Unraveling the Mechanism of Propanoic Acid Hydrodeoxygenation on Palladium using Deuterium Kinetic Isotope Effects

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Abstract

A combined experimental and computational kinetic isotope effect (KIE) study was performed for the catalytic hydrodeoxygenation (HDO) of deuterium-labeled propanoic acid (PAC-2, 2-D₂) over Pd catalyst. For the experimental study, the kinetics were measured in a plug flow reactor over a 5 wt% Pd/C catalyst at 200°C and 1 atm under differential conversion using a reactor feed consisting of 1.2% PAC and 5% or 20% H₂, with balance helium. Different experimental KIE values for the high ($k_H/k_D = 1.13 \pm 0.04$) and low ($k_H/k_D = 1.62 \pm 0.05$) partial pressures of hydrogen were observed. Density functional theory calculations were performed to obtain the reaction parameters of the elementary steps involved in the HDO of PAC on Pd (111), and a microkinetic model was developed to estimate the KIE for the low hydrogen partial pressure case from first principles. The computed result ($k_H/k_D = 1.49$) is in good agreement with the experiment. In addition, the product distribution favored C₂H₆ and CO, suggesting decarbonylation (DCN) is the main reaction pathway. This provides strong evidence for the proposed mechanism for the formation of C₂H₆ on both Pd (111) and supported Pd nanoparticles presenting primarily that exposed crystal face.

Keywords

Kinetic Isotope Effect; Density functional theory; Propanoic acid; Dehydrogenation; Palladium

1. Introduction

An extensive amount of research has explored the catalytic performance for the hydrodeoxygenation (HDO) of biomass-derived carboxylic acids and acid esters [1, 2]. Supported palladium is one of the most investigated catalysts in the area of catalytic hydrodeoxygenation of biomass-derived platform molecules [3-14]. For instance, early studies showed that supported palladium offers a strong activity and selectivity for the HDO of PAc [15-19]. While kinetic studies reveal overall reaction rates, reaction orders, and apparent activation barriers, they do not provide enough information for determining the fundamental elementary steps involved in the reaction mechanism [20, 21]. For HDO reactions, the network of these underlying steps is complex and not yet fully understood.

In our previous DFT studies [22-24] the HDO of PAc was investigated over Pd (111) model surfaces. The elementary reaction steps involved in the decarbonylation (DCN) and decarboxylation (DCX) were identified from first principles (Figure 1). A microkinetic model was developed to determine the dominant pathway and rate-controlling steps under realistic reaction conditions of 200 °C and low, medium, and high partial pressures of hydrogen (0.001, 1 and 30 bar) in the presence and absence of solvents. Our results suggest that under gas phase reaction conditions, DCN is favored over the DCX, while in the presence of water, DCN and DCX mechanisms become essentially competitive [22]. This is in agreement with our experimental study of the gas-phase HDO of PAc over supported group VIII noble metals, where we found that on various metals the DCN pathway dominates [25].

Figure 1. Network of elementary reaction steps considered in the hydrodeoxygenation of Pac over Pd (111). Elementary reactions involved in the DCX mechanism are shown with blue color arrows, DCN reactions are illustrated with red color arrows, and those reactions involved in both mechanisms such as dehydrogenation reactions and removal of the hydrocarbon pool are shown with gray color arrows.

Additionally, computations found that in all reaction environments, and at a low hydrogen partial pressure, dehydrogenation of the α -carbon in Pac is the primary rate-controlling step. With increasing hydrogen partial pressure, C-OH bond dissociation becomes the rate-controlling and the importance of C-H bond cleavage is diminished [22]. The dissociation of the C-OH bond is one of the key reactions in the DCN and was previously also identified as the rate-determining step for the HDO of acetic acid [26, 27]. Our studies, however, clearly suggest that at all

conditions, dehydrogenation steps of the α -carbon of the acid have at least some importance for the HDO of the acid to hydrocarbons. Barteau et al. and Zhong et al. have also examined the deoxygenation of carboxylic acids over Pd [1, 28, 29]. They suggest that a carboxylate intermediate undergoes dehydrogenation, which is accompanied by C-O bond cleavage, resulting in CO and hydrocarbon formation by C-C bond cleavage. Similar work has been reported previously, such as the experimental work of Maier et al. on the gas-phase deoxygenation of octanoic acid [30] and recent computational work on the DCX of butanoic acid by Lamb et al. Their work suggested that dehydrogenation of the α -carbon occurs during DCN/DCX of aliphatic carboxylic acids over Pd [31].

The present study explores the deuterium kinetic isotope effect (KIE) [32-39] for the HDO of PAc in order to further confirm the importance of C-H bond cleavage in the reaction pathway. PAc substituted with deuterium at the α -carbon position ($\text{CH}_3\text{CD}_2\text{COOH}$) was deoxygenated over 5wt% Pd/C catalyst and its reaction rate and TOF compared with that obtained from unlabeled PAc ($\text{CH}_3\text{CH}_2\text{COOH}$). From these data, experimental rate constant ratio ($k_{\text{H}}/k_{\text{D}}$) was determined under various hydrogen partial pressures. Density functional theory (DFT) calculations were performed for labeled PAc and its intermediates on Pd (111) to obtain the reaction parameters of all the elementary steps involved. The DFT-derived parameters were then implemented in a microkinetic model that allowed prediction of $k_{\text{H}}/k_{\text{D}}$ under the same conditions used for the experiments. The experimental and computational results are consistent with each other, and confirm the importance of C-H bond cleavage in governing the rates of HDO of PAc on Pd.

2. Experimental Section

2.1 Materials and Catalyst characterization

The experimental conditions have been previously reported in detail and thus will only be discussed briefly [16]. Propanoic Acid ($\text{CH}_3\text{CH}_2\text{COOH}$, 99%) and propanoic acid-2, 2-d₂ ($\text{CH}_3\text{CD}_2\text{COOH}$, 98%) were purchased from Alfa Aesar and Cambridge Isotope Laboratories, respectively, and used without further purification. The gases for the reactor studies were H_2 (UHP), He (UHP, 99.99%), Ar (UHP, 99.99%) and ethane (CP grade, 99.99%) supplied by Airgas National Welders. The 5wt% Pd/C catalyst (CP-97, $\text{SA}_{\text{BET}} = 615 \text{ m}^2/\text{g}$) was supplied by BASF and reduced *in-situ* at 350°C. The dispersion (16.9%) and mean particle size (6.8 nm) of 5wt% Pd/C was determined by pulsed hydrogen titration of oxygen pre-covered sites utilizing a Micromeritics 2920 AutoChem II Analyzer. Additionally, analysis based on Van Hardeveld and Hartog statistics suggests that for a 6.8 nm particle size, 70-72% of exposed Pd faces correspond to Pd(111), whereas only 16-17% correspond to Pd(100), with the remaining sites made up from corners and edges (which were found to be essentially inactive) [25].

2.2 Reaction Evaluation

The reaction experiments were performed in a single pass, packed bed, plug flow reactor system connected to a GC system (Supporting Information, Scheme S.1). The experiments were carried out under differential (<5%) conversion at 200°C under atmospheric pressure. Two sets of experiments were conducted: (1) 1.2% PAc/20% H_2 /balance He and (2) 1.2% PAc/5% H_2 /balance He in a total flow of 50 sccm. This catalyst under these reaction conditions has previously been shown to be free of both external and internal mass transfer effects [16]. In addition, the carbon support was tested separately and found to exhibit no activity at these reaction conditions [16]. The reaction rate was determined based on the formation of product (which is proportional to the rate of acid disappearance) in $\mu\text{mol product formed}/\text{min} \cdot \text{g}_{\text{cat}}$. The turn over frequency (TOF) was

determined based on the reaction rate per active site in min^{-1} of the 5wt% Pd/C catalyst. Unlabeled and labeled PAc were kept in separate vapor-liquid equilibrium (VLE) saturators (Supporting Information, Scheme S.1) and the concentrations of the both acids (e.g. labeled and unlabeled) in the gas feed were set equal prior to starting the reaction. Once the reaction with unlabeled PAc reached steady-state, the reactor feed was switched to the labeled PAc. This process was cycled until steady state reaction was attained for each species. In this way, the KIE can be determined as the ratio between the unlabeled and labeled TOF (i.e., $k_{\text{H}}/k_{\text{D}}$). Carbon mass balances closed to within 1% in all the experiments and the activity was stable (i.e., no deactivation was observed) over the entire course of the reaction time on stream.

Measurements of the isotopic composition of the products were conducted by mass spectroscopy. To ensure only the products were analyzed by MS, the PAc (unreacted) was condensed in a cold trap (-55°C) (Supporting Information, Scheme S.1). This was verified by analyzing the gas effluent with gas chromatography to confirm only products such as C_2H_6 and CO were detected. The gas products were diluted with argon carrier gas (for a total of 50 sccm) before being sampled by a Stanford Research Systems Residual Gas Analyzer (RGA100) mass spectrometer with an electron multiplier. The detailed description of this apparatus and sampling procedure is included in the Supplemental Information. The masses 29, 30 and 31 were monitored to track various ethane species, while water, nitrogen, oxygen, hydrogen and argon were also monitored to rule out leakage. For the MS study the PAc conversion was increased ($\sim 10\%$) by adjusting the catalyst loading (0.9g).

2.3 Computational Methodology

All density functional theory calculations have been conducted with the Vienna Ab Initio Simulation Package (VASP) [41-43]. The Kohn-Sham valence states are expanded in a plane

wave basis sets with an energy cut-off of up to 400 eV. The interaction between core electrons is described with the projector-augmented wave (PAW) [43, 44] method. The exchange correlation energy is calculated within the generalized gradient approximation (GGA) using the functional form proposed by Perdew and Wang, which is known as Perdew-Wang 91 (PW91) [45-47]. Similar pseudopotentials were used for hydrogen and deuterium atoms with only the mass modified for deuterium atoms.

The lattice constant obtained from the optimization of the fcc-Pd bulk is 3.953 Å, which is in reasonable agreement with the experimental value of 3.891 Å. The surface Brillouin zone is sampled with $4 \times 4 \times 2$ Monkhorst-pack k-point grid. Pd (111) is modeled by a 4-layer slab with a (3×4) surface unit cell and the palladium layers separated by a 15 Å vacuum.

The bottom two layers were fixed to their bulk configuration during all calculations while the top two layers were free to relax in all directions. Adsorption energies of all intermediates were calculated at their most stable geometry by the following equation:

$$E_{ads} = E_{slab+adsorbate} - E_{slab} - E_{adsorbate}(g) \quad (1)$$

where $E_{slab+adsorbate}$ is the total energy of the adsorbed intermediate on the Pd slab, E_{slab} is the total energy of the Pd slab and $E_{adsorbate}(g)$ is the total energy of the adsorbate in the gas phase.

Transition states were obtained from our previous DFT studies [22-24] on PAc and finally, vibrational frequency calculations have been performed to obtain the frequency modes for all labeled intermediates and transition state structures.

The zero-point energy correction for all the structures was taken into account by using the following equation:

$$\Delta E_{ZPE} = \sum_i \frac{1}{2} h \nu_i \quad (2)$$

where h is the Plank constant and ν_i is the vibrational frequency of mode i .

2.4.1 Microkinetic modeling

For surface reactions, the forward rate constant (k_{for}) of each reaction is calculated as:

$$k_{for} = \frac{k_B T}{h} \frac{q_{TS,vib}}{q_{IS,vib}} e^{\frac{-E_{a,for}}{k_B T}} \quad (3)$$

where k_B is the Boltzmann constant, T denotes the reaction temperature, h is the Planck constant, $E_{a,for}$ stands for the zero-point-energy-corrected activation barrier for the forward reaction derived from DFT calculations, and $q_{TS,vib}$ and $q_{IS,vib}$ are the (harmonic) vibrational partition functions for the transition state and the initial state, respectively, i.e., q_{vib} is calculated as:

$$q_{vib} = \prod_i \frac{1}{1 - e^{\frac{-h\nu_i}{k_B T}}} \quad (4)$$

where ν_i is the vibrational frequency of each vibrational mode of the adsorbed intermediate derived from our DFT calculations.

The reverse rate constant (k_{rev}) is calculated similarly and the thermodynamic equilibrium constant K is given by:

$$K = \frac{k_{for}}{k_{rev}} \quad (5)$$

For an adsorption reaction $A(g) + * \rightarrow A^*$, the equilibrium constant K is defined as:

$$K = \frac{(q_{vib})_{A^*}}{(q_{vib} q_{rot} q_{trans})_{A(g)}} e^{\frac{-\Delta E_{ads}}{k_B T}} \quad (6)$$

where $(q_{vib})_{A^*}$ is the vibrational partition function of adsorbed A, and q_{vib} , q_{rot} , q_{trans} stand for vibrational, rotational, and translational partition functions, respectively. ΔE_{ads} represents the zero-point corrected adsorption energy.

For an adsorption reaction $A(g)+* \rightarrow A^*$, the forward rate is given by collision theory with a sticking probability of 1.

$$k_{for} = \frac{1}{N_0 \sqrt{2\pi m_A k_B T}} \quad (7)$$

where N_0 is the number of sites per area ($1.478 \times 10^{19} \text{ m}^{-2}$) and m_A denotes the molecular weight of A.

The reverse rate constant is again given as:

$$k_{rev} = \frac{k_{for}}{K} \quad (8)$$

With the forward and reverse rate constants defined, we solve the full set of steady-state rate equations to obtain the surface coverage of all possible reaction intermediates and the fraction of free sites using the BzzMath library[48] developed by Buzzi-Ferraris. No assumptions were made regarding rate-controlling steps.

3. Results and Discussion

3.1 Kinetic Isotope Effect Measurements

Figure 2A shows the results of the TOF over time during switching between unlabeled ($\text{CH}_3\text{CH}_2\text{COOH}$) and labeled ($\text{CH}_3\text{CD}_2\text{COOH}$) PAc at 200°C and 1 atm with a reactor feed of 1.2% PAc/20% H_2 /balance He. The reaction resulted in differential conversion ($<5\%$) with a 100% selectivity toward C_2H_6 (i.e., there were no side products), with CO indicating decarbonylation (DCN) as the major reaction pathway as described previously [16]. The reaction rates based on the products formed and TOF are summarized in Table 1. The labeled PAc TOF ($0.015 \pm 0.001 \text{ min}^{-1}$) was calculated from the

Figure 2. A) TOF measurements as a function of time on stream for HDO during switching between unlabeled (C-H) and labeled (C-D) PAC. B) Feed analysis as a function of time on stream during the same experiment. Reaction conditions: 200°C, 1 atm, ~1.2% PAC, 20% H₂, balance He.

Table 1. Deuterium isotope effect for PAc HDO over 5wt% Pd/C. Reaction conditions: 200°C and 1 atm, Total flow: 50 sccm. <5% conversion, 100% selectivity C₂H₆. ^a Rxn rate - $\mu\text{mol}/\text{min}\cdot\text{g}_{\text{cat}}$. Rxn 1 = CH₃CH₂COOH/H₂, Rxn 2 = CH₃CD₂COOH/H₂.

20% H ₂ /balance He					5% H ₂ /balance He			
Rxn	Feed conc.	Rxn rate ^a	TOF	$k_{\text{H}}/k_{\text{D}}$	Feed conc.	Rxn rate ^a	TOF	$k_{\text{H}}/k_{\text{D}}$
	(%PAc)		(min ⁻¹)	Exp.	(%PAc)		(min ⁻¹)	Exp.
1	1.19±0.02	1.61±0.16	0.018±0.002		1.22±0.02	1.28±0.15	0.016±0.002	
2	1.16±0.03	1.39±0.05	0.015±0.001	1.13±0.04	1.23±0.01	0.80±0.09	0.010±0.001	1.62±0.05

average of measurements between 45 and 50 hr on stream, while the unlabeled PAc TOF (0.018±0.002 min⁻¹) was calculated from the average of measurements between 37 and 44 hrs on stream. Taking the ratio of these two values, the KIE effect was found to be $k_{\text{H}}/k_{\text{D}} = 1.13 \pm 0.04$. Given this small value, as a comparison, Figure 2B shows the measurement of acid feed concentration (labeled and unlabeled PAc) as a function of time during the same experiment. The feed concentration analysis were conducted every ~2.5 hours to verify there was no change. The variability from labeled to unlabeled feed composition is around 3.0% and a mass balance between 0.99-1.02 is obtained. Given that the reaction order with respect to PAc is ~0.5 order under these conditions [16], such variability does not account for the observed rate difference. Nevertheless, this small ratio of $k_{\text{H}}/k_{\text{D}} = 1.13 \pm 0.04$, indicates that the isotopic substitution at the α -carbon position had little effect under these conditions.

In our previous DFT study, we performed a sensitivity analysis on HDO of propionic acid over Pd (111) model surfaces [22, 23]. Our model suggested that by lowering the partial pressures of hydrogen, the influence of the dehydrogenation of α -carbon on the overall TOF will increase. To

further explore the KIE effect and trend in its relationship with partial pressure of hydrogen, steady-state measurements at 200°C and 1 atm total pressure were conducted at lower hydrogen partial pressure. Figure 3A shows the TOF data as a function of time during switching between unlabeled and labeled PAc using a feed consisting of 1.2% PAc/5% H₂/balance He. The labeled PAc TOF ($0.010 \pm 0.001 \text{ min}^{-1}$) was calculated from the average of measurements between 16 and 19 hr on stream, while the unlabeled PAc TOF ($0.016 \pm 0.002 \text{ min}^{-1}$) was calculated from the average of measurements between 19.5 and 23 hrs on stream. A $k_{\text{H}}/k_{\text{D}}$ ratio of 1.62 ± 0.05 is obtained, suggesting that a significant KIE is present at this lower partial pressure of hydrogen. Once again, Figure 3B shows the measurement of acid feed concentration as a function of time during the same experiment, revealing negligible variation. The significant KIE therefore indicates that the rate-controlling step involves dehydrogenation of the α -carbon (i.e., C-H bond breaking). Indeed, a lower partial pressure of hydrogen should allow for the dehydrogenation of the α -carbon to occur to a greater extent, accounting for the increased KIE.

3.2 Kinetic Isotope Effect Calculations

The positive experimental KIE values obtained above point to the kinetic importance of α -carbon dehydrogenation in the HDO of PAc. According to our previous DFT studies [22, 23], we know that the dehydrogenation of the α -carbon is not the only rate-controlling step under the investigated reaction conditions of 200°C and partial pressures of 0.01 bar of acid and 0.05 bar of H₂. Indeed, the observation that the $k_{\text{H}}/k_{\text{D}}$ ratio varies under different reaction conditions appears to be similar to the changes in the computed degree of rate control [49] of the α -carbon dehydrogenation. Thus, the interpretation of the observed KIE is not straightforward. To initially obtain a meaningful range for the KIE in our system, two limiting theoretical cases were considered. In Section 3.2.1, an upper limit for the KIE is predicted for the case where α -carbon

Figure 3. A) TOF measurements as a function of time on stream for HDO during switching between unlabeled (C-H) and labeled (C-D) PAc. B) Feed analysis as a function of time on stream during the same experiment. Reaction conditions: 200°C, 1 atm, ~1.2% PAc, 5% H₂, balance He.

dehydrogenation is the only rate-controlling step. Next, in Section 3.2.2, it is shown that the k_H/k_D ratio is expected to be approximately 1.0 when C-H bond dissociation is not rate controlling. While labeling PAc could in principle affect other rate-controlling steps through a secondary kinetic isotope effect, this is also shown to be negligible in this system for the limiting case of C-OH bond dissociation being the rate limiting step. Finally, Section 3.2.3 presents a detailed DFT and microkinetic modeling study to estimate the KIE under reaction conditions for a Pd (111) surface from first principles.

3.2.1 Upper Limit for the Primary Kinetic Isotope Effect

Assuming that the dehydrogenation of the α -carbon is the only rate controlling step in the HDO of PAc, the ratio of the turn over frequencies of $\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CD}_2\text{COOH}$ can be approximated using transition state theory as [50-52]:

$$\frac{\text{TOF}_{\text{CH}_3\text{CH}_2\text{COOH}}}{\text{TOF}_{\text{CH}_3\text{CD}_2\text{COOH}}} \approx \frac{k_H}{k_D} \approx \frac{e^{\frac{-(E_a + \Delta\text{ZPE}_H)}{K_B T}}}{e^{\frac{-(E_a + \Delta\text{ZPE}_D)}{K_B T}}} = e^{\frac{-h}{2K_B T} \nu_H (\frac{\nu_D}{\nu_H} - 1)} \quad (9)$$

where E_a is the activation barrier, ΔZPE_H is the zero-point energy correction to the activation barrier for the unlabeled PAc, ΔZPE_D is the zero-point energy correction to the activation barrier for the labeled PAc and ν_H and ν_D are the C-H and C-D (in the α -carbon position) vibrational frequencies, respectively, in PAc.

The maximum C-H frequency for α -carbons observed in carboxylic acids [53] is 3000 cm^{-1} . In addition,

$$\frac{\nu_D}{\nu_H} \approx \sqrt{\frac{\mu_H}{\mu_D}} \quad , \quad \frac{1}{\mu_H} = \frac{1}{m_H} + \frac{1}{m_{\text{CH}_3\text{CHCOOH}}} \quad , \quad \text{and} \quad \frac{1}{\mu_D} = \frac{1}{m_D} + \frac{1}{m_{\text{CH}_3\text{CDCOOH}}} \quad (10)$$

where μ_D and μ_H are the reduced masses for $\text{CH}_3\text{CDCOOH-D}$ and $\text{CH}_3\text{CHCOOH-H}$, respectively, and m_H , m_D , $m_{\text{CH}_3\text{CHCOOH}}$, $m_{\text{CH}_3\text{CDCOOH}}$ are the molecular masses in g mol^{-1} of H (1), D (2), CH_3CHCOOH (73), and CH_3CDCOOH (74), respectively. Combining equations (10) with equation (9) then yields the maximum $\text{KIE} = \frac{\text{TOF}_{\text{CH}_3\text{CH}_2\text{COOH}}}{\text{TOF}_{\text{CH}_3\text{CD}_2\text{COOH}}}$ is calculated to be 3.73. This value is considerably higher (by over a factor of two) than that observed experimentally, suggesting that α -carbon dehydrogenation is not the only rate-controlling step.

3.2.2 Secondary Kinetic Isotope Effect

To estimate the maximum secondary KIE effect for labeled PAc assuming C-OH bond dissociation, we use Equation 9 with a C-OH bond frequency of 1360 cm^{-1} (which is the largest frequency observed in experimental studies [53] for carboxylic acids, which ranges from 1000 to 1360 cm^{-1}). Next, the ratio of ν_D over ν_H can be approximated as:

$$\frac{1}{\mu_H} = \frac{1}{m_{\text{OH}}} + \frac{1}{m_{\text{CH}_3\text{CH}_2\text{CO}}} , \text{ and } \frac{1}{\mu_D} = \frac{1}{m_{\text{OH}}} + \frac{1}{m_{\text{CH}_3\text{CD}_2\text{CO}}} \quad (11)$$

where m_{OH} , $m_{\text{CH}_3\text{CH}_2\text{CO}}$, $m_{\text{CH}_3\text{CD}_2\text{CO}}$ are the molecular masses of OH, $\text{CH}_3\text{CH}_2\text{CO}$, and $\text{CH}_3\text{CD}_2\text{CO}$ which are 17, 57 and 59 g/mol, respectively. As a result, the KIE for the secondary kinetic isotope effect is calculated to be 1.01 which is negligible.

3.2.3 DFT and Microkinetic Modeling Study

Our previous study analyzed the elementary reaction steps involved in the DCN and DCX of PAc on Pd (111) from first principles [22-24]. To computationally investigate the activity of labeled PAc, the adsorption and TS geometries obtained previously for unlabeled PAc were used. DFT frequency calculations were performed for all intermediates involved in the HDO of

labeled PAc to obtain the frequencies of the labeled intermediates needed to compute the zero-point energy corrections and vibrational partition functions of the labeled species. The calculated free energies of reaction (ΔG_{rxn}) and free energies of activation ($G^\ddagger$) for all the labeled elementary reactions, as well as the reaction parameters for the corresponding unlabeled reactions, are listed in Table 2.

Previously, it was found [22, 23] that the dehydrogenation of the α -carbon of PAc ($\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CHCOOH}^{**} + \text{H}^*$) is one of the rate-controlling steps. At 200°C, this step has a free energy of reaction, ΔG_{rxn} , of -0.02 eV and a free energy of activation of 0.70 eV. The correspondent labeled reaction, i.e., the de-deuteration of the α -carbon of labeled PAc (Reaction 2: $\text{CH}_3\text{CD}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CDCOOH}^{**} + \text{D}^*$), has a free energy of reaction, ΔG_{rxn} , of -0.01 eV and a free energy of activation of 0.77 eV indicating that the overall turnover frequency (TOF) of labeled PAc will be slightly slower than that of unlabeled PAc as the barrier of this step was increased by nearly 0.1 eV.

To investigate the overall effects of changes in the reaction parameters on the TOFs, previously developed microkinetic models for the HDO of PAc over Pd (111) [22, 23] were applied to labeled and unlabeled PAc under the reaction conditions identical to the above experimental study (Section 3.1). Accordingly, simulations were carried out at 200°C and partial pressures of H_2 and PAc of 0.05 (5% H_2) and 0.01 (1% PAc) bar, respectively. The partial pressures of H_2O , CO_2 and CO were set to 10^{-3} ; however, the analysis shows that the microkinetic modeling result is insensitive to the partial pressures of these intermediates in the range of 10^{-4} to 10^{-2} bar. In doing so, the partial pressures of these products are fixed, which is necessary since the model does not contain a reaction network for the water-gas shift reaction. Finally, the primary kinetic

Table 2. Reaction free energies (eV), equilibrium and forward rate constants for all elementary reaction steps in the hydrodeoxygenation of labeled PAc over Pd (111) model surfaces at a temperature of 200°C. For comparison reaction free energies and free energies of activation are also shown for unlabeled PAc. Note: * symbolizes a free site.

#	Reaction	Labeled PAc		Unlabeled PAc		Labeled PAc	Labeled PAc
		ΔG_{rxn}	$G^\ddagger$	ΔG_{rxn}	$G^\ddagger$	K_{eq}	$k_{\text{forward}} (\text{s}^{-1})$
1	$\text{CH}_3\text{CD}_2\text{COOH}^* + 3^* \rightarrow \text{CH}_3\text{CD}_2\text{CO}^{***} + \text{OH}^*$	0.45	0.95	0.45	0.97	1.78×10^{-5}	7.30×10^2
2	$\text{CH}_3\text{CD}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CDCOOH}^{**} + \text{D}^*$	-0.01	0.77	-0.02	0.70	1.25	6.95×10^4
3	$\text{CH}_3\text{CD}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CD}_2^* + \text{CO}^* + ^*$	-0.68	0.99	-0.68	1.02	1.85×10^7	2.58×10^2
4	$\text{CH}_3\text{CD}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CDCO}^{**} + \text{D}^*$	0.07	0.89	0.04	0.84	1.99×10^{-1}	3.63×10^3
5	$\text{CH}_3\text{CDCO}^{**} + ^* \rightarrow \text{CH}_3\text{CDCO}^{**} + \text{OH}^*$	0.23	0.88	0.23	0.87	2.83×10^{-6}	3.89×10^3
6	$\text{CH}_3\text{CDCO}^{**} + 2^* \rightarrow \text{CH}_2\text{CDCO}^{***} + \text{H}^*$	-0.35	0.57	-0.36	0.57	5.64×10^3	7.61×10^6
7	$\text{CH}_3\text{CDCO}^{**} + 2^* \rightarrow \text{CH}_3\text{CCO}^{***} + \text{D}^*$	0.01	1.21	-0.03	1.16	7.88×10^{-1}	1.20
8	$\text{CH}_3\text{CDCO}^{**} + ^* \rightarrow \text{CH}_3\text{CD}^{**} + \text{CO}^*$	-0.83	0.99	-0.84	0.98	7.64×10^8	2.81×10^2
9	$\text{CH}_3\text{CDCO}^{**} + 2^* \rightarrow \text{CH}_3\text{CCO}^{***} + \text{D}^*$	-0.34	0.61	-0.37	0.57	3.73×10^3	2.90×10^6
10	$\text{CH}_3\text{CDCO}^{**} + 2^* \rightarrow \text{CH}_2\text{CDCO}^{***} + \text{H}^*$	-0.26	0.58	-0.27	0.58	6.57×10^2	6.69×10^6
11	$\text{CH}_2\text{CDCO}^{***} + ^* \rightarrow \text{CH}_2\text{CDCO}^{***} + \text{OH}^*$	0.61	1.22	0.61	1.22	3.30×10^{-7}	9.51×10^{-1}
12	$\text{CH}_2\text{CDCO}^{***} + ^* \rightarrow \text{CHCD}^{***} + \text{H}^*$	0.06	0.91	0.06	0.91	2.17×10^{-1}	1.98×10^3
13	$\text{CH}_3\text{CCO}^{***} + ^* \rightarrow \text{CH}_3\text{CCO}^{***} + \text{OH}^*$	0.18	0.82	N/A	N/A	1.34×10^{-2}	1.75×10^4
14	$\text{CH}_3\text{CCO}^{***} \rightarrow \text{CH}_3\text{C}^* + \text{CO}^* + ^*$	-1.39	0.47	N/A	N/A	5.76×10^{14}	1.01×10^8
15	$\text{CH}_2\text{CDCO}^{***} + ^* \rightarrow \text{CH}_2\text{CD}^{***} + \text{CO}^*$	-0.79	0.84	-0.76	0.87	2.52×10^8	1.03×10^4
16	$\text{CH}_2\text{CDCO}^{***} + 2^* \rightarrow \text{CHCD}^{***} + \text{H}^*$	0.01	0.68	0.00	0.68	8.79×10^{-1}	5.10×10^5
17	$\text{CHCD}^{***} + 2^* \rightarrow \text{CHCD}^{***} + \text{OH}^*$	0.55	1.10	0.55	1.09	1.34×10^{-6}	2.03×10^1
18	$\text{CHCD}^{***} \rightarrow \text{CHCD}^{***} + \text{CO}^*$	-1.11	0.59	-1.11	0.57	7.16×10^{11}	4.93×10^6
19	$\text{CHCH}^{***} + \text{H}^* \rightarrow \text{CH}_2\text{CH}^{***} + ^*$	0.32	0.93	N/A	N/A	4.27×10^{-4}	1.34×10^3
20	$\text{CH}_2\text{CH}^{***} + \text{H}^* \rightarrow \text{CH}_2\text{CH}_2^{**} + 2^*$	-0.11	0.86	N/A	N/A	1.40×10^1	7.10×10^3
21	$\text{CH}_2\text{CH}^{***} \rightarrow \text{CH}_2\text{C}^{**} + \text{H}^*$	-0.42	0.45	N/A	N/A	3.07×10^4	1.73×10^8
22	$\text{CH}_2\text{C}^{**} + \text{H}^* \rightarrow \text{CH}_3\text{C}^* + 2^*$	-0.27	0.87	N/A	N/A	8.27×10^2	5.44×10^3
23	$\text{CH}_2\text{CH}^{***} + \text{H}^* \rightarrow \text{CH}_3\text{CH}^{**} + 2^*$	0.22	0.78	N/A	N/A	4.27×10^{-3}	4.81×10^4
24	$\text{CH}_3\text{C}^* + \text{H}^* \rightarrow \text{CH}_3\text{CH}^{**}$	0.92	1.11	N/A	N/A	1.68×10^{-10}	1.59×10^1
25	$\text{CH}_3\text{CH}^{**} + \text{H}^* \rightarrow \text{CH}_3\text{CH}_2^* + 2^*$	0.12	0.85	N/A	N/A	5.45×10^{-2}	8.85×10^3
26	$\text{CH}_3\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3\text{CH}_3^* + ^*$	-0.03	0.64	N/A	N/A	2.20	1.64×10^6

27	$\text{CH}_3\text{CH}_2^* + 2^* \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$	-0.44	0.45	N/A	N/A	4.87×10^4	1.72×10^8
28	$\text{CH}_3\text{CD}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CD}_2\text{COO}^{**} + \text{H}^*$	-0.35	0.35	-0.34	0.43	5.10×10^3	1.68×10^9
29	$\text{CH}_3\text{CD}_2\text{COO}^{**} \rightarrow \text{CH}_3\text{CD}_2^* + \text{CO}_2^*$	0.17	1.41	0.16	1.37	1.62×10^{-2}	9.46×10^{-3}
30	$\text{CH}_3\text{CD}_2\text{COO}^{**} + 2^* \rightarrow \text{CH}_3\text{CDCOO}^{***} + \text{D}^*$	0.47	1.33	0.44	1.28	9.30×10^{-6}	6.79×10^{-2}
31	$\text{CH}_3\text{CDCOOH}^{**} + ^* \rightarrow \text{CH}_3\text{CDCOO}^{**} + \text{H}^*$	0.13	0.85	0.12	0.84	3.79×10^{-2}	8.74×10^3
32	$\text{CH}_3\text{CDCOOH}^{**} + ^* \rightarrow \text{CH}_3\text{CD}^{**} + \text{COOH}^*$	0.31	1.40	0.40	1.38	4.64×10^{-4}	1.26×10^{-2}
33	$\text{CH}_3\text{CDCOO}^{***} \rightarrow \text{CH}_3\text{CD}^{**} + \text{CO}_2^*$	-0.39	0.89	-0.39	0.92	1.43×10^4	3.16×10^3
34	$\text{CH}_3\text{CDCOO}^{***} + ^* \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{D}^*$	-0.05	0.89	-0.09	0.85	3.84	2.99×10^3
35	$\text{CH}_3\text{CCOOH}^{***} + ^* \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	0.07	1.01	N/A	N/A	1.85×10^{-1}	1.55×10^2
36	$\text{CH}_3\text{CCOOH}^{***} \rightarrow \text{CH}_3\text{C}^* + \text{COOH}^{**}$	-0.58	0.98	N/A	N/A	1.65×10^6	3.29×10^2
37	$\text{CH}_2\text{CDCOOH}^{***} + ^* \rightarrow \text{CH}_2\text{CD}^{***} + \text{COOH}^*$	0.45	1.79	0.75	2.10	1.78×10^{-5}	9.12×10^{-7}
38	$\text{CH}_3\text{CCOO}^{***} \rightarrow \text{CH}_3\text{C}^* + \text{CO}_2^* + ^*$	-1.13	0.64	N/A	N/A	1.15×10^{12}	1.65×10^6
39	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$	-0.57	0.37	N/A	N/A	1.09×10^6	1.07×10^9
40	$\text{COOH}^{**} \rightarrow \text{CO}^* + \text{OH}^*$	-0.63	0.39	N/A	N/A	4.66×10^6	6.64×10^8
41	$\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* + ^*$	-0.28	0.66	N/A	N/A	1.06×10^3	9.00×10^5

Table 2 (cont.)

#	Reaction	Labeled PAc		Unlabeled PAc		Labeled PAc	Labeled PAc
		ΔG_{rxn}	$G^\ddagger$	ΔG_{rxn}	$G^\ddagger$	K_{eq}	$k_{\text{forward}} (\text{s}^{-1})$
42	$\text{CH}_3\text{CD}^{**} + \text{H}^* \rightarrow \text{CH}_3\text{CDH}^* + 2^*$	0.12	0.84	0.12	0.85	5.64×10^{-2}	1.05×10^4
43	$\text{CH}_3\text{CDH}^* + \text{H}^* \rightarrow \text{CH}_3\text{CDH}_2^* + ^*$	-0.03	0.63	-0.03	0.64	2.35	1.79×10^6
44	$\text{CH}_2\text{CD}^{***} + \text{H}^* \rightarrow \text{CH}_2\text{CDH}^{**} + 2^*$	-0.10	0.86	-0.11	0.86	1.15×10^1	7.46×10^3
45	$\text{CH}_2\text{CD}^{***} + \text{H}^* \rightarrow \text{CH}_3\text{CD}^{**} + 2^*$	0.22	0.78	0.22	0.78	4.62×10^{-3}	4.71×10^4
46	$\text{CH}_3\text{CDH}^* + 2^* \rightarrow \text{CH}_2\text{CDH}^{**} + \text{H}^*$	-0.44	0.45	-0.44	0.45	4.40×10^4	1.49×10^8
47	$\text{CH}_2\text{CDH}_2^* + 2^* \rightarrow \text{CH}_2\text{CDH}^{**} + \text{H}^*$	-0.43	0.46	-0.44	0.45	4.05×10^4	1.25×10^8
48	$\text{CH}_2\text{CDH}_2^* + \text{H}^* \rightarrow \text{CH}_3\text{CDH}_2^* + ^*$	-0.03	0.64	-0.03	0.64	2.16	1.80×10^6
49	$\text{CHCD}^{***} + \text{H}^* \rightarrow \text{CH}_2\text{CD}^{***} + ^*$	0.32	0.93	0.32	0.93	4.00×10^{-4}	1.35×10^3
50	$\text{CHCD}^{***} + \text{H}^* \rightarrow \text{CHCDH}^{***} + ^*$	0.32	0.93	0.32	0.93	4.25×10^{-4}	1.29×10^3
51	$\text{CHCDH}^{***} + \text{H}^* \rightarrow \text{CHCDH}_2^{**} + 2^*$	0.22	0.78	0.22	0.78	4.89×10^{-3}	4.84×10^4
52	$\text{CHCDH}_2^{**} + \text{H}^* \rightarrow \text{CH}_2\text{CDH}_2^* + 2^*$	0.12	0.85	0.12	0.85	5.46×10^{-2}	9.14×10^3
53	$\text{CH}_3\text{CD}_2^* + \text{H}^* \rightarrow \text{CH}_3\text{CD}_2\text{H}^* + ^*$	-0.03	0.63	-0.03	0.64	2.29	1.88×10^6
54	$\text{CH}_3\text{CD}_2^* + 2^* \rightarrow \text{CH}_3\text{CD}^{**} + \text{D}^*$	-0.09	0.77	-0.12	0.73	8.20	6.22×10^4
55	$\text{CH}_3\text{CD}_2\text{H}^* + ^* \rightarrow \text{CH}_3\text{CDH}^* + \text{D}^*$	0.07	0.72	0.03	0.67	2.02×10^{-1}	2.33×10^5
56	$\text{CH}_2\text{CD}_2^{**} + 2^* \rightarrow \text{CH}_2\text{CD}^{***} + \text{D}^*$	0.99	0.13	0.11	0.97	3.96×10^{-2}	2.56×10^2
57	$\text{CH}_2\text{CD}^{***} \rightarrow \text{CH}_2\text{C}^{**} + \text{D}^*$	-0.39	0.49	-0.42	0.45	1.57×10^4	5.71×10^7
58	$\text{CH}_3\text{CD}^{**} \rightarrow \text{CH}_3\text{C}^* + \text{D}^*$	-0.89	0.19	-0.92	0.19	2.81×10^9	8.73×10^{10}
59	$\text{CH}_3\text{CD}_2\text{COOH} + ^* \rightarrow \text{CH}_3\text{CD}_2\text{COOH}^*$	0.76	N/A	0.74	N/A	8.85×10^{-9}	9.40×10^7
60	$\text{CH}_3\text{CH}_3 + ^* \rightarrow \text{CH}_3\text{CH}_3^*$	0.63	N/A	N/A	N/A	2.09×10^{-7}	1.50×10^8
61	$\text{CH}_2\text{CH}_2 + 2^* \rightarrow \text{CH}_2\text{CH}_2^{**}$	-0.08	N/A	N/A	N/A	7.74	1.55×10^8
62	$\text{H}_2\text{O} + ^* \rightarrow \text{H}_2\text{O}^*$	0.41	N/A	N/A	N/A	4.14	1.93×10^8
63	$\text{CO}_2 + ^* \rightarrow \text{CO}_2^*$	0.74	N/A	N/A	N/A	1.33×10^{-8}	1.24×10^8
64	$\text{CO}^* \rightarrow \text{CO} + ^*$	-1.19	N/A	N/A	N/A	828.13	1.55×10^8
65	$\text{H}_2 + 2^* \rightarrow 2\text{H}^*$	-0.58	N/A	N/A	N/A	6.04	5.80×10^8
66	$\text{CH}_3\text{CDH}_2 + ^* \rightarrow \text{CH}_3\text{CDH}_2^*$	-0.63	N/A	0.63	N/A	2.19×10^{-7}	1.47×10^8
67	$\text{CH}_3\text{CD}_2\text{H} + ^* \rightarrow \text{CH}_3\text{CD}_2\text{H}^*$	-0.63	N/A	0.63	N/A	1.76×10^{-7}	1.45×10^8
68	$\text{CH}_2\text{CDH} + 2^* \rightarrow \text{CH}_2\text{CDH}^{**}$	-0.08	N/A	-0.08	N/A	6.81	1.52×10^8
69	$\text{CH}_2\text{CD}_2 + 2^* \rightarrow \text{CH}_2\text{CD}_2^{**}$	-0.08	N/A	-0.08	N/A	6.90	1.50×10^8
70	$\text{CHCD} + ^* \rightarrow \text{CHCD}^*$	-1.15	N/A	-1.16	N/A	$\frac{1.87 \times 10^1}{2}$	1.58×10^8
71	$\text{HD} + 2^* \rightarrow \text{H}^* + \text{D}^*$	-0.57	N/A	-0.58	N/A	1.24×10^6	4.73×10^8

isotope effect, $KIE = \frac{TOF_{CH_3CH_2COOH}}{TOF_{CH_3CD_2COOH}}$ was calculated to be 1.49 under the experimental reaction conditions. This value is in good agreement with our experimental result of 1.62 under the same reaction conditions. Table 3 summarizes and compares the KIE obtained based on the computational, calculated and experimental approach.

Table 3. Comparison of KIE values based on experimental, calculated and theoretical approaches. * Based on the upper limit for the primary kinetic isotope effect calculations discussed in Section 3.2.1.

Gas phase comp. 1.2% PAC/5% H ₂ /balance He		
k_H/k_D <i>Experimental</i>	k_H/k_D <i>Theoretical(comp.)</i>	k_H/k_D <i>Calculated*</i>
1.62	1.49	3.73

3.3 Extent of Dehydrogenation

Given the confirmation of α -carbon dehydrogenation as an important rate controlling step, the extent of this step under actual reaction conditions was further examined. Mass spectrometric analysis was performed on the reaction products formed for the HDO of labeled and unlabeled PAC, since GC cannot distinguish between various deuterium-labeled ethane products. Masses corresponding to CH₃CH₃ (m/e = 30), CH₃CDH₂ (m/e = 31), and CH₃CD₂H (m/e = 32) were considered. If one C-D bond is broken at the rate-determining step, the product CH₃CDH₂ should be detected. Similarly, if two C-D bonds are broken at the rate-determining step, the product CH₃CH₃ is detected. Lastly, if there is no C-D bond broken at the rate determining step, the product CH₃CD₂H is detected. The latter, however, was not able to be detected since it overlapped with a background of signal at m/e = 32 arising from background O₂⁺ in the MS chamber. Nevertheless, it is highly unlikely that CH₃CD₂H species are formed, given that it

requires C-C bond breaking to occur to form a CH_3CD_2 fragment before H addition, which is not favorable. According to our DFT calculations (Table 2), the C-C bond dissociation in deuterated propanoyl (Reaction 3: $\text{CH}_3\text{CD}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CD}_2^* + \text{CO}^* + *$) has an activation barrier of 0.99 eV, while the activation barrier of C-C bond dissociation in Reaction 14 ($\text{CH}_3\text{CCO}^{***} \rightarrow \text{CH}_3\text{C}^* + \text{CO}^* + *$) was lowered to 0.47 eV. This suggests that propionic acid or propanoyl most likely go through dehydrogenation steps prior to C-C bond dissociations. In this context, if $\text{CH}_3\text{CD}_2\text{H}$ was a dominant product, no KIE would be observed; however, we observe a clear primary KIE.

Analysis of the mass spectrum recorded for the HDO of labeled PAc (Figure S2) shows that both CH_3CDH_2 and CH_3CH_3 are produced (see Supporting Information for detailed description). As can be seen from Table S2, the $\text{CH}_3\text{CDH}_2:\text{CH}_3\text{CH}_3$ ratio is 1:2. Thus, C-C bond rupture in $\text{CH}_3\text{-CH}_2\text{-COOH}$ is favored by a factor of two after both C-H bonds at the $\alpha\text{-C-H}$ position have been broken. These results also strongly support the idea that C-H bond-breaking occurs before C-C bond rupture.

4. Conclusion

Kinetic isotope effects in the HDO of deuterated PAc over Pd catalyst were examined with both experimental and computational approaches. Excellent agreement was found between the KIE found experimentally over Pd/C ($k_{\text{H}}/k_{\text{D}} = 1.62$) versus that estimated by DFT calculations coupled with microkinetic models for Pd(111) ($k_{\text{H}}/k_{\text{D}} = 1.49$). The results confirm that the dehydrogenation of the $\alpha\text{-carbon}$ in PAc is one of the rate-controlling steps, especially under lower partial pressures of hydrogen. In addition, measurements of product distribution suggest that the reaction proceeds through the decarbonylation pathway, and that the associated C-C rupture is most favorable after both of the $\alpha\text{-C-H}$ bonds are broken. These results reaffirm the

advantage of isotope labeling experiments for elucidation of kinetically important steps in catalytic reactions. In particular, the coupling of experiments with modern computational modeling allows for a more detailed and deeper analysis than was previously possible. Further research will focus on similar types of combined studies to elucidate the reaction mechanism of HDO, as well as other reactions important to catalytic biomass conversion.

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Supporting Information Available: Experimental details with respect to the reactor system and mass spectroscopy measurements. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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