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High Selectivity for Primary C−H Bond Cleavage of Propane σ-Complexes on the PdO(101) Surface

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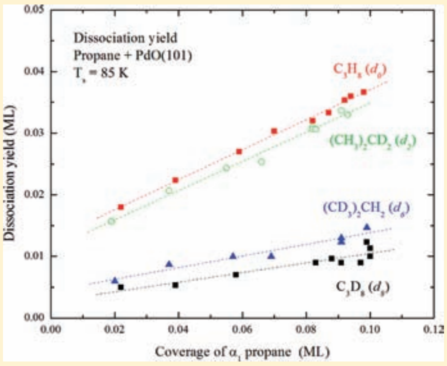
S *Supporting Information*

ABSTRACT: We investigated regioselectivity in the initial C−H bond activation of propane σ-complexes on the PdO(101) surface using temperature programmed reaction spectroscopy (TPRS) experiments. We observe a significant kinetic isotope effect (KIE) in the initial C−H(D) bond cleavage of propane on PdO(101) such that the dissociation yield of C_3H_8 is 2.7 times higher than that of C_3D_8 at temperatures between 150 and 200 K. Measurements of the reactivity of $(CH_3)_2CD_2$ and $(CD_3)_2CH_2$ show that deuteration of the methyl groups is primarily responsible for the lower reactivity of C_3D_8 relative to C_3H_8, and thus that 1° C−H bond cleavage is the preferred pathway for propane activation on PdO(101). By analyzing the rate data within the context of a kinetic model for precursor-mediated dissociation, we estimate that 90% of the propane σ-complexes which dissociate on PdO(101) during TPRS do so by 1° C−H bond cleavage.



INTRODUCTION

Alkane activation by transition metals has attracted considerable interest due to the desire to more effectively utilize these abundant natural resources as energy sources and to develop improved processes to convert alkanes to more valuable chemicals. A significant challenge in this area is the development of catalysts that afford both high activity and precise selectivity toward the initial C−H bond activation of low molecular-weight alkanes. Catalysts capable of selectively activating the primary C−H bonds of alkanes are particularly interesting since the thermodynamic preference is the cleavage of secondary or tertiary C−H bonds. Moreover, selective activation of the CH_3 groups would offer flexibility in developing synthetic processes for directly transforming alkanes to value-added products such as 1-alkenes and primary alcohols.

Alkane activation on transition-metal surfaces has been widely investigated,[1] but only a few studies have focused on characterizing regioselectivity in the initial C−H bond cleavage. On transition metal surfaces, the initial C−H bond selectivity tends to follow the thermodynamically preferred route, at least for the systems that have been investigated in detail. For example, molecularly adsorbed propane exhibits an energetic preference for 2° C−H bond cleavage on Pt(110),[2] Ir(111),[3] and Ru(0001),[4] with the activation energies for 1° versus 2° C−H bond cleavage scaling with the homolytic bond dissociation energies; 410 kJ/mol for 1° C−H bonds, 398 kJ/mol for 2° C−H bonds. For comparison, the zero-point energy difference between C−H and C−D bonds of propane is about 4.5 kJ/mol. Computational studies also report a preference for 2° C−H bond cleavage in the activation of propane on molybdenum oxides[5] and a binary Fe−Sb oxide,[6] which are representative of catalysts used in applications of propane ammoxidation. Likewise, several metal oxide clusters exhibit a preference for 2° C−H bond activation of propane in the gas phase.[7,8] A recent investigation of alkane activation by the gas-phase $MgO^{+\bullet}$ ion is an exceptional case in which 1° C−H bond cleavage of both propane and *n*-butane is preferred.[9]

In prior work we have found that propane activation is highly facile on the PdO(101) surface, with initial C−H bond cleavage occurring readily in ultrahigh vacuum (UHV) below 200 K.[10] Our results reveal that propane activation on PdO(101) occurs by a precursor-mediated mechanism wherein a molecularly adsorbed state acts as a precursor for initial C−H bond cleavage and a kinetic competition between desorption and dissociation of the precursor determines the net dissociation probability. We have presented evidence based on experimental measurements as well as density functional theory (DFT) calculations that alkanes form σ-complexes on PdO(101) by bonding with coordinatively unsaturated (cus) Pd atoms at the surface, and that these complexes act as precursors for initial C−H bond activation.[11,12] DFT calculations show clearly that dative bonding with the cus-Pd atoms significantly weakens the C−H bonds, making them easier to cleave. Finally, our experimental results show that the propyl groups generated during propane activation remain stable on the surface up to at least 400 K, at which point these species

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are completely oxidized by the PdO surface to produce CO_2 and H_2O which desorb.[10] Although partial oxidation products are more desirable, the stability of propyl groups on PdO(101) over a wide temperature range (~200 K) may provide opportunities for steering the chemistry toward more valuable products. Overall, the alkane/PdO(101) system is ideally suited for investigating fundamental aspects of the activation of alkane σ-complexes and the oxidation chemistry of the resulting alkyl groups.

In this paper, we report results of an experimental study of C−H bond selectivity in the low-temperature activation of propane on the stoichiometric PdO(101) surface. Differences in the reactivity among propane isotopologues reveal a strong preference for 1° C−H bond cleavage of propane on PdO(101), with the overall selectivity for generating 1-propyl groups equal to 90% at surface temperatures below 200 K. As far as we know, this study is the first to report a strong preference for 1° C−H bond cleavage in the activation of an alkane adsorbed on a solid surface.

EXPERIMENTAL DETAILS

Previous studies[13,14] provide details of the three-level UHV chamber utilized for the present experiments. The Pd(111) crystal employed in this study is a circular disk (8 mm × ~1 mm) spot-welded to W wires and attached to a copper sample holder that is held in thermal contact with a liquid nitrogen cooled reservoir. Resistive heating, controlled using a PID controller that varies the output of a programmable dc power supply, supports maintaining or linearly ramping the sample temperature from 81 to 1250 K. Initially, sample cleaning consisted of sputtering with 600 eV Ar^+ ions at a surface temperature of 900 K, followed by annealing at 1100 K for several minutes. Subsequent cleaning involved routinely exposing the sample held at 856 K to an atomic oxygen beam for several minutes, followed by flashing the sample to 923 K to desorb oxygen and carbon oxides. As discussed previously,[15] we limited the sample temperature to 923 K to maintain oxygen-saturation in the subsurface reservoir, and thereby ensure reproducibility in preparing the PdO(101) thin films used in this study.

A two-stage differentially pumped chamber attached to the UHV chamber houses the inductively coupled RF plasma source (Oxford Scientific Instruments) utilized to generate beams containing oxygen atoms for this study. We refer the reader to prior work for details of the beam system.[13,14] To produce a PdO(101) thin film, we expose a Pd(111) sample held at 500 K to an ~12 ML dose of gaseous oxygen atoms supplied in a beam, where we define 1 ML (monolayer) as equal to the Pd(111) surface atom density of 1.53×10^{15} cm^{-2}. This procedure generates a high-quality PdO(101) film that has a stoichiometric surface termination, contains ~3.0 ML of oxygen atoms, and is about 12 Å thick.[16,17] The structure of the PdO(101) surface is discussed in detail below.

We studied the reactivity of C_3H_8 (Matheson, 99.993%), $(CH_3)_2CD_2$ (Isotec, 98 atom % D), $(CD_3)_2CH_2$ (Isotec, 98 atom % D), and C_3D_8 (Isotec, 99 atom % D), denoted as propane-d_0, -d_2, -d_6, and -d_8, respectively, on the PdO(101) surface using temperature programmed reaction spectroscopy (TPRS). Each gas was delivered to the sample surface through a molecular beam doser and was used at the purity supplied by the vendor. After the propane exposures, we collected TPRS spectra by positioning the sample in front of a shielded mass spectrometer at a distance of about 10 mm and then heating at a constant rate of 1 K s^{-1} until the sample temperature reached 923 K. Because the PdO film decomposes when heated to 923 K, it was necessary to prepare a fresh PdO thin film for each adsorption/reaction experiment. We monitored the desorption of propane, water, CO_2, and O_2 since prior studies show that these are the only products to evolve from propane-covered PdO(101) during TPRS.[10,11] The majority mass fragment of the propane fragmentation pattern corresponds to the ethyl radical, and the mass-to-charge ratio of this fragment is equal to $m/z = 29$, 31, 32, and 34 for C_3H_8, $(CH_3)_2CD_2$, $(CD_3)_2CH_2$, and C_3D_8, respectively. We generated CO_2 TPRS spectra by subtracting contributions from propane desorption from the measured 44 amu spectra. We estimate absolute coverages and desorption yields using procedures described previously.[10−12]

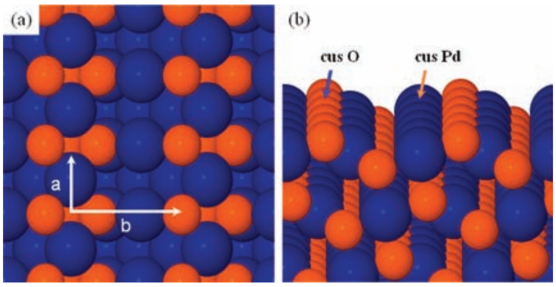

Figure 1. (a) Top and (b) side view of the PdO(101) thin film structure. The orange and blue atoms represent O and Pd atoms, respectively. Rows of 3-fold coordinated (cus) Pd and O atoms are indicated. The *a* and *b* directions correspond to the [010] and $[\bar{1}01]$ crystallographic directions of PdO.

RESULTS AND DISCUSSION

Structure of Stoichiometric PdO(101). A model representation of the stoichiometric PdO(101) surface that we investigated in this study is shown in Figure. 1. Bulk crystalline PdO has a tetragonal unit cell and consists of square planar units of Pd atoms 4-fold coordinated with oxygen atoms. The bulk-terminated PdO(101) surface is defined by a rectangular unit cell, where the *a* and *b* lattice vectors coincide with the [010] and $[\bar{1}01]$ directions of the PdO crystal, respectively. The stoichiometric PdO(101) surface consists of alternating rows of 3-fold or 4-fold coordinated Pd or O atoms that run parallel to the *a* direction shown in Figure 1. Thus, half of the surface O and Pd atoms are coordinatively unsaturated (cus). The side view of PdO(101) shows that the coordinative environment associated with each cus-Pd atom resembles a square planar Pd complex with a coordination vacancy directed away from the surface and three oxygen ligands, one of which is a cus-O atom. The areal density of each type of coordinatively distinct atom of the PdO(101) surface is equal to 35% of the atomic density of the Pd(111) surface. Hence, the coverage of cus-Pd atoms is equal to 0.35 ML, and each PdO(101) layer contains 0.7 ML of Pd atoms and 0.7 ML of O atoms.

Reactivity of Propane Isotopologues on PdO(101) Studied with TPRS. Figure 2 shows TPRS traces for propane and CO_2 obtained in separate experiments in which we adsorbed different propane isotopologues on PdO(101) at 85 K. In these experiments, we initially populated the molecular precursor state (α_1 state) to approximately the saturation coverage (~0.09 ML) where the total coverage of the adsorbed precursor is equal to the amount of molecular precursor which desorbs plus the amount which dissociates and evolves as CO_2 and H_2O. The TPRS traces are presented in units of absolute desorption rates, as determined using established procedures.[10−12] This scaling allows direct comparisons to be made among the TPRS traces obtained from the different propane isotopologues.

Molecularly adsorbed propane desorbs in the two main features centered at 130 and ~195 K, which we denote as the α_2 and α_1 states, respectively. We have previously shown that the more strongly bound α_1 state corresponds to a propane σ-complex(s)

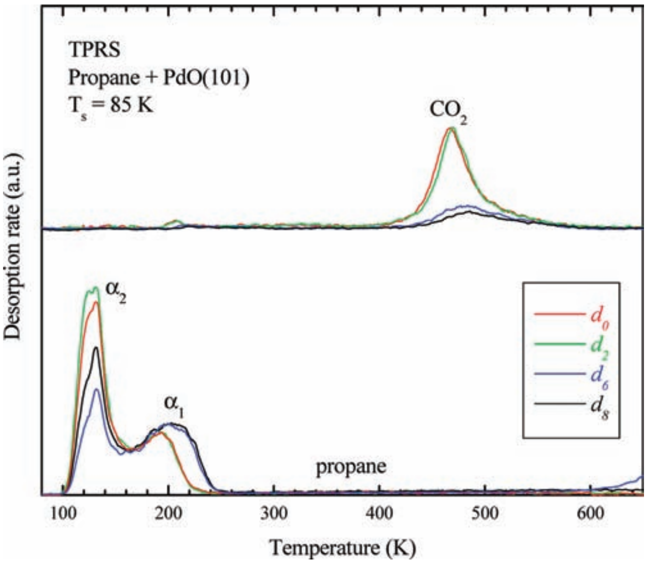

Figure 2. TPRS spectra of CO_2 and the majority propane mass fragment obtained from PdO(101) after saturating the α_1 state of molecularly adsorbed propane at a substrate temperature of 85 K. The initial coverage of propane in the α_1 state was equal to ∼0.09 ML in each experiment. The spectra were obtained in separate experiments using C_3H_8 (d_0), $(CH_3)_2CD_2$ (d_2), $(CD_3)_2CH_2$ (d_6), and C_3D_8 (d_8). The reaction-limited desorption of CO_2 produces the peak at ∼470 K in the CO_2 TPRS traces. The TPRS spectra were obtained using a constant heating rate of 1 K s^{-1}.

and that this state serves as the precursor for initial C−H bond activation.[10−12] A kinetic competition between dissociation and desorption determines the fraction of adsorbed propane σ-complexes which dissociates. Because the resulting molecular fragments are completely oxidized during continued heating, the CO_2 desorption yield is directly proportional to the amount of propane which undergoes C−H(D) bond cleavage below ∼225 K, i.e., below the temperature at which molecularly adsorbed propane completely desorbs. We note that the small features seen near 200 K in the CO_2 TPRS spectra are consistent with trace quantities of CO_2 that are produced by reactions of propane on the UHV chamber walls. We also point out that the total initial coverages in the α_1 state were within 0.005 ML for the TPRS data represented in Figure 2. The initial coverage in the α_2 state exhibits greater variability because it is challenging to ensure saturation of the α_1 state without partially populating the α_2 state. The presence of different amounts of propane in the α_2 state has a negligible influence on the activation of propane adsorbed in the α_1 state.[10]

The TPRS traces reveal a significant kinetic isotope effect (KIE) in the low-temperature activation of propane on PdO(101). When we compare the data obtained from C_3D_8 and C_3H_8, it may be seen that the amount of propane desorbing in the α_1 peak is considerably higher for C_3D_8 than C_3H_8, while the CO_2 yield is proportionally lower. This difference reveals that complete deuteration suppresses the initial bond activation of propane, and thus shifts the kinetic branching away from dissociation of the molecular precursor. On the basis of the CO_2 yields, we estimate that approximately 41% of the C_3H_8 molecules (∼0.037 ML) initially adsorbed in the α_1 state undergo dissociation, and that the dissociation yield for C_3H_8 is about 2.7 times greater than that of C_3D_8 when the α_1 state is initially saturated.

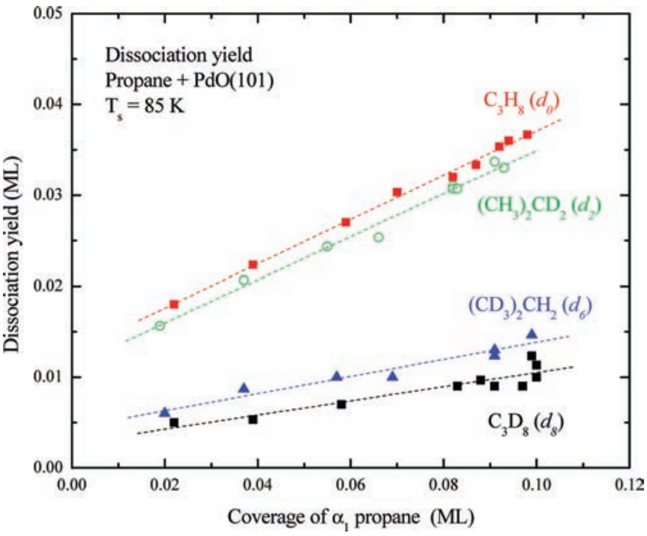

Figure 3. Dissociation yield (ML) versus the initial coverage of propane σ-complexes (α_1 state) on PdO(101) as determined from TPRS experiments at an initial surface temperature of 85 K. The propane dissociation yield is equal to one-third of the CO_2 desorption yield and is estimated from the CO_2 TPRS data. Data is shown for the dissociation of C_3H_8 (d_0), $(CH_3)_2CD_2$ (d_2), $(CD_3)_2CH_2$ (d_6), and C_3D_8 (d_8), and the dashed lines represent linear fits to each data set.

The data further reveals that propane-d_2 is more reactive than propane-d_6 under the conditions examined in the TPRS experiments. In particular, the larger CO_2 peak, as well as the smaller α_1 peak obtained from propane-d_2 compared with propane-d_6, clearly demonstrates that the dissociation probability of propane-d_2 is higher than that of propane-d_6 for the conditions studied. In fact, the results show that the reactivity of propane-d_2 is very similar to that of C_3H_8, while the reactivity of propane-d_6 is close to, although slightly higher than, that of C_3D_8. Thus, selectively deuterating the 1° C−H bonds has a more pronounced effect on the reactivity than does deuteration at the secondary position. The difference in reactivity between propane-d_2 and -d_6 indicates that cleavage of 1° C−H bonds is mainly responsible for the KIE observed upon complete deuteration to C_3D_8 and is therefore the favored pathway for the initial dissociation of propane on PdO(101).

Figure 3 shows the propane dissociation yield as a function of the initial propane coverage in the α_1 state for each isotopologue. The dissociation yield represents the quantity of adsorbed propane which dissociates during TPRS, and is equal to one-third of the measured CO_2 yield. The data shows that the relative differences in reactivity are similar among the propane isotopologues for all of the initial coverages that we investigated, which span about 20% to 100% of the α_1 saturation coverage. This comparison demonstrates that the preference for 1° C−H bond cleavage persists down to low initial coverages of the propane σ-complexes, and must therefore arise primarily from the intrinsic interaction between propane and the PdO(101) surface; intermolecular interactions appear to have only a small influence on the bond selectivity. For each isotopologue, the dissociation yield as a function of the α_1 propane coverage is well-approximated by a linear function over the range of coverages studied. The linear relations serve a practical purpose in analyzing the dissociation data as they provide a convenient way for estimating the dissociation yields of the various isotopologues as a function of the initial propane coverage.

Table 1. Dissociation Yields of Propane Isotopologues as a Function of the Initial Coverage of Propane σ-Complexes (α_1 State) on PdO(101)[a]

α_1 propane coverage (ML)	$\langle S_0 \rangle$	$\langle S_2 \rangle$	$\langle S_6 \rangle$	$\langle S_8 \rangle$	$\tilde{p}_1$ (d_2)	$\tilde{p}_1$ (d_6)	% difference
0.05	0.50	0.46	0.18	0.13	0.84	0.92	8.3%
0.06	0.46	0.42	0.17	0.12	0.86	0.91	6.7%
0.07	0.43	0.40	0.16	0.12	0.87	0.91	4.7%
0.08	0.40	0.38	0.15	0.11	0.88	0.91	3.7%
0.09	0.39	0.36	0.14	0.11	0.88	0.91	2.8%

[a] The dissociation yield is equal to the amount of propane which dissociates divided by the total amount of propane initially adsorbed in the α_1 state. The dissociation yields of C_3H_8 (d_0), $(CH_3)_2CD_2$ (d_2), $(CD_3)_2CH_2$ (d_6), and C_3D_8 (d_8) were calculated from the regression lines shown in Figure 3 and are given in the columns labeled as $\langle S_0 \rangle$, $\langle S_2 \rangle$, $\langle S_6 \rangle$, and $\langle S_8 \rangle$, respectively. The table also shows values of the apparent probability for 1° C−H bond cleavage, $\tilde{p}_1$, that are determined separately using the propane-d_2 and d_6 data. The final column shows the percent difference between the $\tilde{p}_1$ values determined from the d_2 and d_6 data sets.

Quantification of 1° versus 2° C−H Bond Selectivity. To quantify the C−H bond selectivity, we analyzed our data within the context of a kinetic model developed by Weinberg and Sun,[2] after modifying the model to more accurately represent the experimental conditions employed in our study. The Supporting Information provides details of the kinetic model and analysis. The model describes the kinetics for the precursor-mediated dissociation of an alkane on a solid surface, where a molecularly adsorbed state of the alkane serves as the precursor for dissociation and a kinetic branching between desorption and dissociation determines the net dissociation probability. For each TPRS experiment, the measured CO_2 yield relative to the initial coverage of propane in the α_1 state provides an estimate of the net dissociation probability, i.e., the dissociation fraction $\langle S \rangle$.

The kinetic model assumes that an adsorbed propane molecule can dissociate by cleavage of either a 1° or 2° C−H bond, thus affording a 1-propyl versus a 2-propyl group and a hydrogen atom, respectively. The model also neglects secondary kinetic isotope effects and assumes that the desorption rate parameters are identical among the propane isotopologues. Weinberg and Sun[2] define apparent probabilities for 1° versus 2° C−H bond cleavage as $\tilde{p}_1$ and $\tilde{p}_2$, respectively, where $\tilde{p}_1 + \tilde{p}_2 = 1$. The apparent probability $\tilde{p}_1$ represents the conditional probability for the 1° C−H bond cleavage of propane, given that propane reacts. The quantity $\tilde{p}_1$ is also equal to the fraction of 1-propyl fragments that result from the dissociative chemisorption of propane. The definition of $\tilde{p}_2$ follows from that of $\tilde{p}_1$.

Table 1 shows estimates of the dissociation fractions for each isotopologue as a function of the α_1 propane coverage as well as the apparent probabilities for 1° C−H bond cleavage determined separately from the d_2 versus d_6 data sets (see Supporting Information). We limited the analysis to initial propane coverages from 0.05 to 0.09 ML since the measurement uncertainty is higher at lower coverages. The values of $\tilde{p}_1$ vary only slightly with propane coverage in the α_1 state. From the d_2 data, we estimate that $\tilde{p}_1$ increases from 84% to 88%, while the d_6 data predicts a small decrease from 92% to 91% for initial propane coverages increasing from 0.05 to 0.09 ML. Considering experimental uncertainty, the values of $\tilde{p}_1$ are effectively invariant over the range of propane coverages considered. Importantly, the values of $\tilde{p}_1$ determined from the d_2 versus d_6 data are in excellent agreement; the $\tilde{p}_1$ values agree to within better than 3% at the saturation coverage of 0.09 ML. The good agreement between the $\tilde{p}_1$ values lends confidence to the analysis and the validity of the assumptions of the kinetic model.

From the analysis, we estimate that the apparent probability for 1° C−H bond cleavage is equal to 90% when the α_1 state is initially saturated. This result reveals that 90% of the adsorbed propane molecules which dissociate on PdO(101) do so by 1° C−H bond cleavage. After taking into account the different statistical factors for 1° versus 2° C−H bond cleavage, we estimate that the intrinsic probability for 1° C−H bond cleavage is 74%. Thus, the intrinsic probability for 1° C−H bond cleavage of propane on PdO(101) is nearly three times greater than that for 2° C−H bond cleavage for the reaction conditions that we investigated.

The high selectivity for 1° C−H bond cleavage of propane on PdO(101) is interesting and, as far as we know, unprecedented for the activation of alkanes adsorbed on a solid surface. While a preference for 1° C−H bond activation of alkanes appears to be uncommon for heterogeneous transition-metal systems, several organometallic complexes are highly selective toward this reaction.[18−22] For many of these complexes, ancillary ligands cause steric congestion at the metal center which hinders activation of the internal alkane bonds. Strong binding of the 1-alkyl products to the metal center can also promote selectivity toward 1° C−H bond cleavage. DFT calculations that explicitly include dispersion interactions are currently underway to explore the factors which determine regioselectivity in the activation of propane on PdO(101). Although the details are not yet known, the strong preference for 1° C−H bond cleavage is likely associated with the formation of relatively strongly bound propane σ-complexes on the PdO(101) surface. At present, strong dative bonding between alkanes and a solid surface has only been reported for PdO(101).[10−12]

SUMMARY

We conducted TPRS experiments using propane isotopologues to investigate regioselectivity in the initial C−H bond activation of propane on the PdO(101) surface. Our experiments reveal a significant kinetic isotope effect in the C−H(D) bond cleavage of propane on PdO(101) such that the dissociation yield of C_3H_8 is 2.7 times higher than that of C_3D_8 during TPRS at temperatures between ∼150 and 200 K. Experiments using $(CH_3)_2CD_2$ and $(CD_3)_2CH_2$ further demonstrate that deuteration of the methyl groups is largely responsible for the KIE observed upon complete deuteration of propane, and thus that propane activation on PdO(101) occurs preferentially by 1° C−H bond cleavage. By analyzing the dissociation data within the context of a precursor-mediated kinetic model, we estimate that 90% of the propane molecules which dissociate on PdO(101) during TPRS do so by 1° C−H bond cleavage. As far as we know, the present study is the first to report a strong preference for 1° C−H bond cleavage in the initial dissociation of a molecularly adsorbed alkane on a solid surface. Future studies of the interactions of alkanes with the PdO(101) surface may provide opportunities for identifying factors which promote the 1° C−H bond cleavage of alkanes on transition metal oxides.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Description of the kinetic model that was used to analyze the product yield data and obtain estimates of the branching probabilities for 1° and 2° C−H bond cleavage of propane adsorbed on PdO(101). This material is available free of charge via the Internet at http://pubs.acs.org.

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