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Propane σ-Complexes on PdO(101): Spectroscopic Evidence of the Selective Coordination and Activation of Primary C–H Bonds

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Abstract: *Achieving selective C–H bond cleavage is critical for developing catalytic processes that transform small alkanes to value-added products. The present study clarifies the molecular-level origin for an exceptionally strong preference for propane to dissociate on the crystalline PdO(101) surface via primary C–H bond cleavage. Using reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT) calculations, we show that adsorbed propane σ-complexes preferentially adopt geometries on PdO(101) in which only primary C–H bonds datively interact with the surface Pd atoms at low propane coverages and are thus activated under typical catalytic reaction conditions. We show that a propane molecule achieves maximum stability on PdO(101) by adopting a bidentate geometry in which a H–Pd dative bond forms at each* CH_3 *group. These results demonstrate that structural registry between the molecule and surface can strongly influence the selectivity of a metal oxide surface in activating alkane C–H bonds.*

Developing catalytic processes that can transform low molecular-weight alkanes to value-added products remains a significant challenge, yet is critical to improving the utilization of hydrocarbon resources.[1] Catalysts capable of selectively activating the primary C–H bonds of alkanes are particularly important for enabling new routes to synthesize valuable primary alcohols and alkenes. Advances in understanding alkane activation by transition metal compounds are of central importance to these efforts since initial C–H bond cleavage is a critical and often rate-determining step in the catalytic processing of alkanes. Most mechanistic descriptions of alkane functionalization promoted by transition metal complexes consider that an alkane molecule coordinates with the metal center prior to C–H bond cleavage, producing a weakly-bound coordination compound known as an alkane σ-complex.[2,3] Kinetic measurements as well as quantum chemical calculations provide convincing evidence that alkane σ-complexes serve as precursors to C–H bond cleavage by many organometallic complexes.[2,4,5] Notably, however, spectroscopic identification and characterization of alkane σ-complexes is limited to only a few systems.[2,5]

The importance of alkane σ-complexes in heterogeneous catalysis and even the formation of these compounds on solid surfaces is less clear compared with homogeneous systems. A common view is that alkane C–H bond activation on solid surfaces typically occurs via H-atom abstraction by surface radical sites.[6] Short-lived alkane σ-complexes are difficult to detect on a catalyst surface under reaction conditions but their role as precursors to alkane activation has important consequences to our understanding of possible pathways to C–H bond cleavage in heterogeneous catalysis. Early studies using vibrational spectroscopy revealed significant redshifts of C–H stretch bands of alkanes upon adsorption on transition metal surfaces,[7,8] leading researchers to consider the possibility that alkanes experience dative bonding with metallic surfaces. However, contrasting interpretations have highlighted the difficulty in drawing parallels between the binding arising from alkane adsorption on metallic surfaces and the formation of organometallic alkane σ-complexes.[9,10]

In contrast, the binding of adsorbates on transition-metal oxide surfaces seems to more closely resemble the bonding in organometallic complexes,[11,12] suggesting the possibility of establishing clearer connections between the chemical properties of these types of compounds. Indeed, recent studies provide evidence that the formation and facile C–H bond cleavage of alkane σ-complexes is a key feature in the surface chemistry of late transition metal oxides that expose coordinatively unsaturated metal and oxygen atoms.[13]

In the present study, we report spectroscopic evidence for the formation of propane σ-complexes on the PdO(101) surface (Figure 1) and demonstrate their role as precursors for C–H bond cleavage. We show that the preferred configurations of the propane complexes change with increasing propane concentration, and that the dominance of CH_3–Pd coordination is responsible for the high selectivity for primary C–H bond activation under typical reaction conditions. These results represent the first spectroscopic characterization of alkane σ-complexes on an extended crystalline surface, and clarify the molecular origins for the initial C–H bond selectivity of propane on PdO(101).

Figure 2a shows temperature programmed reaction spectroscopy (TPRS) traces of propane, H_2O and CO_2 obtained upon heating a propane monolayer on PdO(101) that was prepared at 90 K in ultrahigh vacuum (UHV). Prior work shows that the PdO(101) films employed in these measurements are highly crystalline with minimal quantities of defects.[11] The propane TPRS trace exhibits peaks at 115 and 132 K that arise from weakly-bound propane, in addition

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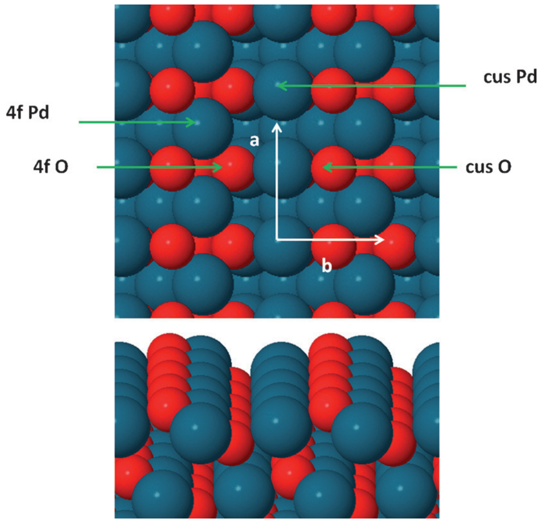

Figure 1. Top and front views of the stoichiometric PdO(101) surface. The red and dark blue atoms represent O and Pd atoms, respectively. Rows of coordinatively unsaturated (cus) and fourfold-coordinated (4f) Pd or O atoms are indicated. The vertical and horizontal arrows a and b represent the [010] and [$\bar{1}$01] crystallographic directions of PdO.

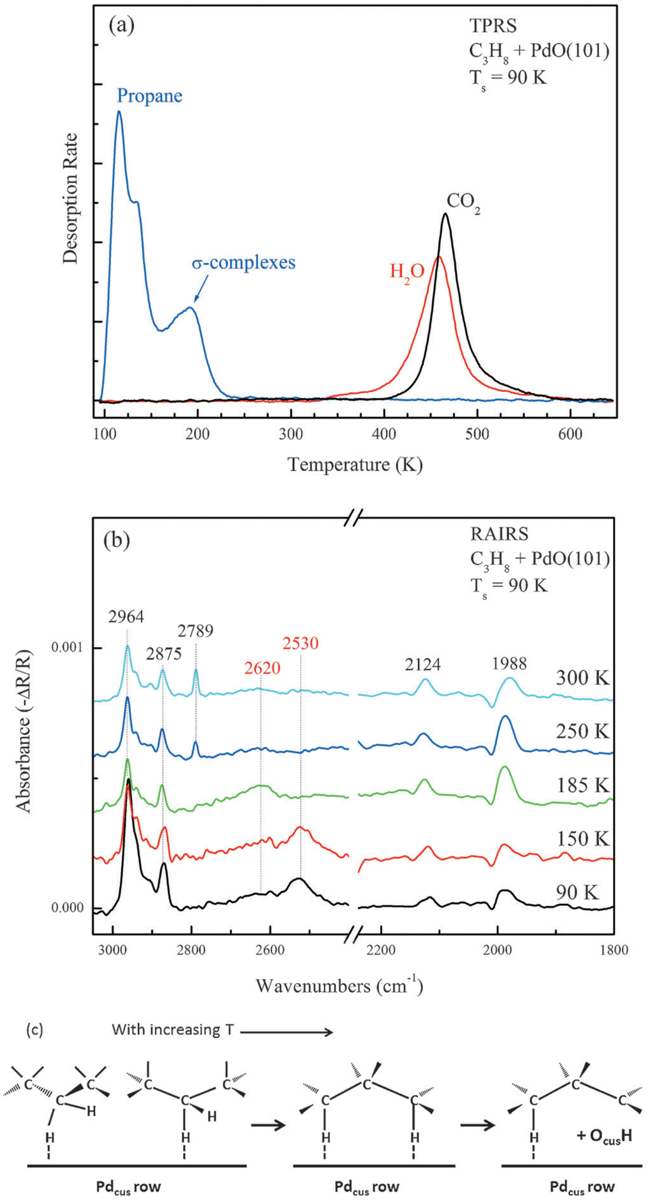

Figure 2. a) TPRS traces of propane, H_2O and CO_2 obtained after saturating a PdO(101) film with undeuterated propane at 90 K.
b) Series of RAIR spectra obtained after heating a saturated propane layer on PdO(101) to the temperatures indicated. Each RAIR spectrum was obtained using a freshly prepared PdO(101) film and the frequencies of softened C–H stretch bands are labeled in red.
c) Schematic illustration showing the evolution of adsorbed configurations of propane on PdO(101) during TPRS.

to a peak at 190 K that originates from more strongly-bound propane σ-complexes.[14] A fraction of the adsorbed propane undergoes C–H bond cleavage rather than desorbing, as evidenced by the production of H_2O and CO_2 above ca. 350 K. Both experiments and DFT calculations demonstrate that the more strongly bound propane σ-complexes are the precursors to propane C–H bond cleavage on PdO(101), and that the weakly bound species contribute negligibly to the observed reactivity.[11]

Figure 2b shows RAIR spectra obtained from a propane layer after heating to selected temperatures between 90 and 300 K. For each RAIRS measurement, we generated a propane monolayer on a freshly prepared PdO(101) film, heated to a specific temperature and then collected the RAIRS data after cooling to 90 K. The RAIRS peaks between 2850 and 3000 cm^{-1} originate from C–H stretch modes of adsorbed propane that are nearly unconstrained ("free") by the surface (i.e., near gas-phase frequencies). The spectrum obtained at 90 K also exhibits two broad C–H stretch bands centered at 2530 and 2620 cm^{-1} that are redshifted by between 300 and 400 cm^{-1} from the nearly free modes. Such significant softening of C–H stretch modes has not been previously reported for alkanes adsorbed on an extended crystalline surface, and is indeed consistent with our earlier reports that the formation of alkane σ-complexes on the PdO(101) surface significantly perturbs C–H bonds.[14]

As seen in Figure 2b, heating to 150 K causes the free C–H stretch bands to attenuate whereas the softened C–H stretch bands change negligibly. Since the weakly-bound species desorb by heating to 150 K, the perseverance of the soft C–H stretch bands indicates that these RAIRS features originate from the more strongly bound propane species. After heating to 185 K, we find that the C–H stretch peak at 2530 cm^{-1} vanishes while the peak at 2620 cm^{-1} intensifies. This change is attributable to a decrease in the coverage of propane σ-complexes that occurs upon heating to 185 K, rather than to other temperature-induced effects. Our interpretation is based on observations that the soft C–H stretch bands change in a similar way as seen in Figure 2b when we vary the propane coverage on PdO(101) at a constant surface temperature of 90 K (see the Supporting Information).

The RAIR spectra also reveal that a fraction of the propane σ-complexes dissociates on PdO(101) and generates adsorbed propyl groups during heating above 185 K. The soft C–H stretch band at 2620 cm^{-1} diminishes significantly after heating to 250 K while a sharp peak at 2789 cm^{-1} becomes evident (Figure 2b). The appearance of a new C–H stretch peak at 2789 cm^{-1}, concurrently with the loss of the soft C–H stretch band, suggests that a fraction of the propane σ-complexes undergo C–H bond cleavage to produce an adsorbed hydrocarbon fragment. RAIRS measurements with propane isotopologues suggest that the peak at 2789 cm^{-1} arises from the interior CH$_2$ group of an adsorbed 1-propyl group. We do not observe RAIRS features that could arise from organic oxygenates after heating to 300 K, and the peaks seen in the C–O stretch region (1988, 2124 cm^{-1}) are consistent with small quantities of CO (<3 % of a monolayer) that adsorb from the vacuum background. The lack of oxidized intermediates observed with RAIRS up to 300 K further supports our interpretation that the peak at 2789 cm^{-1} arises from adsorbed propyl groups. The RAIRS data thus provides spectroscopic evidence that adsorbed propane σ-complexes on PdO(101) serve as precursors to initial dissociation, and that initial C–H bond cleavage produces adsorbed propyl groups that remain stable to temperatures up to at least 300 K. The proposed evolution of propane configurations during TPRS are illustrated in Figure 2c and elaborated below.

We characterized the adsorption of propane isotopologues on PdO(101) to clarify the binding configurations of the propane σ-complexes. Figure 3a and 3b show the RAIRS heating series obtained after generating monolayers of [D$_2$]propane ($CH_3CD_2CH_3$) and [D$_6$]propane ($CD_3CH_2CD_3$) on PdO(101), respectively, for heating temperatures between 90 and 300 K. We note that the soft C–D stretch bands of the alkanes and the C–O stretch bands arising from small quantities of CO contamination lie in a similar range of frequencies, but are sufficiently well-separated to distinguish. We have previously shown that propane exhibits a strong preference for dissociating on PdO(101) via primary C–H bond cleavage, with about 90 % of the reacting propane dissociating by primary C–H bond cleavage during TPRS.[14] Due to primary kinetic isotope effects, [D$_2$]propane is significantly more reactive on PdO(101) compared with [D$_6$]propane, with TPRS dissociation fractions of 36 % versus 14 %. RAIRS measurements in combination with DFT clarify the origin for this high selectivity toward primary C–H bond cleavage.

The RAIR spectrum obtained from a saturated [D$_2$]propane layer prepared on PdO(101) at 90 K exhibits negligible intensity in the region of soft C–H stretch bands (2500 to 2800 cm^{-1}). However, we observe two broad features centered at 1868 and 1920 cm^{-1} that are consistent with soft C–D stretch bands (Figure 3a). The implication is clearly that only CD$_2$ groups of the $(CH_3)_2CD_2$ complexes coordinate with the surface at the saturation coverage, and are thus softened. Interestingly, heating to 150 and 185 K causes the soft C–D stretch bands to diminish while a single, broad feature emerges at roughly 2633 cm^{-1}, which is consistent with the soft C–H stretch band observed for undeuterated propane. Indeed, this change suggests that coordination through the CH$_3$ groups becomes preferred over coordination through the CD$_2$ groups as the coverage of [D$_2$]propane complexes decreases due to desorption.

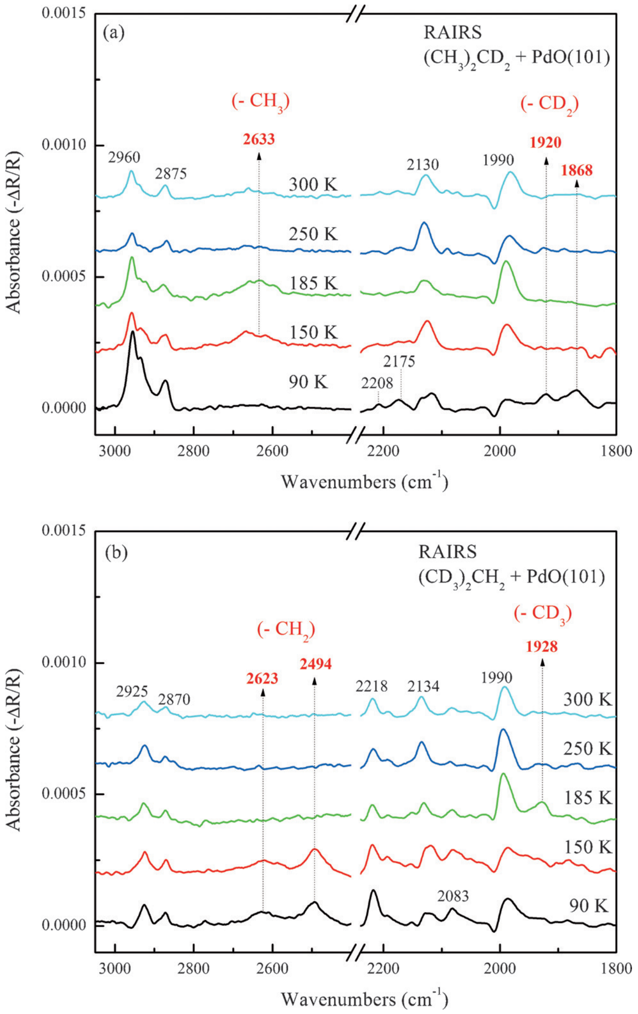

Figure 3. Series of RAIR spectra obtained after heating saturated monolayers of a) [D$_2$]propane and b) [D$_6$]propane on PdO(101) to the indicated temperatures. Each RAIR spectrum was obtained using a freshly prepared PdO(101) film and the frequencies of softened C–H(D) stretch bands are labeled in red.

The soft C–H stretch band diminishes significantly upon heating the [D$_2$]propane layer to 250 and 300 K due to desorption and dissociation of the propane σ-complexes. The RAIR spectra also exhibit a small, yet distinct C–D stretch peak at 2090 cm^{-1} after heating the [D$_2$]propane layer to 250 and 300 K, while a sharp C–H stretch peak near 2789 cm^{-1}, as observed after dissociating undeuterated propane, is absent from the spectra. This difference suggests that the new mode originates from the interior CH$_2$ (CD$_2$) group of adsorbed 1-propyl species.

The RAIR spectra obtained from the [D$_6$]propane layer on PdO(101) (Figure 3b) essentially mirror those seen for [D$_2$]propane. The RAIR spectrum obtained from the initial [D$_6$]propane monolayer prepared at 90 K exhibits soft C–H stretch bands at 2494 and 2623 cm^{-1}, whereas the spectral intensity below about 1950 cm^{-1} is quite small. The intensities of the soft C–H stretch bands remain largely unchanged upon heating to 150 K, and the intensity in the soft C–D stretch region increases slightly but distinct features are difficult to discern. Heating to 185 K causes the soft C–H stretch bands to vanish while a new feature at 1928 cm^{-1} emerges. Consistent with the [D$_2$]propane RAIRS data, these changes indicate that the [D$_6$]propane complexes preferentially coordinate to the surface through the CH$_2$ group at high coverage, but that a decrease in the propane coverage causes the complexes to adopt configurations in which only the CD$_3$ groups coordinate to the surface.

Dispersion-corrected DFT calculations predict that propane σ-complexes on PdO(101) undergo a configurational change with increasing concentration, in a manner that is consistent with our experimental observations. For low propane coverages (25%), the calculations predict that the energetically preferred configurations correspond to bidentate geometries in which the propane molecule aligns along the Pd$_{cus}$ row and each CH$_3$ group forms a single H-Pd η^1 bond with a Pd$_{cus}$ atom, resulting in two H–Pd dative bonds per molecule (Figure 4). We refer to these configurations as "p-2η^1" where the "p" indicates that only "primary" C–H bonds coordinate with Pd$_{cus}$ atoms, and the number two indicates that two H–Pd dative bonds form per propane molecule. The calculations indicate that two p-2η^1 conformers are possible, with binding energies of 73.4 and 73.0 kJ mol^{-1}. According to DFT, the p-2η^1 configurations are favored at low coverage because each such complex forms two H–Pd dative bonds, whereas each stable s-η^1 and s-η^2 complex forms only one dative H–Pd bond. Note that the label "s" indicates that the propane complex datively bonds to the surface only through a "secondary" C–H bond.

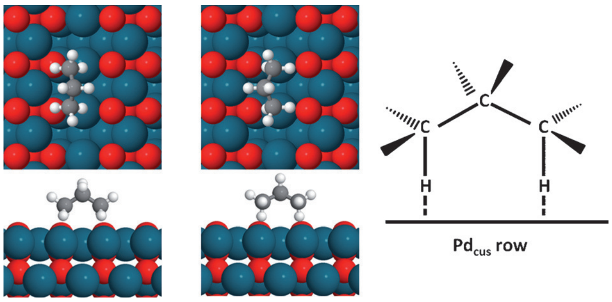

Figure 4. Top and side views of the preferred p-2η^1 configurations of propane complexes on PdO(101) as predicted by DFT calculations. A H–Pd dative bond forms at each CH$_3$ group of these complexes as illustrated in the schematic (right).

Normal mode analysis predicts that each p-2η^1 complex possesses two soft C–H stretch modes, with frequencies between 2630 and 2670 cm^{-1}. These computed frequencies agree well with the position of the broad soft C–H band (2620 cm^{-1}) that we observe at low propane coverage. The DFT calculations thus support the conclusion that propane complexes preferentially coordinate to the PdO(101) surface through the CH$_3$ groups at low propane coverages. As such, the high selectivity toward primary C–H bond cleavage of propane on PdO(101) may be understood in terms of the strong tendency for the propane complexes to adopt a bidentate geometry in which only primary C–H bonds coordinate with the surface Pd atoms and are thus activated.

The DFT calculations also predict that the formation of neighboring p-2η^1 complexes is destabilizing at 50% coverage due to intermolecular repulsion and that configurations with CH$_2$–Pd coordination become energetically preferred as a result. The calculations predict that structures with either two s-η^2 or two s-η^1 complexes per four Pd$_{cus}$ atoms achieve slightly higher energetic stability than structures with two neighboring p-2η^1 complexes at 50% coverage (see the Supporting Information). Each structure with all s-η^2 or s-η^1 complexes exhibits only one soft C–H stretch band, with computed frequencies of 2498 and 2584 cm^{-1}, respectively. The difference in these frequencies is close to that observed experimentally (86 versus 90 cm^{-1}), suggesting the possibility that coexisting domains with all s-η^2 and all s-η^1 complexes develop on PdO(101) at high propane coverage. A structure with neighboring s-η^2 and s-η^1 complexes is also viable according to the DFT calculations.

Advances in understanding alkane activation on solid surfaces are critical to developing new catalytic processes to selectively transform alkanes to value-added products. The present study provides the first spectroscopic evidence of the formation and facile C–H bond cleavage of alkane σ-complexes on an extended crystalline surface, and thus demonstrates that alkane activation can occur by a common mechanism on both homogeneous and heterogeneous transition metal catalysts. We find that propane σ-complexes preferentially adopt bidentate geometries on PdO(101) in which a H–Pd dative bond forms at each CH$_3$ group, thus resulting in a high selectivity for primary C–H bond cleavage under typical catalytic reaction conditions. These findings demonstrate that the bonding geometry of the adsorbed σ-complex precursors can play a decisive role in determining alkane C–H bond selectivity on metal oxide surfaces, and reveal that geometrical registry between the molecule and surface can strongly influence the preferred σ-complex configurations. Our results can provide guidance to future efforts aimed at designing catalyst structures with potential to achieve selective alkane conversions. Infrared spectroscopy can be a key tool in such efforts due to its sensitivity to the bonding geometries of adsorbed alkane σ-complexes.

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[1] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514.
[2] C. Hall, R. N. Perutz, *Chem. Rev.* **1996**, *96*, 3125–3146.

[3] R. N. Perutz, S. Sabo-Etienne, *Angew. Chem. Int. Ed.* **2007**, *46*, 2578–2592; *Angew. Chem.* **2007**, *119*, 2630–2645.
[4] R. H. Crabtree, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789–805; *Angew. Chem.* **1993**, *105*, 828–845.
[5] J. E. Bercaw, J. A. Labinger, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 6899–6900.
[6] R. Horn, R. Schlogl, *Catal. Lett.* **2015**, *145*, 23–39.
[7] J. E. Demuth, H. Ibach, S. Lehwald, *Phys. Rev. Lett.* **1978**, *40*, 1044–1047.
[8] T. Koitaya, J. Yoshinobu, *Chem. Rec.* **2014**, *14*, 848–856.
[9] H. Ostrom, L. Triguero, M. Nyberg, H. Ogasawara, L. G. M. Pettersson, A. Nilsson, *Phys. Rev. Lett.* **2003**, *91*, 046102.
[10] K. A. Fosser, R. G. Nuzzo, P. S. Bagus, C. Woll, *J. Chem. Phys.* **2003**, *118*, 5115–5131.
[11] J. F. Weaver, *Chem. Rev.* **2013**, *113*, 4164–4215.
[12] H. Over, *Chem. Rev.* **2012**, *112*, 3356–3426.
[13] J. F. Weaver, C. Hakanoglu, A. Antony, A. Asthagiri, *Chem. Soc. Rev.* **2014**, *43*, 7536–7547.
[14] J. F. Weaver, C. Hakanoglu, A. Antony, A. Asthagiri, *J. Am. Chem. Soc.* **2011**, *133*, 16196–16200.

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