Quantum Treatment of Hydrogen Nuclei in Primary Kinetic Isotope Effects in a Thermal [1,5]-Sigmatropic Hydrogen (or Deuterium) Shift from (*Z*)-1,3-Pentadiene

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The geometric and kinetic isotope effects (GIE and KIE) for thermal [1,5]-sigmatropic H and D shifts of (*Z*)-1,3-pentadiene were studied by including the direct quantum effect of the migrating H or D nucleus in the multi-component molecular orbital−Hartree−Fock (MC_MO-HF) method. Based on the results, the C^1-D bond lengths are 0.007 Å shorter than the C^1-H bond lengths in both the reactant (**A**) and the transition states (**TS**), whereas other bond lengths resemble those between H and D. The ratio of the rate constant (k_H/k_D) of the reaction for the thermal [1,5]-H and D shifts determined using the MC_MO-HF method (8.28) is closer to the experimental value (12.2) than that determined using either the conventional restricted Hartree−Fock (4.10) or restricted Møller−Plesset second-order perturbation (3.79) methods.

I. Introduction

The thermal [1,5]-sigmatropic hydrogen-shift reaction is not only one of the most important sigmatropic rearrangement reactions,[1] but it is also the most fundamental hydrogen-transfer reaction, and has found many applications in organic synthesis,[2] such as a key step in the synthesis of chiral methyl groups.[2a] (*Z*)-1,3-Pentadiene **A** (Figure 1) is the simplest model for representing thermal [1,5]-sigmatropic hydrogen-shift reactions.[1,3−5] The reaction path of (*Z*)-1,3-pentadiene was first reported by Wolinsky in 1962, who suggested that this reaction proceeds via a six-member transition structure.[6] A suprafacial mode in this reaction is rationalized by the Woodward−Hoffmann rule (Figure 1).[5] The experimental hydrogen/deuterium (H/D) in the kinetic isotope effects (KIE) of the homogeneous gas-phase reaction for (*Z*)-1,3-pentadiene was examined by Roth and König, and is illustrated in Figure 2.[7] The large KIE value of $k_H/k_D = 12.2$ (k_H and k_D refer to the rate constant of the reaction for H and D compounds, respectively) at 298 K, which is derived from the extrapolation from the values in the temperature range 463.4−478.5 K[7] and modified intermediate neglect of differential overlap (MINDO)/2[8] calculations, suggests that the reaction proceeds according to a mechanism that includes a transition structure with C_s symmetry (**TS** in Figure 1).[9] A C_{2v} transition structure was proposed by Kwart et al. based on experimental results[10] and by Dormans and Buck based on unrestricted Hartree−Fock (UHF)/3-21G theoretical calculations,[11] in which five carbon atoms and a migrating hydrogen atom lie in a plane. However, based on Hartree−Fock (HF) calculations by Hess et al.[12,19] and Møller−Plesset second-order perturbation (MP2) calculations by Jensen and Houk,[13] it is now generally accepted that the transition structure has C_s symmetry rather than C_{2v} symmetry. Thermal [1,5]-sigmatropic hydrogen-shift reactions of (*Z*)-1,3-pentadiene and its derivatives have been extensively studied at higher levels of computational methods, including the CBS-QB3 level.[14] Theoretical studies on the substituent effects in the transition structure have also been reported.[15−17]

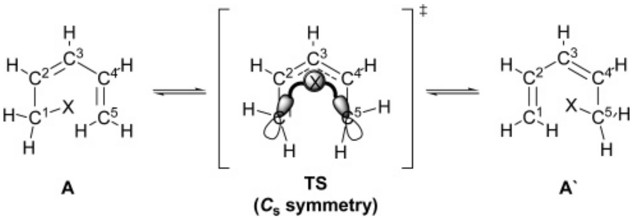

Figure 1. Scheme of the [1,5]-hydrogen shift from (Z)-1,3-pentadiene in a suprafacial mode (X = H or D).

The KIE has also been investigated by using semiempirical and *ab initio* molecular orbital (MO) calculations with the Born−Oppenheimer approximation[18] and with the rigid-rotor−harmonic-oscillator approximation to evaluate zero-point vibrational corrections.[11,19−21] The theoretical k_H/k_D of 3.9[11] (restricted Hartree−Fock (RHF)/3-21G, 298 K) is still much smaller than the measured k_H/k_D of 12.2 at 298 K.[7] At 473 K, the calculated k_H/k_D of 2.53 at the MP2/3-21G level[21] is similar to the calculated k_H/k_D of 2.5 at the HF/3-21G level.[11] However, differences between these theoretical values and the experimental value of 5.1[7] are significant. Although the KIE of the thermal [1,5]-sigmatropic H (or D) shift of (*Z*)-1,3-pentadiene has been known since the 1960’s, the discrepancy is still large between the measured and calculated k_H/k_D values using the

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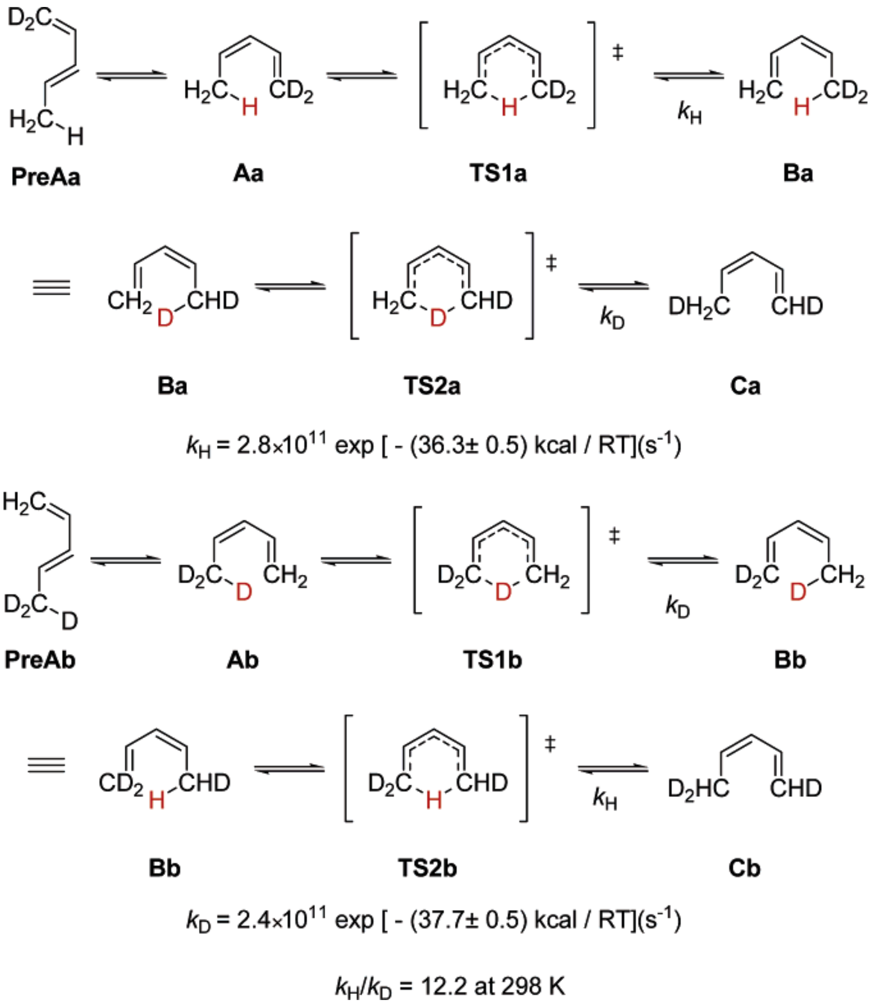

$$k_H = 2.8\times10^{11}\ \exp[-(36.3\pm 0.5)\ \mathrm{kcal}/RT](\mathrm{s}^{-1})$$

$$k_D = 2.4\times10^{11}\ \exp[-(37.7\pm 0.5)\ \mathrm{kcal}/RT](\mathrm{s}^{-1})$$

$$k_H/k_D = 12.2 \text{ at } 298\ \mathrm{K}$$

Figure 2. Experimental KIE value of the thermal [1,5]-sigmatropic hydrogen-shift reaction reported by Roth and König (ref 7).

conventional MO method. This implies that the direct quantum effect of the migrating H or D nuclei must be included in the calculations. Although semiclassical tunneling corrections[22] for the theoretical k_H/k_D values have been used to correct this discrepancy,[20,23] such corrections are little more than adjustments to a model that does not properly account for the quantum effects of the migrating H or D nuclei.[22]

Representing thermal hydrogen-transfer reactions using the conventional MO method with the Born−Oppenheimer approximation is incorrect, because it does not account for the direct response from the wavefunction of nuclear particles to the wavefunction of electronic particles. The wavefunction based on the Born−Oppenheimer approximation is not sensitive to the difference between the nucleic weights of a proton and a deuteron, and the proper behavior of the wavefunction therefore cannot be reproduced with the Born−Oppenheimer approximation. The direct quantum effect of the nuclei of a migrating H atom or D atom is expected to be important for investigating the KIE for the thermal hydrogen-shift reaction. The multicomponent MO (MC_MO) method[24,25] was previously used to determine the KIE for hydrogen abstraction reactions from water or alcohol molecules by an OH radical from the geometric difference created by replacing an H atom with a D atom (the geometric isotope effect, or GIE).[26] Using X-ray crystallographic analysis, in O−H···O hydrogen bonds substituting D for H resulted in small changes in the lattice dimensions showed by Ubbelohde, et al.[27,28] The phrase, "geometric isotope effect" (GIE) was used for the first time in a Finholt and Williams paper on a neutron diffraction study of $D_3O^+CH_3C_6H_4SO_3^-$ in 1973.[29] The correlation between the O−H bond length versus the O···O distance and GIE were actively studied and analyzed by Ichikawa,[30a] followed by many physicists and chemists.[30] GIE cannot be calculated by using the conventional MO method. This is a critical limitation of the conventional MO method with the Born−Oppenheimer approximation for calculating the KIE. In contrast to the conventional MO method, the MC_MO method accounts for the direct quantum effect of the proton (deuteron), because this method simultaneously determines both the electronic and protonic (deuteronic) wavefunctions. The MC_MO method can also account for the different effective potential-energy surfaces, which means the motion of the proton and deuteron is included in the analysis of KIE. The H and D compounds have different geometries because they have different effective potential-energy surfaces. The MC_MO method can successfully analyze the geometric changes induced by the GIE.[26−33] After the first report on the MC_MO method was published, equivalent methods were also reported, such as the nuclear orbital molecular orbital (NOMO)[34] and the nuclear−electronic orbital (NEO) method.[35,36] The hydrogen transfer in malonaldehyde has been examined by using the NEO method with a nuclear basis set with fixed exponents.[35]

The previous computational studies[11,20,21,23] involving a thermal [1,5]-sigmatropic hydrogen (or deuterium) shift of (*Z*)-1,3-pentadiene of pericyclic reactions used the conventional MO method with the Born−Oppenheimer approximation for calculating the KIE; however, the calculated KIE did not match well with the experimental KIE (vide supra). The GIE in these previous computational studies was not used in calculating the

k_H/k_D induced by the H/D KIE. In this study, we therefore report on the continued research of pericyclic reactions[37] and use the MC_MO method to analyze pericyclic reactions by demonstrating the importance of the quantum mechanical treatment of the KIE for the proton or deuteron transfer in a thermal [1,5]-sigmatropic hydrogen (or deuterium) shift of (*Z*)-1,3-pentadiene. Here, the migrating proton or deuteron was modeled by using quantum mechanics, without using semiclassical tunneling corrections. We used the GIE to calculate the k_H/k_D induced by the H/D KIE because the quantum effect of the migrating proton (deuteron) is directly reflected in the geometry and the potential-energy surface of the reaction in the MC_MO method. In addition, both the electronic and protonic (deuteronic) wavefunctions were evaluated, and the difference in the distribution between protonic and deuteronic wavefunctions was determined.

II. MC_MO Method

We first describe the MC_MO method in the framework of the HF approximation. The MC_MO method has been proposed for directly and simultaneously calculating both the electronic and nuclear wavefunctions. The total Hamiltonian of a system composed of N_P nuclear and N_e electronic particles is given by

$$\hat{H}_{\mathrm{MCMO}} = \hat{H}_P + \hat{H}_e + \hat{V}_{p,e} \qquad (1)$$

where $\hat{H}_P$, $\hat{H}_e$, and $\hat{V}_{P,e}$ refer to the contribution from the nuclear particles (*P*), electronic particles (*e*) and from different kinds of particles (*P* and *e*), respectively, and can be represented as

$$\hat{H}_P = \sum_{i\in P}^{N_P}\left\{-\frac{1}{2M_P}\nabla_i^2 + \sum_{i'>i\in P}^{N_i}\frac{Z_P}{r_{ii'}}\right\} \qquad (2)$$

$$\hat{H}_e = \sum_{j\in e}^{N_e}\left\{-\frac{1}{2M_e}\nabla_j^2 + \sum_{j'>j\in e}^{N_j}\frac{Z_e}{r_{jj'}}\right\} \qquad (3)$$

$$\hat{V}_{P,e} = \sum_{i\in P}^{N_P}\sum_{j\in e}^{N_e}\frac{Z_P Z_e}{r_{ij}} \qquad (4)$$

In eqs 2−4, the indices (i,i') and (j,j') represent the nuclear and electronic particles, respectively, M_P and M_e represent the masses of nuclei and electrons, respectively, and Z_P and Z_e represent the nuclear and electronic charges, respectively. In the MC_MO method, a wide variety of particles can be treated as quantum waves. Under the independent-particle (HF) approximation, the total wavefunction is given by

$$\psi_{\mathrm{MCMO}} = \Phi_0^P\cdot\Phi_0^e \qquad (5)$$

where Φ_0^P is either the antisymmetrized wavefunction for fermions (nuclear particles) or the symmetrized wavefunction for bosons (nuclear particles). Φ_0^e is the antisymmetrized wavefunction for electrons. The total energy of this system is given by

$$\begin{aligned}E_{\mathrm{MCMO}} = {} & \sum_{i\in P}^{PMO} n_i^P h_{ii}^P + Z_P^2\sum_{i,i'\in P}^{PMO}[\alpha_{ii'}^P(\phi_i\phi_i|\phi_{i'}\phi_{i'}) + \beta_{ii'}^P \\ & (\phi_i\phi_{i'}|\phi_i\phi_{i'})] + \sum_{j\in e}^{eMO} n_j^e h_{jj}^e + Z_e^2\sum_{j,j'\in e}^{eMO}[\alpha_{jj'}^e(\phi_j\phi_j|\phi_{j'}\phi_{j'}) + \beta_{jj'}^e \\ & (\phi_j\phi_{j'}|\phi_j\phi_{j'})] + Z_p Z_e\sum_{i\in P}^{PMO}\sum_{j\in e}^{eMO} n_i^P n_j^e(\phi_i\phi_i|\phi_j\phi_j)\end{aligned} \qquad (6)$$

where ϕ_i and ϕ_j are the MOs of the nuclear and electronic particles, h_{ii}^P and h_{jj}^e are one-particle integrals, $[(\phi_i\phi_i|\phi_{i'}\phi_{i'}),(\phi_j\phi_j|\phi_{j'}\phi_{j'})]$ and $[(\phi_i\phi_{i'}|\phi_i\phi_{i'}),(\phi_j\phi_{j'}|\phi_j\phi_{j'})]$ are Coulomb and exchange integrals between the same kinds of particles, respectively, and $(\phi_i\phi_i|\phi_j\phi_j)$ is the Coulomb integral between different kinds of particles. The coefficients n_i and n_j are the occupation numbers of ϕ_i and ϕ_j, respectively, α and β are Coulomb and exchange coupling constants, respectively, and *PMO* and *eMO* are the number of MOs in the nuclear and electron particles, respectively.

The electronic and nuclear MOs are expressed as a linear combination of primitive Cartesian Gaussian-type functions (GTFs)

$$\phi_i = \sum_a^{PAO} C_{ai}^P \chi_a^P \qquad (7)$$

$$\phi_j = \sum_b^{eAO} C_{bj}^e \chi_b^e \qquad (8)$$

where *PAO* and *eAO* are the number of GTFs in nuclear and electronic particles, respectively. Equations 7 and 8 include three types of parameters: (a) a linear combination of the GTF (LCGTF) coefficients $C_{ai}^P(a = 1, 2, \cdots, PAO)$ and $C_{bj}^e(b = 1, 2, \cdots, eAO)$, (b) the exponent α of the nucleus in χ_a^P, and (c) the center (*R*) of $\exp\{-\alpha(r-R)^2\}$ in χ_a^P and χ_b^e.

In the conventional linear-combination (LC) GTF-MO method, only LCGTF coefficients are optimized with the variational theorem, whereas the other parameters are fixed. In our approach, we use the fully variational method for molecular orbitals,[38] where all parameters are optimized for both electronic and nuclear GTFs, including LCGTF coefficients, GTF exponents, and their centers, Ω. Because the GTF exponents and centers are mutually dependent, nonlinear optimization must be done. We used the analytical gradient method to do nonlinear optimization, which can be expressed as

$$\begin{aligned}\frac{\partial E_{\mathrm{MCMO}}}{\partial\Omega} = {} & \sum_{i\in P}^{PMO} n_i^P \sum_{u,v}^{PAO} C_u^i C_v^i \frac{\partial h_{uv}^P}{\partial\Omega^P} + Z_P^2\sum_{i,i'\in P}^{PMO}\Bigg[(\alpha_{ii'}^P C_u^i C_v^i C_w^{i'} C_x^{i'} + \\ & \beta_{ii'}^P C_u^i C_v^{i'} C_w^i C_x^{i'})\frac{\partial(uv|wx)}{\partial\Omega^P}\Bigg] - \sum_{i\in P}^{PMO} n_i^P \epsilon_i^P \sum_{u,v\in P}^{PAO} C_u^i C_v^i \frac{\partial S_{uv}^P}{\partial\Omega^P} + \\ & \sum_{j\in e}^{eMO} n_j^e \sum_{q,r}^{eAO} C_q^j C_r^j \frac{\partial h_{qr}^e}{\partial\Omega^e} + Z_e^2\sum_{j,j'\in e}^{eMO}\Bigg[(\alpha_{jj'}^e C_q^j C_r^j C_s^{j'} C_t^{j'} + \\ & \beta_{jj'}^e C_q^j C_r^{j'} C_s^j C_t^{j'})\frac{\partial(qr|st)}{\partial\Omega^e}\Bigg] - \sum_{j\in e}^{eMO} n_j^e \epsilon_j^e \sum_{q,r\in e}^{eAO} C_q^j C_r^j \frac{\partial S_{qr}^e}{\partial\Omega^e} + \\ & Z_p \sum_{i\in P}^{PMO} n_i^P \sum_{u,v\in P}^{PAO} Z_e \sum_{j\in e}^{eMO} n_j^e \sum_{q,r\in e}^{eAO} C_u^i C_v^i C_q^j C_{r\,\partial(uv|qr)/\partial\Omega^{P,e}}^j\end{aligned} \qquad (9)$$

where ϵ_i^P and ϵ_j^e are the nuclear and electronic orbital energies, respectively, $(\partial h_{uv}^P/\partial\Omega^P, \partial h_{qr}^e/\partial\Omega^e)$ and $(\partial(uv|wx)/\partial\Omega^P, \partial(qr|st)/\partial\Omega^e)$ are derivatives of one and two particles of the same kind, respectively, $\partial S_{qr}^e/\partial\Omega^e$ is a derivative of overlapping particles, and $\partial(uv|qr)/\partial\Omega^{P,e}$ is a derivative of two different kinds of particles.

III. Computational Method

The geometries of the reactant (**A**) and the transition state (**TS**) were optimized at the RHF, RMP2, and MC_MO-HF/6-

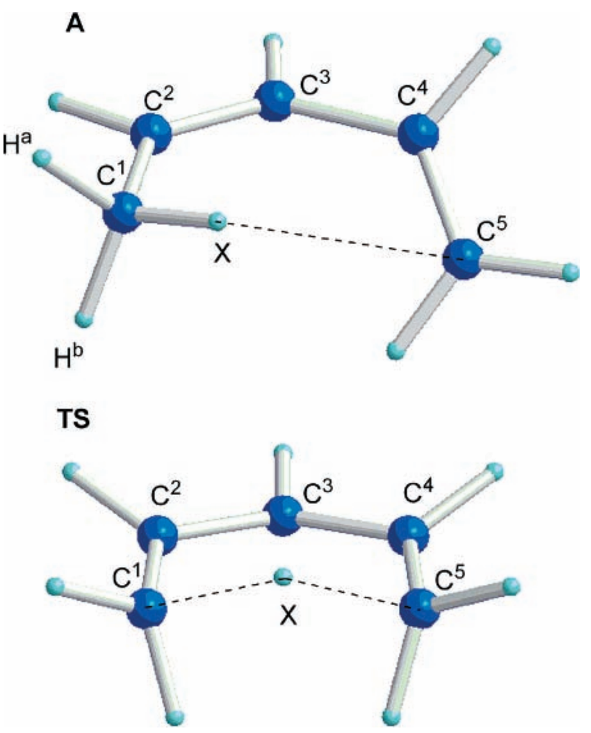

Figure 3. Optimized structures of the reactant (**A**) and transition states (**TS**) for the thermal [1,5]-sigmatropic hydrogen-shift reaction from (Z)-1,3-pentadiene at the MC_MO-HF/6-31++G(d,p) level.

31++G(d,p) levels (Figure 3) with a modified version of the Gaussian 03 code.[39] With the MC_MO-HF method, we follow the minimization with C_s symmetry to obtain the **TS** of the thermal [1,5]-sigmatropic proton (or deuteron) shift from (*Z*)-1,3-pentadiene because it is generally accepted that the transition structure has C_s symmetry.[19,12,13] In our MC_MO-HF calculations, the geometric difference induced by H/D was calculated based on the single *s*-type [1s] GTF, $\exp\{-\alpha(r-R)^2\}$, for each protonic and deuteronic wavefunction. The orbital exponent, α, for the nuclei were optimized numerically. The reactant/product and the **TS** optimized at the RHF/6-31++G(d,p) and RMP2/6-31++G(d,p) levels were fully characterized by normal coordinate analyses. All of the energies reported here were corrected with harmonic zero-point vibrational energies obtained at the RHF/6-31++G(d,p) and RMP2/6-31++G(d,p) levels as in conventional MO calculations. The MC_MO-HF energies themselves include the anharmonic zero-point vibrational energies of the quantum H or D nuclei (in this work, we call these migrating H or D nuclei).

IV. Results and Discussion

A. Geometric Isotope Effect (GIE). We first discuss the H/D GIE obtained using the MC_MO-HF method. Figures 1 and 2 show the reaction path and structures of either the reactant **A** or product **A′** (**A** and **A′** are equivalent) and the **TS** of the thermal [1,5]-sigmatropic proton (or deuteron) shift from (*Z*)-1,3-pentadiene. Table 1 lists bond lengths in the optimized structures of reactant **A** and transition states **TS**. Table 2 lists the bond and dihedral angles.

The calculated C^1-D bond lengths are shorter by 0.007 Å than those of the C^1-H bond in both **A** and **TS** due to the anharmonicity of the potential. Reflecting this geometric change in covalent bonds, the C^5-D hydrogen bond is longer than the C^5-H bond in **A**. It is difficult to directly describe this geometric difference with conventional MO methods. Other bond lengths resemble the difference between MC_MO-HF (X = H) and MC_MO-HF (X = D). In **A**, the angles of $\angle C^1-H-C^5$, $\angle H-C^1-C^2-C^5$, $\angle C^2-C^1-H$, and $\angle H^b-C^1-C^2-C^4$ in the H-transfer are similar to those of the $\angle C^1-D-C^5$, $\angle D-C^1-C^2-C^5$, $\angle C^2-C^1-D$, and $\angle H^b-C^1-C^2-C^4$ angles in the D-transfer reaction, respectively. But in **TS**, only the $\angle C^2-C^1-X$ angles resemble those between MC_MO-HF (X = H) and MC_MO-HF (X = D). Namely, the differences in the angles for calculated structures with the MC_MO-HF method in **TS** are larger than those in **A** between (X = H) and (X = D).

B. Kinetic Isotope Effect (KIE). Next, we discuss the value of k_H/k_D in the thermal [1,5]-sigmatropic H (or D) shift of (*Z*)-1,3-pentadiene. Table 3 lists the activation energies (ΔE_X) and activation enthalpies (ΔH_X) of the reaction from *cisoid* conformer **A** and **TS**. Table 4 lists the calculated k_H/k_D. We estimated k_H/k_D at 298 K as

$$\frac{k_H}{k_D} = \frac{e^{-(\Delta E_H^{\neq}/RT)}}{e^{-(\Delta E_D^{\neq}/RT)}} \tag{10}$$

where *R* is the gas constant and *T* is the absolute temperature. ΔE_X for the D compound is 5.24 kJ/mol higher than that for the H compound, due to the different potential energies between the H and D compounds. The k_H/k_D of 8.28 calculated using the MC_MO-HF/6-31++G(d,p) method is much closer to the experimental k_H/k_D of 12.2[7] than the calculated the k_H/k_D 4.10 and 3.79 using conventional RHF and RMP2 methods, respectively (Table 4). The remaining difference between the MC_MO-HF-calculated and measured k_H/k_D might be due to the lack of nucleus−electron correlations and nucleic diffuse functions in our numerical model and due to the limitation of the transition state theory (TST) approximation.[40]

Next, we compared the calculated k_H/k_D between the MC_MO and conventional MO methods. With the conventional RHF and RMP2 methods, ΔE_X for the D compound is only 3.50 and 3.30 kJ/mol higher than that for the H compound, respectively. The calculated k_H/k_D using the RHF and RMP2 methods are 4.10 and 3.79, respectively. Even using Wigner's tunneling corrections,[41,42] the calculated k_H/k_D values do not agree well with the measured values.[7] Because both the RHF and RMP2 methods are based on the Born−Oppenheimer approximation, these methods give similar values of k_H/k_D. Consequently, the electron−electron correlation method cannot improve the accuracy of the value of k_H/k_D in either the H or D shift reaction. Larger basis sets, however, yield slightly larger k_H/k_D values (4.58) in comparison with previously reported theoretical values (3.9, using RHF/3-21G at 298 K) that were calculated without using semiclassical tunnel corrections.[21] TST has been frequently used to calculate k_H/k_D, and the theoretical values agree well with the measured values for many organic reactions.[43] However, conventional treatments, such as zero-point vibrational corrections, are inadequate for calculating the KIE for the proton and deuteron shifts in this reaction. Therefore, KIE should not be reproduced by methods based on the Born−Oppenheimer approximation. These results clearly demonstrate that the k_H/k_D value of the [1,5]-sigmatropic hydrogen (or deuterium) shift of (*Z*)-1,3-pentadiene is influenced by the direct quantum effect of each X = H (or D) nucleus.

The main reason for achieving acceptable values of the KIE can be clarified by the spatial distribution of either a proton or deuteron. Table 5 lists the optimized orbital exponents for protons and deuterons (α(H) and α(D)) in the **A** and **TS**. These parameters reflect the distribution of the wavefunction of either the proton or deuteron. The wavefunction of the deuteron is more localized than that of the proton, because a deuteron is a

TABLE 1. Bond lengths (Å) in Optimized Structures of the Reactant A and the Transition State TS with 6-31++G(d,p) Basis Sets

	C^1-C^2	C^2-C^3	C^3-C^4	C^4-C^5	C^1-X	C^5-X
			A			
MC_MO (X = H)[a]	1.326	1.480	1.330	1.504	1.105	2.793
MC_MO (X = D)[a]	1.326	1.480	1.330	1.504	1.098	2.795
$\Delta^{\mathbf{A}}_{\mathrm{D-H}}$	0.000	0.000	0.000	0.000	−0.007	0.002
			TS			
MC_MO (X = H)[a]	1.407	1.390	1.390	1.407	1.468	1.468
MC_MO (X = D)[a]	1.408	1.390	1.390	1.408	1.461	1.461
$\Delta^{\mathbf{TS}}_{\mathrm{D-H}}$	0.001	0.000	0.000	0.001	−0.007	−0.007

[a] MC_MO-HF is abbreviated as MC_MO in this table. $\Delta^{\mathbf{A}}_{\mathrm{D-H}}$ is the difference in bond lengths in **A**. $\Delta^{\mathbf{TS}}_{\mathrm{D-H}}$ is the difference in bond lengths in **TS**.

TABLE 2. Bond Angles (Degrees) and Dihedral Angles (Degrees) in Optimized Structures of Reactant A and Transition State TS with 6-31++G(d,p) Basis Sets

	$\angle C^1-X-C^5$	$\angle C^2-C^1-X$	$\angle X-C^1-C^2-C^5$	$\angle H^a-C^1-C^2-C^4$	$\angle H^b-C^1-C^2-C^4$
			A		
MC_MO (X = H)	112.4	112.2	28.6	134.9	−106.9
MC_MO (X = D)	112.5	112.2	28.6	134.8	−106.9
$\Delta^{\mathbf{A}}_{\mathrm{D-H}}$[a]	0.1	0.0	0.0	−0.1	0.0
			TS		
MC_MO (X = H)	129.9	97.3	21.9	151.0	−69.4
MC_MO (X = D)	130.3	97.3	21.7	150.7	−69.6
$\Delta^{\mathbf{TS}}_{\mathrm{D-H}}$[a]	0.4	0.0	−0.2	−0.3	−0.2

[a] $\Delta^{\mathbf{A}}_{\mathrm{D-H}}$ is the difference in bond angles and dihedral angles in **A**. $\Delta^{\mathbf{TS}}_{\mathrm{D-H}}$ is the difference in bond angles and dihedral angles in **TS**.

TABLE 3. Activation Energies (ΔE_X) and Activation Enthalpies (ΔH_X) (kJ/mol) for the Reaction of X = H Compounds and X = D Compounds at 298 K with 6-31++G(d,p) Basis Sets

	ΔE_X[a]	ΔH_X
	(X = H)	
MC_MO	211.69	
RHF	219.88	216.19
RMP2	130.65	126.96
	(X = D)	
MC_MO	216.93	
RHF	223.38	219.60
RMP2	133.95	130.16

[a] ΔE_X of the RHF and RMP2 methods are the zero-point corrected energies. ΔE_X in the MC_MO method is the activation energy without correction of the zero-point energies.

TABLE 4. k_H/k_D Values of the [1,5]-Sigmatropic H Shift at 298 K with 6-31++G(d,p) Basis Sets

	k_H/k_D[a]	k_H/k_D[b]
MC_MO	8.28	
RHF	4.10	4.58 (6.57)
RMP2	3.79	4.22 (5.62)
experiment	12.2[c]	

[a] k_H/k_D was calculated using eq 10. [b] k_H/k_D was calculated using Bigeleisen's equation, and corrected with Wigner's tunneling corrections in parentheses. [c] Reference 7a.

TABLE 5. Optimized Orbital Exponents α(X) for X = H and X = D in Reactants and Product (A) and in Transition State (TS) at the MC_MO-HF/6-31++G(d,p) Level

	A	**TS**
α (H)	24.80	20.60
α (D)	36.45	30.55

heavier particle than a proton. Both $\alpha_{\mathbf{TS}}$ values (i.e., for α(H) and α(D)) are smaller than the respective $\alpha_{\mathbf{A}}$ values, indicating that the proton and deuteron waves become more diffusive (i.e., radiate farther from each atomic center) in **TS** than in **A**. This difference in the wavefunctions of the proton and deuteron between **TS** and **A** is one of the principal factors affecting the KIE.

V. Conclusions

We used the MC_MO-HF method to study the KIE and GIE in the thermal [1,5]-sigmatropic H (or D) shift of (*Z*)-1,3-pentadiene. Our results indicate that the C^1-D bond length is 0.007 Å shorter than the C^1-H bond length in both **A** and **TS**. From the GIE, we found that the C^5-D bond length is longer than the C^5-H bond length in **A**. The differences in the calculated structures using the MC_MO-HF method in **TS** is the difference in **A** between (X = H) and (X = D). With the MC_MO method, the significant difference in GIE between the H and D compounds is the difference in bond angles observed in both **A** and **TS**.

By including the quantum effect of the migrating H or D nucleus in the MC_MO-HF method, the KIE can be directly evaluated from the difference in structure, and the k_H/k_D of 8.28 calculated using the MC_MO-HF method is substantially closer to the measured k_H/k_D of 12.2[7] than the range of 3.79−4.10 calculated using the conventional MO method. Both $\alpha_{\mathbf{TS}}$ values (i.e., for α(H) and α(D)) are smaller than the respective $\alpha_{\mathbf{A}}$ values, indicating that the proton and deuteron waves become more diffusive in **TS** than in **A**. This difference in the wavefunctions of the proton and deuteron between **TS** and **A** is one of the principal factors affecting the GIE. This improvement clearly shows the need for the quantum treatment of the H (or D) nucleus in proton (or deuteron) shift reactions.

Note Added in Proof. The non-Born−Oppenheimer approximation by using *n*-particle correlated Gaussian functions has been reported by Kinghorn and Adamowicz. See: Kinghorn, D. B.; Adamowicz, L. *J. Chem. Phys.* **1997**, *106*, 4589−4595. Cafiero, M.; Bubin, S.; Adamowicz, L. *Phys. Chem. Chem. Phys.* ***2003***, *5*, 1491−1501.

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Supporting Information Available: Cartesian coordinates, energies, and harmonic frequencies of the reactants/product **A**, and transition state **TS** at the RHF/6-31++G(d,p) and the RMP2/6-31++G(d,p) levels, as well as Cartesian coordinates and energies of the reactants, product **A**, and transition state **TS** at the MC_MO-HF/6-31++G(d,p) levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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