination of more EIE's would help to understand this reaction, but experimental results in this field are not easy to obtain and, as a consequence, only relatively limited thermodynamic data are available. This is the case for one of the Kubas complexes (the first isolated dihydrogen complexes), whose EIE for the tautomerism has not been strictly resolved because of the lack of experimental data.

$$(\eta^2\text{-}D_2)ML_n + (H)_2ML_n \xrightleftharpoons{EIE_T} (D)_2ML_n + (\eta^2\text{-}H_2)ML_n \quad (1)$$

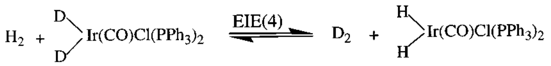
Bender, Kubas, Hoff, and co-workers (BKH) have recently studied[3] the EIE on H_2 binding in the dihydrogen complex $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$. In that work the measured vibrational frequencies arising from the corresponding infrared spectra are used to obtain partition function ratios as described in the general treatment of equilibrium isotope effects by Bigeleisen and Goeppert-Mayer.[4] Once they have the EIE for the H_2 binding in the Kubas complex, they also try to determine the EIE for eq 1 (EIE_T). It can be defined as the quotient between the EIE for the H_2 binding in the dihydrogen form and the EIE for the H_2 binding in the dihydride form. Determining a generic EIE_T is quite ambitious if we remind that, up to now, no regular behavior has been found among all the studied complexes. To overcome this impasse, BKH employ a particular strategy which consists of assuming that the EIE for the addition of H_2 to the Vaska's complex $Ir(CO)Cl(Ph_3)_2$ (0.46 at 300 K) is typical for the $(H)_2ML_n$ case and that the EIE for Kubas complex $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ (0.78 at 300 K) is typical for the $(H_2)ML_n$ case. This allow them to estimate the EIE in eq 1, $EIE_T = EIE(2)/EIE(4)$, and hence to predict in general a normal EIE_T—i.e., that deuterium favors the classical site at 300 K. Finally, they try to test the so predicted EIE_T for the $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ tautomeric equilibrium, but such a validation cannot be achieved because no vibrational frequencies for the dihydride form are available.



$$H_2 + (\eta^2\text{-}D_2)W(CO)_3(PCy_3)_2 \xrightleftharpoons{EIE(2)} D_2 + (\eta^2\text{-}H_2)W(CO)_3(PCy_3)_2 \quad (2)$$



$$H_2 + (D)_2W(CO)_3(PCy_3)_2 \xrightleftharpoons{EIE(3)} D_2 + (H)_2W(CO)_3(PCy_3)_2 \quad (3)$$



$$H_2 + (D)_2Ir(CO)Cl(PPh_3)_2 \xrightleftharpoons{EIE(4)} D_2 + (H)_2Ir(CO)Cl(PPh_3)_2 \quad (4)$$

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Starting from this point, our aim is to contribute to the understanding of the dihydride/dihydrogen tautomerism in the Kubas complex $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ by theoretically obtaining the EIE_T, strictly defined as EIE(2)/EIE(3). In a first step we will calculate it within the harmonic approximation. After that, we will try to improve the results by being more rigorous. In a previous work[5] of our group we concluded that anharmonicity has to be taken into account in order to reproduce and theoretically predict the experimental results concerning many properties of dihydrogen and, probably, polyhydride complexes especially in what refers to isotope effects. Then, in a second step, we will include anharmonicity to correct some normal modes in order to obtain a more accurate EIE_T. This anharmonicity will be introduced by a new scheme derived from quantum nuclear calculations which has been already successfully applied to several dihydrogen complexes.[5]

Calculational Details

In this section we will present the scheme followed to obtain the results of this study. At the same time, we will establish the working conditions, that is, the models that have been assumed, the methods that have been required, and the information that has been borrowed from previous works. The whole process can be divided in two steps: electronic structure calculations; nuclear motion calculations. Both sets of computations are detailed here.

A. Electronic Structure Calculations. In a first step, electronic structure calculations have been done to find the geometry of the minimum energy structures, to compute its molecular partition functions from the harmonic frequencies, and to build up a sizable part of the potential energy surfaces (PES). To save computational effort, the complex under study has been modeled by turning the three cyclohexyl groups into three hydrogen atoms.

All electronic structure calculations have been carried out with the GAUSSIAN 98 series of programs.[6] To solve the electronic Schrödinger equation, the density-functional theory[7] (DFT) methodology has been used. This methodology meets the requirements of high accuracy and reasonable cost and has been employed with great success in the study of several organometallic systems, including dihydrogen and polyhydride complexes.[8,9] The three-parameter hybrid functional of Becke and the Lee, Yang, and Parr correlation functional, widely known as Becke3LYP,[10] has been used. Geometry optimizations have been performed using the Schlegel gradient optimization algorithm using redundant internal coordinates.[11,12]

To reduce the cost of the computations an effective core operator has been used to replace the 60 innermost electrons of the tungsten atom. For the 14 outer electrons of the metal atom the basis set was that associated with the pseudopotential of Hay and Wadt[13] with a standard valence double-ξ LANL2DZ contraction.[11] The basis set for the hydrogen atoms directly attached to the metal was a double-ξ supplemented with a polarization p shell.[14,15] A 6-31G basis set[14] was used for the H atoms attached to a P or a C atom, as well as for carbon and oxygen atoms. The phosphorus atoms were described with the 6-31G(d) basis set.[16]

For each minimum energy structure analytical second derivatives of the energy with respect to the Cartesian coordinates have been computed to obtain the frequencies and eigenvectors associated with each vibrational normal mode within the harmonic approximation. For complexes described by means of pseudopotentials this is a new feature included in GAUSSIAN 98.[6] In this thermochemical calculation, molecular partition functions have also been obtained at 1 atm and 300 K within the ideal gas, rigid rotor, and harmonic oscillator models.

For the dihydrogen form of the studied complex, the minimum energy structure and the harmonic molecular partition functions for the two isotopic versions (H/D) have been taken from a previous paper of our group.[5] For the dihydride form, the geometry for the minimum energy structure has been taken from the authors of ref 17, but all the other magnitudes have been calculated in this work. That dihydride structure accounts[17] for both the spectroscopic and the thermodynamic experimental data.

B. Nuclear Motion Calculations. In this second step, nuclear motion calculations have been carried out to determine vibrational (anharmonic) energy levels and their associated (anharmonic) molecular partition functions.

Anharmonic vibrational energy levels arise from the solution (eigenvalues) of the nuclear Schrödinger equation over a suitable PES built up from electronic calculations. Hence, previously to the nuclear motion study, an adequate PES is required for each minimum energy structure. For the dihydrogen complex, a two-dimensional PES as a function of the interatomic distance between the two hydrogen (deuterium) atoms of the H_2 (D_2) unit of the complex and the distance between the metal atom and the point halfway between those two hydrogen (deuterium) atoms has been taken from our previous work.[5] For the dihydride complex a two-dimensional PES as a function of the interatomic distance between the metal atom and one of the H(D) atoms and the interatomic distance between the metal atom and the other H(D) atom has been constructed. It has to be noted that the two PES coordinates are different from those of the dihydrogen form. This is because the molecular symmetry between the two complexes is different (the criterion we have used to choose these new coordinates is explained in the next section). When the PES is calculated, global relaxation of the rest of geometrical parameters has been allowed.

These two interatomic distances behave as orthogonal coordinates, in such a way that no coupled terms between them appear in the nuclear kinetic operator of the corresponding nuclear Schrödinger equation; that is,

$$\hat{T} = \frac{-\hbar^2}{2\mu_x}\frac{\partial^2}{\partial x^2} + \frac{-\hbar^2}{2\mu_y}\frac{\partial^2}{\partial y^2} \qquad (5)$$

where x and y stand respectively for the H−H and $W-H_2$ distances in the dihydrogen complex and $W-H_A$ and $W-H_B$ distances in the dihydride complex.

To solve the nuclear Schrödinger equation the generic discrete variable representation (DVR) proposed by Colbert and Miller[18] has been used. This method has already been applied with success in the field of organometallic chemistry.[8,19] Computationally, the DVR has great advantages over the more traditional variational basis representation, in which the energy levels are obtained by diagonalization of the matrix representation of the projection of the Hamiltonian operator on a given basis set. In short, the DVR is a grid-point representation instead of a basis set representation, and thus, it facilitates the calculation of the potential energy integrals V_{ij}. In this representation, the potential energy matrix is diagonal,

$$V_{ii'} = \delta_{ii'}V(x_i) \qquad (6)$$

and the kinetic energy matrix is very simple,

$$T_{ii'} = \frac{\hbar^2(-1)^{i-i'}}{2\mu_x\Delta x^2}\begin{Bmatrix} \pi^2/3 & i = i' \\ \dfrac{2}{(i-i')^2} & i \neq i' \end{Bmatrix} \qquad (7)$$

leading to a very sparse Hamiltonian matrix easier to diagonalize than those coming from a basis set representation,

$$H_{ij,i'j'} = T_{ii'}\delta_{jj'} + T_{jj'}\delta_{ii'} + \delta_{ii'}\delta_{jj'}V(x_i, y_j) \qquad (8)$$

Once the grid-point representation of the nuclear Hamiltonian has been built up and diagonalized, the nuclear energy levels obtained have been used to calculate the associated two-dimensional anharmonic vibrational partition function as

$$Q_{\mathrm{anh}} = \sum_j \mathrm{e}^{-Ej/k_{\mathrm{B}}T} \qquad (9)$$

where k_B is Boltzmann's constant and the summatory extends over all the significantly populated vibrational levels of the 2-D PES.

The total vibrational partition function is then calculated by assuming an independent normal mode framework for the rest of the degrees of freedom (i.e. no mode−mode coupling). In this case the vibrational partition function is the product of Q_{anh} with the individual partition functions corresponding to each additional normal mode. To obtain these individual partition functions, one-dimensional PES should be built up as a function of each normal mode. Our transition-metal complex has 17 nuclei, which implies dealing with 45 vibrtional modes. Application of this procedure to each normal mode is a task out of reach. To simplify the calculations we have assumed that all the modes except the ones included in Q_{anh} behave as harmonic oscillators. This assumption is reasonable if most of the anharmonic correction comes from the two modes chosen to define the 2-D PES and, in any case, provides a first approximation to the total anharmonic vibrational partition function of the molecule.

Results and Discussion

In this section we will present the results obtained from the electronic and nuclear calculations. As we outlined in the Introduction, the discussion will be centered on the understanding of the EIE and it will be presented as follows: In a first step, we will consider the harmonic EIE obtained by the standard approach, and in a second step, we will analyze the anharmonic EIE obtained by following our new procedure.

According to the well-known formulas of the statistical thermodinamics,[20] the deuterium equilibrium isotope effect has been calculated as the equilibrium constant of the equilibrium displayed in eq 1. This equilibrium can also be described as eq 2/eq 3, and hence, the EIE_T has been obtained and presented as EIE(2)/EIE(3), that is, as the quotient between EIE for the dihydrogen formation and the EIE for the dihydride formation.

A. Harmonic EIE. First of all, within the harmonic approximation, we have used the molecular partition functions provided by GAUSSIAN 98 for each chemical species in Figure 1 to evaluate the harmonic EIE's. In addition, we have decomposed each EIE as the product of three factors: the translational−rotational contribution (TRANSROT); the factor corresponding to the contribution of the ground vibrational states, that is, only including the zero-point energy levels (ZPE); the factor that appears when the excited vibrational energy levels are taken into account (EXC). The corresponding results are shown in Table 1.

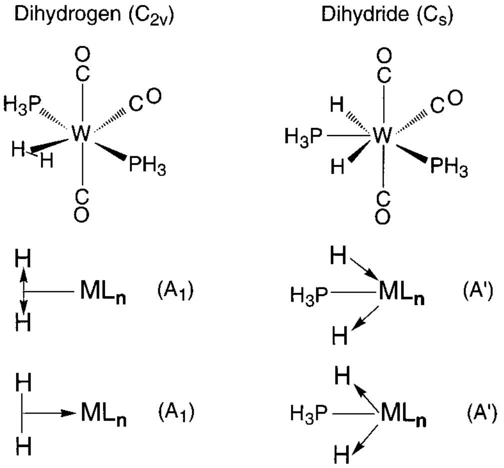

Figure 1. Relevant symmetry coordinates associated with the dihydrogen and the dihydride complexes.

The DFT-calculated harmonic EIE for the dihydrogen formation turns out to be inverse, although numerically is somewhat lesser (that is to say, the isotope effect turns out to be more intense) than the value calculated by BKH[3] from the infrared spectra. The difference stems fundamentally from the ZPE factor, which is the main responsible of the inverse behavior, but that variation is not large enough to be considered a qualitative disaccord. On the other hand, the dihydride formation hardly gives harmonic isotope effect. This is a little surprising if we think that the dihydride complex is almost the same molecule as the dihydrogen one. What has changed? The reason seems to reside on a structural alteration. The dihydrogen structure has a C_{2v} geometry. In turn, the dihydride structure can be described as a pentagonal-bipyramidal C_s complex with axial carbonyls and the two hydrides lying in the equatorial plane being separated by a phosphine ligand[17] (see Figure 1). The P−W−P angle (136.6°) seems large enough to accommodate encumbered phosphines such as PCy_3. In that structure, the two H's cannot be considered as a H_2 unity, and hence, the H−H stretching as such is not a symmetry coordinate contributing to a normal mode anymore. Another result of that coordination change is that the hydrogen motion appears to be more spread out among the normal modes. It participates in a larger number of normal modes, and furthermore, it is more coupled with the motion of the rest of the atoms of the molecule. As a consequence, the relative contribution of the H motion in the dihydride vibrations is less than in the dihydrogen vibrations, and therefore, the normal modes are, in general, less sensitive to the isotopic substitution. That is, the EIE is less important.

Finally, we obtain an inverse EIE_T (EIE for the tautomerism) that differs from the normal EIE predicted by BKH[3], at least within the harmonic approximation. This is not an inconsistency if we bear in mind that they estimate EIE_T as EIE(2)/EIE(4), that is, mixing two different complexes: $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$ as a typical dihydrogen and $(H)_2Ir(CO)Cl(PPh_3)_2$ as a typical dihydride.

B. Anharmonic EIE. As we have previously seen, the first thing we need to do to be able to calculate the anharmonic EIE is to choose which normal modes are to be corrected. A priori, it is not possible to know with certainty which are the most anharmonic normal modes in a molecule, but if we focus on the normal modes which can influence the EIE, we obviously have to consider those associated with the dihydrogen or dihydride ligand.

In the dihydrogen complex the major anharmonicity effect is probably related to the H−H stretching. This motion and the

TABLE 1: Harmonic EIE's and Contributions to Them[a]

	eq 2 $H_2 + (D_2){-}WL_n \rightleftharpoons D_2 + (H_2){-}WL_n$	eq 3 $H_2 + (D)_2{-}WL_n \rightleftharpoons D_2 + (H)_2{-}WL_n$	eq 1 $(D_2){-}WL_n + (H)_2{-}WL_n \rightleftharpoons (H_2){-}WL_n + (D)_2WL_n$
TRANSROT	5.519 (5.77)	5.543	0.996
ZPE	0.131 (0.20)	0.254	0.514
EXC	0.675 (0.67)	0.712	0.948
EIE	0.486 (0.78)	1.002	0.485

[a] Numbers in parentheses correspond to the values calculated by Bender, Kubas, Hoff, and co-workers[3] from the infrared spectra.

W−H_2 stretching are the two A_1 symmetry coordinates associated with the dihydrogen ligand[5] and are pictured in Figure 1. Then, the A_1 normal modes derived from these symmetry coordinates have to be considered as anharmonic modes in the sense defined above. In addition, since that anharmonicity couples significantly the two modes of the same symmertry, the independent normal mode framework has been assumed neglecting all the mode−mode couplings but the coupling between the two A_1 modes that has not been separated. On the other hand, in the dihydride complex the reorganization of the ligands leads to a loss of symmetry and, hence, to a change in the normal modes. Since there is a phosphine between, the two H's behave as independent ligands and not as a H_2-bound molecule. For that reason H−H stretching is not a representative component of the normal modes in the dihydride complex, and consequently, it has not been used as a symmetry coordinate. Among the normal modes that include the motion of the two hydrogen atoms, those where heavy atom motions are negligible have been chosen as the anharmonic modes to be corrected (Figure 1) and, as in the dihydrogen case, not to be separated by the independent normal mode framework. In both dihydrogen and dihydride cases, the two normal modes chosen have been studied together over a two-dimensional PES.

The two-dimensional PES for the dihydrogen complex was already presented in a previous paper as a function of the two symmetry coordinates.[5] A collection of 120 electronic structure calculations, each corresponding to a different set of H−H and W−H_2 distances, covered ranges from 0.6 to 2.0 Å for the H−H distance and from 1.4 to 2.5 Å for the W−H_2 distance. The resulting points were fitted into a two-dimensional cubic splines functional form,[21] which is a smooth and continuous function. Figure 2 depicts the two-dimensional PES as a contour plot.[5] For the dihydride complex a two-dimensional PES has been built up by calculating 56 points, each one corresponding to a different set of W−H_A and W−H_B distances, covering ranges from 1.5 to 2.2 Å for the W−H_A distance and from 1.5 to 2.1 Å for the W−H_B distance. These 56 points are necessary to cover the PES until an energy of at least 10 kcal/mol above the minimum is reached. Since the two hydride ligands are not equivalent, the extent of the W−H_A distance and the W−H_B distance is not exactly the same. It has to be noted that, in this case, the symmetry coordinates used to represent the anharmonic normal modes do not coincide with the axes of the bidimensional PES but with its two diagonals. It has been necessary to expand this PES made of electronic structure calculations. The reason is that DVR results are sometimes difficult to converge due to the fictitious energy gap present at the edge of the PES (the method works as if there were an infinite potential wall at the border). To save computational effort, this enlargement has been done by using a two-dimensional analytic harmonic potential that generates the harmonic frequencies of the two corrected normal modes. The anharmonicity which can affect the EIE is that of the region next to the minimum. Therefore, the use of this supplementary harmonic potential is not incompatible with the introduction of anharmonicity. Figure 3 depicts the resulting two-dimensional PES as a contour plot.

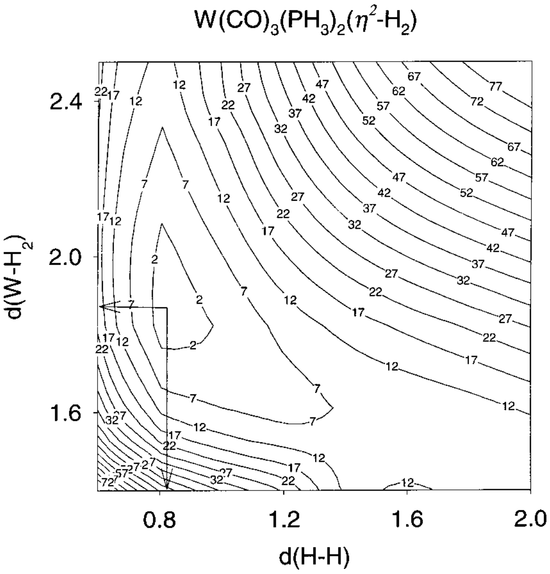

Figure 2. Contour plot of the two-dimensional potential energy surface for the dihydrogen complex $W(CO)_3(PH_3)_2(\eta^2\text{-}H_2)$. Distances are given in Å. Energy contours appear every 5 kcal/mol. The arrows indicate the position of the minimum energy structure (d(H−H) = 0.832 Å and d(W−H_2) = 1.872 Å).

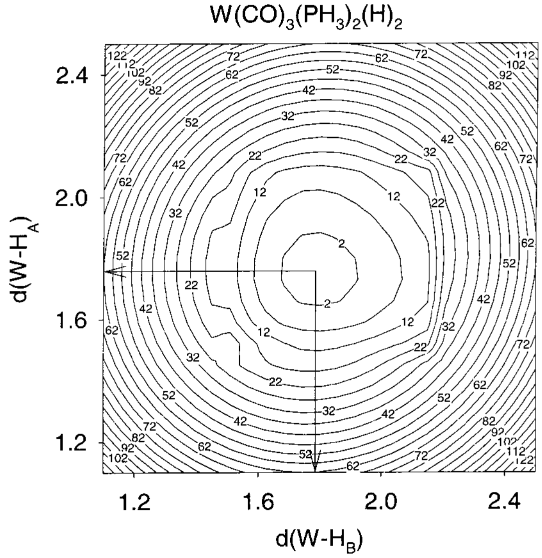

Figure 3. Contour plot of the two-dimensional potential energy surface for the dihydride complex $W(CO)_3(PH_3)_2(H)_2$. Distances are given in Å. Energy contours appear every 10 kcal/mol. The arrows indicate the position of the minimum energy structure (d(W−H_A) = 1.788 Å and d(W−H_B) = 1.753 Å).

Comparison between Figures 2 and 3 discloses some remarkable differences regarding the shape of the two PES in the region of the minima. The dihydride complex presents a typical harmonic pattern with the two normal modes, symmetric and antisymmetric H_A−M−H_B stretching, being the sum and the subtraction of the two W−H distances respectively (that is, the

TABLE 2: Anharmonic EIE's (See Text) and Contributions to Them[a]

	eq 2 $H_2 + (D_2){-}WL_n \rightleftharpoons D_2 + (H_2){-}WL_n$	eq 3 $H_2 + (D)_2{-}WL_n \rightleftharpoons D_2 + (H)_2{-}WL_n$	eq 1 $(D_2){-}WL_n + (H)_2{-}WL_n \rightleftharpoons (H_2)\text{-}WL_n + (D)_2WL_n$
TRANSROT	5.519 (5.77)	5.543	0.996
ZPE	0.143 (0.20)	0.254	0.563
EXC	0.676 (0.67)	0.710	0.952
EIE	0.534 (0.78)	1.001	0.534

[a] Numbers in parentheses correspond to the values calculated by Bender, Kubas, Hoff, and co-workers[3] from the infrared spectra.

two diagonals of the PES in Figure 3). In view of this shape, we can expect that the introduction of anharmonicity will not change significantly the EIE results. Conversely, the potential energy valley for the dihydrogen complex is almost parallel to the W−H_2 axis with a trend to curve along the H−H direction as the W−H_2 distance shortens (Figure 2). As a consequence, the two normal modes of A_1 symmetry, although mixed to some extent (as already pointed out by BKH[3]), can still be identified respectively with the two A_1 symmetry coordinates. That is to say, one normal mode is basically the H−H stretching and the other one is essentially the symmetric M−H_2 stretching. Unlike the dihydride, this energy valley shows some anharmonic character, and hence, in this case we can expect that the introduction of anharmonicity do will change the EIE results.

Once the potential energy surfaces have been obtained, the corresponding nuclear Schrödinger equations can be solved using the DVR method. Prior to that, a certain reduced mass has to be assigned to each degree of freedom in the Hamiltonian. As in our previous works,[7,22] the reduced masses for the motion along the coordinates have been calculated (for the perprotio complexes) as

$$\frac{1}{\mu_{\mathrm{d(H-H)}}} = \frac{1}{m_{\mathrm{H_A}}} + \frac{1}{m_{\mathrm{H_B}}}$$

$$\frac{1}{\mu_{\mathrm{d(M-H_2)}}} = \frac{1}{m_{\mathrm{H_2}}} + \frac{1}{m_{[\mathrm{ML}_n]}} \tag{10}$$

for the dihydrogen complex and

$$\frac{1}{\mu_{\mathrm{d(M-H_A)}}} = \frac{1}{m_{\mathrm{H_A}}} + \frac{1}{m_{[\mathrm{ML}_n\mathrm{H_B}]}}$$

$$\frac{1}{\mu_{\mathrm{d(M-H_B)}}} = \frac{1}{m_{\mathrm{H_B}}} + \frac{1}{m_{[\mathrm{ML}_n\mathrm{H_A}]}} \tag{11}$$

for the dihydride complex. Note that the reduced masses of the dideuterated complexes can be calculated in an analogous way. Then, the matrix representation of the nuclear Hamiltonian over a rectangular grid of equally spaced points has been constructed. Different sizes of each grid have been tested until convergence of the energy levels has been achieved. The characteristics of the final grids chosen for the different systems have been as follows: 35 × 27 = 945 for both the perprotio and the dideuterated dihydrogen complexes and 35 × 35 = 1225 for both the perprotio and the dideuterated dihydride complexes (the format used is the following: number of points along the *x* coordinate × number of points along the *y* coordinate = total number of points). Diagonalization of the corresponding matrixes provides the sets of vibrational wave functions (eigenvectors) and anharmonic energy levels (eigenvalues). These energy levels permit the calculation of the anharmonic vibrational partition function of each molecule according to the procedure outlined in the previous section so that the anharmonic EIE's are obtained. The corresponding anharmonic EIE's are shown in Table 2.

Table 2 exhibits the anharmonic EIE's and their decomposition in factors (evidently the TRANSROT contribution is the same as in Table 1). Comparison of Tables 1 and 2 shows that anharmonicity does not significantly alter the EXC factor. The important changes only concern the ZPE factor. For the dihydride, no changes appear in the anharmonic EIE(3), which means that the harmonic approximation is valid to study the thermochemistry of this complex. For the dihydrogen complex, instead, anharmonicity augments slightly the ZPE contribution and, therefore, the EIE(2). The anharmonic EIE(2), still clearly inverse, is somewhat closer to the experimental values than the harmonic EIE(2). If one takes into account the range of uncertainty of the experimental values[3] (0.78 from infrared spectra or 0.70 ± 0.15 from displacement of N_2) and that anharmonicity has been only partially incorporated, the agreement is rather good. As we saw in our previous work, anharmonicity tends to favor the addition of H_2 because it weakens the lowering of the vibrational energy levels due to the isotopic substitution. The larger the anharmonicity of the normal modes sensitive to the isotopic substitution in the dihydrogen complex, the smaller the gap between the equivalent HH and DD vibrational energy levels. Along the addition in eq 2, the change in the HH/DD zero-point energy gap for the normal mode corresponding originally to the H−H (D−D) stretching in the free hydrogen molecule gives a normal ZPE factor (a value greater than unity). On the contrary, conversion of the 5 translational and rotational modes in free hydrogen to vibrational normal modes in the dihydrogen complex leads to an inverse ZPE factor (a value smaller than unity). As a consequence of all this, anharmonicity increases the numerical value of the ZPE factor associated with the dihydrogen ligand (the normal and inverse factors become more normal and less inverse, respectively), so tending to produce a normal EIE.

The anharmonicity of the dihydrogen complex is reflected in the anharmonic EIE_T for the tautomerism. As in the harmonic results, anharmonic EIE_T turns out to be inverse, although in a less extent.

Conclusions

In this work we have theoretically studied the equilibrium isotope effect for the dihydride/dihydrogen tautomerism (EIE_T) in the Kubas complex $W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)$. Experimental determination of this magnitude has not been achieved due to the lack of vibrational frequencies for the dihydride form. There is only an estimation by Bender, Kubas, Hoff, and co-workers[3] that predicts a normal EIE_T, that is, that deuterium favors the classical site at 300 K.

We have first calculated the harmonic EIE_T arising from the standard thermodynamic analysis (within the ideal gas, rigid rotor, and harmonic oscillator models). Prior to that it has been necessary to characterize the geometry of the minimum energy structures and to compute its molecular partition functions. These electronic DFT calculations have given an inverse EIE_T = 0.485 at 300 K. In view of the difference from the predicted normal behavior, a deeper treatment has been done in order to obtain a more accurated EIE_T. Beyond the harmonic approach, nuclear calculations over bidimensional potential energy surfaces have been performed. Particularly, DVR methodology has been used to obtain the corresponding vibrational energy levels of each structure, and finally, following a new scheme developed by our group in a previous work,[5] anharmonic partition functions have been obtained and used to compute the corrected EIE_T. These nuclear calculations have given again an inverse $EIE_T = 0.534$ at 300 K. Therefore, although being less inverse than the harmonic result, the anharmonic EIE_T also indicates that deuterium favors the nonclassical site at 300 K. This result contrasts with the small normal kinetic isotope effect (KIE) for conversion of the dihydride to the dihydrogen tautomers measured by Hoff and co-workers.[23] However, it has to be realized that the KIE (a kinetic magnitude) and its corresponding EIE (a thermodynamic magnitude) can behave in a different way.

The conclusion outlined above for the Kubas complex is not a general rule which can be applied to any dihydride/dihydrogen tautomerism. The EIE_T has been rigorously calculated here only for the Kubas complex. Actually, several experimental EIE_T's have been reported[2] and conclusions diverge from one complex to another. It seems that this is such an intricate chemical process that no direct extrapolation would be valid to make predictions for whatever dihydride/dihydrogen tautomerism at whatever temperature. With the aim of understanding the dihydride/dihydrogen tautomerism, additional experimental and theoretical studies would be necessary. Work on this topic is now in progress in our laboratory.

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