Kinetic and Mechanistic Assessment of Alkanol/Alkanal Decarbonylation and Deoxygenation Pathways on Metal Catalysts

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ABSTRACT: This study combines theory and experiment to determine the kinetically relevant steps and site requirements for deoxygenation of alkanols and alkanals. These reactants deoxygenate predominantly via decarbonylation (C–C cleavage) instead of C–O hydrogonylation on Ir, Pt, and Ru, leading to strong inhibition effects by chemisorbed CO (CO*). C–C cleavage occurs via unsaturated species formed in sequential quasi-equilibrated dehydrogenation steps, which replace C–H with C–metal bonds, resulting in strong inhibition by H2, also observed in alkane hydrogenolysis. C–C cleavage occurs in oxygenates only at locations vicinal to the C–O group in RCHOH* intermediates, because such adjacency weakens C–C bonds, which also leads to much lower activation enthalpies for oxygenates than hydrocarbons. C–O hydrogonylation rates are independent of H2 pressure and limited by H* assisted C–O cleavage in RCHOH* intermediates on surfaces with significant coverages of CO* formed in decarbonylation events. The ratio of C–O hydrogonylation to decarbonylation rates increased almost 100-fold as the Ir cluster size increased from 0.7 to 7 nm; these trends reflect C–O hydrogonylation reactions favored on terrace sites, while C–C hydrogonylation prefers sites with lower coordination, because of the relative size of their transition states and the crowded nature of CO* covered surfaces. C–O hydrogonylation becomes the preferred deoxygenation route on Cu-based catalysts, thus avoiding CO inhibition effects. The relative rates of C–O and C–C cleavage on these metals depend on their relative ability to bind C atoms, because C–C cleavage transitions states require an additional M–C attachment.

1. INTRODUCTION

Oxygen must be removed from biomass-derived molecules to render them useful as fuels and chemicals, but such processes remain challenging because of their significant energy and H2 requirements. Oxygen removal strategies include C–O hydrogonylation, using H2 to remove oxygen as H2O (deoxygenation), and C–C hydrogonylation reactions that form a shorter carbon backbone and CO (decarbonylation) or CO2 (decarboxylation) as coproducts. Alkanols and alkanals are ubiquitous in biomass-derived streams, and a more detailed understanding of the relevant mechanisms by which these molecules react on metal surfaces is essential to choose catalytic systems for their efficient conversion in reforming5,9 direct fuel cells,5 and oxidation reactions.5 The conversion of many complex alkanol substrates1,6–8 has been studied on several metal catalysts in the aqueous phase, but without detailed mechanistic conclusions, at least in part, because of the mass transfer limitations and nonideal thermodynamics, ubiquitous in such aqueous media. Rates of ethanol and 1-propanol decarbonylation reactions were 10–100 times larger than C–O hydrogonylation rates on single crystals of Pt,5,15 Pd9–11 and Ni.12 Density functional theory (DFT) treatments of the conversion pathways for ethanol, 14–17 ethylene glycol, 18 and glycerol19 on Group VIII metals (Pt, Pd, Ir, Ru, Rh) indicate that H-removal steps occur before C–C or C–O cleavage, similar to the extensive dehydrogenation that precedes C–C cleavage of alkanes. 20,21 High-resolution electron energy loss spectra,9 the identity and desorption dynamics of the products formed from preadsorbed ethan- 10–12 and DFT calculations14–17 on single crystals, however, have not led to a consensus about the structure and the degree of unsaturation of the relevant intermediates and transition states. Also, while C–O hydrogonylation of biomass-derived furanic species was reported on Cu in gaseous22,23 and aqueous24,25 media, its turnover rate and the C–C and C–O bond cleavage selectivities have not been systematically compared among Cu and Group VIII metals. These unresolved or unaddressed matters have prevented precise assessments of the origins of reactivity in C–C and C–O cleavage of alkanols/ alkanals and of how C–C cleavage differs in mechanistic detail among alkanols, alkanals, and alkanes.

Here, we report turnover rates and their dependence on reactant and product concentrations for reactions of 1-butanol/ H2 mixtures on supported Ir, Pt, Ru, and Cu clusters at conditions relevant to their practical use. Decarbonylation...
occur with much higher turnover rates than C–O hydrogenolysis on small clusters of Ir, Pt, and Ru (∼1 nm mean diameter), and no other C–C cleavage reactions occur. DFT-derived activation barriers indicate that the presence of C–O double bonds (in alkanol/alkan al-derived intermediates) significantly weakens adjacent C–C bonds, resulting in lower barriers for C–C cleavage vicinal to –CO groups (decarbonylation) than for C–C cleavage at other backbone positions. H2 pressure inhibits decarbonylation and has no effect on C–O hydrogenolysis, and these H2 effects are consistent with kinetically relevant transition states of decarbonylation that are more dehydrogenated than those for C–O hydrogenolysis, confirmed here using DFT methods. The ratio of C–O hydrogenolysis to decarbonylation for 1-butanol is much lower than for C–C hydrogenolysis (Figure 1). Turnover rates (Figure 1) were unaffected by dilution (SiO2/Ir-SiO2 = 0–4), indicating that neither bed temperature gradients nor contributions from the support influenced measured turnover rates. All samples were treated in flowing H2 (Praxair, 99.999%; 50 cm3 g−1 s−1) at ambient pressure by heating to 673 K and holding for 2 h before rate measurements.

Reactant and product concentrations were measured by gas chromatography (Agilent GC, 5890) using a methyl silicone capillary column (HP-1, Agilent, 50 m × 0.32 mm × 0.8 μm) with a flame ionization detector and a packed column (Porapak Q, Alltech, 80/100, 12’ × 1/8’ with a thermal conductivity detector. All rates are reported at differential conversions (<5%) in reference to the alkanal/alkanol reactant pool to avoid axial concentration gradients. Turnover rates are normalized by the number of surface metal atoms determined by H2 consumption.

2. EXPERIMENTAL METHODS

2.1. Synthesis and Characterization of SiO2-Supported Ir, Pt, Ru, and Cu Clusters. SiO2 (Davisil 646, 300 m2 g−1) was treated in flowing dry air (Praxair, 99.99%, 5.0 cm3 g−1 s−1) by heating to 823 K at 0.03 K s−1 and holding for 5 h. Ir (1.0% wt), Ru (0.5% wt) and Cu (5% wt) precursors were deposited onto the treated silica using impregnation methods. The ratio of C–O hydrogenolysis to decarbonylation for 1-butanol is much lower than on unity small (7 nm Ir) clusters, indicating that C–O hydrogenolysis occurs on low-index terrace sites that become more prevalent on larger clusters, while decarbonylation is much less sensitive to surface coordination. C–O hydrogenolysis is the predominant route on Cu because CO* and C* form weaker bonds on Cu than Group VIII metals, consistent with much lower decarbonylation turnover rates on Cu (10–100 times smaller) than on Ir, Pt, and Ru catalysts.
chemisorption for Ir, Pt, and Ru and by TEM for Cu. Selectivities are reported as the percentage of the C atoms in the 1-butanol/butanal equilibrated pool converted that appears within a given product.

2.3. Computational Methods. Periodic DFT calculations were performed using the Vienna ab initio simulation package (VASP)\textsuperscript{31–34} with planewaves constructed using projector augmented-wave (PAW) potentials.\textsuperscript{35,36} Exchange and correlation energies were determined using revised Perdew–Burke–Ernzerhof (RPBE) form of the generalized gradient approximation (GGA).\textsuperscript{37–39} Transition-state structures were obtained for each elementary reaction using the nudged elastic band (NEB) method\textsuperscript{40,41} and the dimer method.\textsuperscript{42} The details of these electronic structure calculations may be found in the SI.

3. RESULTS AND DISCUSSION

3.1. 1-Butanol Turnover Rates and Selectivity on Ir/SiO\textsubscript{2}. 1-Butanol can react reversibly on Ir/SiO\textsubscript{2} to form butanal and H\textsubscript{2} (dehydrogenation) with an approach to equilibrium (\(\eta\)):

\[
\text{C}_6\text{H}_{12}\text{O} \quad \xrightleftharpoons{\text{K}_{\text{deh}}} \quad \text{C}_4\text{H}_8\text{O} + \text{H}_2, \quad \eta = \frac{P_{\text{H}_2}P_{\text{butanal}}}{P_{\text{butanal}}K_{\text{deh}}} \tag{1}
\]

value of 0.7–1 even at the low 1-butanol conversions in this study (0.8% to 6.4%), allowing butanol and butanal to be treated as a lumped reactant pool in all reported turnover rates and selectivities. 1-Butanol can also form (i) propane and CO (decarbonylation; C–C hydrogenolysis), (ii) butane and H\textsubscript{2}O (C–O hydrogenolysis), and (iii) CH\textsubscript{4} and H\textsubscript{2}O (methanation) via a secondary reaction of CO and H\textsubscript{2} (Scheme 1).

1-Butanol decarbonylation rates were >10 times higher than C–O hydrogenolysis rates (Ir/SiO\textsubscript{2}; Figure 1a, 0.7 nm clusters; 473–523 K, 1–3 MPa H\textsubscript{2}), as also reported for ethanol\textsuperscript{43–45} and propanol\textsuperscript{13} on Pt, Pd, Ru, and Ni catalysts at lower H\textsubscript{2} pressures (<0.1 MPa, 400–523 K). Propanol, ethanol, and ethane were not detected as products, indicating that only C–C bonds vicinal to the O atom are cleaved, consistent with 1-propanol reactions on Pd\textsuperscript{11} and Pt.\textsuperscript{13} CO\textsubscript{2} was also not detected, indicating CO did not react with H\textsubscript{2}O formed in situ. 1-Butanol decarbonylation and C–O hydrogenolysis turnover rates were unaffected by the presence of additional SiO\textsubscript{2} present as physical mixture (SiO\textsubscript{2}/Ir-SiO\textsubscript{2} = 0–4, Cab-O-Sil HS-5, washed with deionized water and treated in flowing dry air at 793 K for 5 h), indicative of monofunctional reactions. Propane and butane selectivities depended weakly on residence time and reactant pool conversion (Figure 1b), even though they form directly from equilibrated butanol-butanal mixtures, because their formation rates are inhibited to different extents by the CO formed in decarbonylation reactions. CH\textsubscript{4} selectivity was low and increased with residence time (Figure 1b), together with a decrease in CO selectivity, because of methanation reactions. Propane and C\textsubscript{1} molecules (CO, CH\textsubscript{4}) formed in equimolar amounts at all conditions.

Decarbonylation and C–O hydrogenolysis turnover rates decreased with increasing residence time (Ir/SiO\textsubscript{2}, Figure 1a), even at very low reactant pool conversions (2–6%), indicating that products (CO and/or H\textsubscript{2}O) inhibit these reactions. Rates were unaffected by added H\textsubscript{2}O (Figure 1c) at pressures (1 kPa H\textsubscript{2}O) above those prevalent during 1-butanol reactions (<0.003 kPa H\textsubscript{2}O); therefore, H\textsubscript{2}O-derived intermediates do not account for the observed product inhibition. CO added to 1-butanol/H\textsubscript{2} reactants (1 kPa vs <0.07 kPa during reaction; Figure 1c) led to more than a 10-fold decrease in rates; rates were no longer influenced by conversion when CO was present. Turnover rates were stable with time on stream (Figure S1), indicating that CO* did not irreversibly poison the Ir metal, but...
instead inhibited rates through quasi-equilibrated adsorption/desorption events. These data show that CO strongly inhibits rates by competitive adsorption, leading to kinetically detectable CO* coverages, even at very low conversions (2–6%) and CO pressures (0.04–0.07 kPa). Such CO inhibition effects are also evident in aqueous and gas-phase reforming of oxygenates (ethylene glycol, glycerol, sorbitol)\textsuperscript{15,44} on Pt and Ni surfaces and in ethanol decarbonylation on Pt surfaces;\textsuperscript{16} these strong inhibitory effects of CO* remain influential even at the higher and more relevant H\textsubscript{2} pressures (1–3 MPa) and low conversions of the present study.

3.2. Effects of 1-Butanol, H\textsubscript{2}, and CO Pressures on Decarbonylation Turnover Rates. Decarbonylation turnover rates were proportional to 1-butanol pressure (Figure 2a) and inversely dependent on H\textsubscript{2} (Figure 2b) and CO (Figure 2c) pressures on Ir/SiO\textsubscript{2}. The observed decrease in decarbonylation rates with increasing H\textsubscript{2} pressure is consistent with the involvement of unsaturated species, formed via quasi-equilibrated dehydrogenation steps, as intermediates in the formation of the transition states that mediate kinetically relevant steps.

Scheme 2 depicts a sequence of elementary steps that accounts for the observed kinetic effects of alkanol, CO, and H\textsubscript{2} pressures on 1-butanol decarbonylation rates (Figure 2) and C\textsubscript{2}H\textsubscript{5}CH\textsubscript{2}CO (Scheme 2, step 2) as the sole kinetically relevant step. The values of $a$ (2.9 ± 0.13 kPa\textsuperscript{0.5} s\textsuperscript{-1}) and $K\text{CO}$ (6.3 × 10\textsuperscript{-11} ± 2.4 × 10\textsuperscript{-2} kPa\textsuperscript{-1}) were obtained by regressing all rate data (Figure 3, S3).

![Scheme 2. Proposed Intermediates and Sequence of Elementary Steps Involving Decarbonylation of 1-Butanol on Ir Clusters\textsuperscript{*}](Image)

where the denominator terms account for the relative coverages of vacant sites (\textsuperscript{*}) and (CO*) species and $K\text{CO}$ is the equilibrium constant for CO* adsorption and $K\text{H}_{2}$ is the equilibrium constant for H* adsorption. The $\alpha$ term in eq 2 represents an effective rate constant for decarbonylation:

\[
\alpha = K\text{BuOH}K\text{OH,H}K\text{CH}_{x}K_{\text{CH}_{2}}K_{\text{H}_{2}}^{1/5}K_{\text{CH}_{3}} ^{-1/5}
\]

with the rate and equilibrium constants defined for the elementary steps in Scheme 2. The $\alpha$ term reflects the contributions of C-H activation in C\textsubscript{2}H\textsubscript{5}CH\textsubscript{2}CO\textsuperscript{*} species (Scheme 2, step 2.6) as the sole kinetically relevant step. The values of $\alpha$ (2.9 ± 0.13 kPa\textsuperscript{0.5} s\textsuperscript{-1}) and $K\text{CO}$ (6.3 × 10\textsuperscript{-11} ± 2.4 × 10\textsuperscript{-2} kPa\textsuperscript{-1}) were obtained by regressing all rate data (Figure 3, S3).

523 K, 0.7 nm Ir) to the functional form of eq 2. Fractional CO* coverages derived from this $K\text{CO}$ value range from 0.30 to 0.85 as CO pressures increased from 0.8 to 8 kPa at 523 K. Alternate decarbonylation pathways, such as those involving kinetically relevant C-C activation in C\textsubscript{2}H\textsubscript{5}CH\textsubscript{3}CO\textsuperscript{*} (instead of C-H activation in C\textsubscript{2}H\textsubscript{5}CH\textsubscript{2}CO\textsuperscript{*}) would have led to rates also given by eq 2, but are ruled out here because of their significantly larger DFT-derived barriers compared with the steps in Scheme 2 (discussed in detail below). Eq 2 assumes that H* species are minority surface species, even at 1–3 MPa H\textsubscript{2} pressures (Figure 3). This conclusion is consistent with the insensitivity of C-O hydrogenolysis rates to H\textsubscript{2} pressure and with the similar effects of H\textsubscript{2} pressure on Ir particles with different mean diameters (0.7–7 nm), which suggest that H* coverages are not kinetically detectable at these conditions (1–5 kPa 1-butanol, 1–3 MPa H\textsubscript{2} 0.8–8 kPa CO at 523 K), as further discussed in the SI (Figures S2 and S3).

Previous rate data and theoretical assessments for alkane hydrogenolysis\textsuperscript{20,21} have indicated that one or more C atoms undergo C-H activation to form C-M bonds before C-C cleavage. The requirement for bound C atoms and the equilibrated nature of alkane-alkane interconversions (Section 3.1) suggest the involvement of RCH*O, RCO*O, and RC*OH species (where $R = \text{CH}_{3}\text{CH}_{2}, \text{CH}_{3}\text{CH}_{\text{3}},$ and $\text{CH}_{2}\text{CH}_{\text{3}}$) in decarbonylation (C-C cleavage). DFT calculations were carried out for these species instead of 1-butanol/butanal to decrease conformational diversity and computational intensity.
and because C–C hydrogenolysis occurs exclusively at the C–C bond vicinal to the –OH group (Section 3.1).

Adsorbed propanal can react with a vacant site and undergo C–C cleavage to form vicinal CH₃CH₂* and CH₃CHO* species (Scheme 3, Step 2); ΔH_{act} values (151 kJ mol⁻¹) for this step are much larger than C–H bond activation at the α-C position in adsorbed propanal to form an CH₃CH₂*CHOH* and H* (Step 3, ΔH_{act,3} = 88 kJ mol⁻¹). Subsequent C–H activation at the α-C position would then form CH₃C=CH₂* (Step 7, ΔH_{act,7} = 48 kJ mol⁻¹), thus C–H activations at the α-C are more facile than direct C–C activation of propanal. Intrinsic (ΔH_{act} enthalpy differences between transition states and the corresponding precursors) and effective (ΔH^eff, difference between the transition state and propanal in the gas-phase) enthalpy barriers for C–C cleavage reactions both decrease as more H atoms are removed from the α-C atom (Figures 4 and 5) for all RCH*OH species (R = CH₃CH₂, CH₃CH₂*, CH₃C*=). Propanal can also undergo C–H activation at the carbonyl C atom in RCHO* to form RCO* species (CH₃CH₂C=O*, CH₃CH*=CO*, and CH₂C*=CO*). C–C cleavage in RCHO* occurs with smaller ΔH_{act,5} and ΔH^eff than for C–C cleavage in RCHO (Figures 4 and 5). ΔH_{act,5} and ΔH^eff values decreased as H atoms are removed from the α-C atom in both RCHO* and RCO* species, because H-removal occurs with the concomitant formation of C–M bonds (Figure 5), which weakens C–C bonds, as also shown for C–C cleavage steps alkane hydrogenolysis.

Successive C–H activation events in propanol-derived species can form RCO*OH species (R = CH₃CH₂, CH₃CH₂*, CH₃C*=), which can undergo C–C cleavage (Scheme S1, SI). C–C cleavage in RCO*OH (R = CH₃CH₂, CH₃CH₂*, CH₃C*) occurs with higher ΔH_{act,5} and ΔH^eff than in RCHO (Figures 4 and 5). ΔH_{act,5} and ΔH^eff values for C–C cleavage in RCO*OH both decreased as α-C atoms lose H atoms, as also found for RC*O and RCO*O species (Figure 5). Transition states for C–C cleavage in RCO*OH exhibit much longer C–O bonds than in RCO* (Figure 5), and the bonding geometry at the C atom for RC*O and RCO*O species indicates a shift from sp³ to sp² hybridization (from RC*O to RCO*). These changes in local geometry indicate that C–O bonds are present in

**Scheme 3.** DFT-Calculated Effective Enthalpy Barriers (ΔH^eff, black, bold font), Intrinsic Activation Enthalpies (ΔH_{act,5} blue, left of slash), and Reaction Enthalpies (ΔH_{rxn, red, right of slash}) for Propanol Decarbonylation Pathways

**Figure 4.** (A) ΔH_{act} (open symbols, difference between transition states and relevant precursors); (B) ΔH^eff (closed symbols, difference between transition states and gas-phase propanol); and (C) ΔG (at 483 K, 1 bar) and for C–C activations of RCH*O (●), RC*OH (▲), and RC*O (■) intermediates where R = CH₃CH₂, CH₃CH₂*, and CH₂C*. The reversible steps are represented by double arrows (↔) and irreversible steps are represented by single arrows (→). Reaction numbers used throughout the text are given within circles (①–⑤) for all RCH*O species (Figures 4 and 5).

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RC*O but not in RC*OH; these C=O bonds weaken adjacent C–C bonds, thus favoring C–C bond cleavage in RC*O over similar reactions in RC*OH. C–C cleavage in CH₃C=C*O (Step 14) shows the lowest ΔHᵣₑₓ (48 kJ mol⁻¹) and ΔH⧧ (123 kJ mol⁻¹) values among all nine C–C cleavage steps considered (Steps 2, 5, 6, 12, and 14 in Scheme 3, and Steps 27, 30, and 33 in Scheme S1). The relative rates of C–C cleavage in these nine intermediates (RCH*O, RCOH*, and RCO* with R = CH₃C=O, CH₃CH₂C=O, and CH₃C*) were evaluated by determining the maximum possible rate of each C–C cleavage step. This maximum rate requires that all previous steps be quasi-equilibrated, thus resulting in a thermodynamically limited pool of reactant precursors. Transition-state theory formalisms then give these maximum rates for each C–C cleavage step as

\[
\frac{r_{\text{max}}}{[L]} = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT} \left( \frac{1}{(H_2)^{3/2}} \right) \left( 1 + \frac{K_{\text{CO}}(\text{CO})}{S_U^O(\text{CO})} \right)^2
\]

(4)

where \(k_B\) and \(h\) are the Boltzmann and Planck constants, respectively, and \(S_U^O\) represents the number of H atoms removed before C–C cleavage. Since rates depend on Gibbs free energies (ΔG⧧), entropy (ΔS⧧) was accounted for by calculating the relative magnitudes of the C–C cleavage in the nine intermediates in Figures 4 and 5. ΔS⧧ values increase with increasing extent of dehydrogenation because H₂ (g) is evolved upon forming each transition state. C–C cleavage in CH₃C=C*O (with the lowest ΔH⧧, Figure 4B) shows the largest ΔS⧧ values and the smallest ΔG⧧ (Figure 4C), indicating that C–C cleavage occurs almost exclusively via CH₃C=C*O intermediates.

In alkane hydrogenolysis on metals, C–C cleavage steps are irreversible and kinetically relevant, while C–H activation steps are quasi-equilibrated. If this were the case for alkanol/alkanal decarbonylation reactions, C–C cleavage via CH₃C=C*O species would be given by

\[
r_{\text{rel}} = \frac{\alpha(\text{BuOH})}{(H_2)^{3/2}(1 + K_{\text{CO}}(\text{CO}))^2}
\]

(5)

inconsistent with measured rates \((r \sim (H_2)^{-1.5})\), eq 2. These DFT treatments, taken together with measured rates, indicate that while C–C cleavage may indeed occur preferentially in CH₃C=C*O species during decarbonylation, some preceding C–H activation steps may not achieve equilibrium. The measured H₂ effects on decarbonylation rates implicate the activation of a C–H bond in CH₃CH₂C*O* species (Step 9) as the kinetically relevant decarbonylation step. These inferences are made rigorous by the seamless coupling of theory and experiment in this study; mechanistic conclusions would have been inaccurate if based on kinetic analysis or theoretical treatments alone. Next, we assess the differences in C–C activation events among alkanols/alkanals and alkanes.

3.3. Effects of Proximity to Carbon–Oxygen Bond on the Cleavage Rates of C–C Bonds. C–C bonds in alkans cleave after four H atoms are removed from the C atoms involved in the cleaved C–C bond based on experimental and DFT results shown in Section 3.2, as for C–C hydrogenolysis of 1C–1C, 1C–2C, and 2C–2C bonds (1C and 2C represent primary and secondary carbons, respectively, with C–C activation as the kinetically relevant step) in acyclic and cyclic alkanes. In contrast with alkanes, C–C hydrogenolysis in alkans involves: (i) O–H activation to form C=O bonds that weaken vicinal C–C bonds; (ii) C–H activation, instead of C–C activation, as kinetically relevant step; and (iii) the
selective activation of C–C bonds adjacent to C–O groups. The weakening of C–C bonds by the vicinal C–O moieties is evident from the DFT-calculated \( \Delta H_{act} \) values for C–C cleavage in \( \text{CH}_2\text{C}^*\text{C}^*\text{O} \) (48 kJ mol\(^{-1}\)) and \( \text{CH}_2\text{C}^*\text{C}^*\text{H} \) (65 kJ mol\(^{-1}\)). These \( \Delta H_{act} \) values lead to much smaller \( \Delta H^2 \) values for decarbonylation (123 kJ mol\(^{-1}\)) than for alkane hydrogenolysis (170 kJ mol\(^{-1}\)), consistent with 1-butanol/butanol decarbonylation turnover rates that are >10\(^4\) times larger than for C–C hydrogenolysis in n-butane on Ir (0.7 nm) at similar conditions (523 K, 2 MPa H\(_2\)).

Here, we also examine the C–C cleavage of alkanols at bonds without neighboring O atoms. Intrinsic activation enthalpies (\( \Delta H_{act, in} \)) are much higher for C–C cleavage in \( \text{CH}^*\text{C}^*\text{CH}_2\text{OH} \) (90 kJ mol\(^{-1}\)) and in \( \text{CH}^*\text{C}^*\text{CHO} \) (97 kJ mol\(^{-1}\)) than for the respective propane-derived intermediates (65 kJ mol\(^{-1}\) for \( \text{CH}^*\text{C}^*\text{CH}_3 \)) (Figure 6). Decarbonylation has the lowest \( \Delta H^2 \) among these C–C bond activations (Figure 6), consistent with the exclusive formation of \( \text{C}_3 \) and \( \text{C}_1 \) molecules from 1-butanol reactants (Section 3.1).

3.4. Effects of 1-Butanol, \( \text{H}_2 \), and \( \text{CO} \) Pressures on C–O Hydrogenolysis Turnover Rates. Measured C–O hydrogenolysis rates are proportional to 1-butanol pressure (Figure 2a) and inversely dependent on \( \text{CO} \) pressure (Figure 2c) on Ir/SiO\(_2\), as also observed for decarbonylation rates (Figure 2a). C–O hydrogenolysis rates do not depend on \( \text{H}_2 \) pressure, while decarbonylation reactions are inhibited by \( \text{H}_2 \) (cf. Figure 2b). These data indicate that kinetically relevant C–O hydrogenolysis transition states contain the same number of H atoms as 1-butanol, making them much less dehydrogenated than the transition states for decarbonylation, as also proposed based on theoretical treatments of ethanol reactions on Pt(111). \(^{17}\)

Scheme 4 depicts a plausible sequence of elementary steps for C–O hydrogenolysis of 1-butanol; these steps are consistent with the observed effects of alkanol and \( \text{H}_2 \) pressures on rates (Figure 2) and with theoretical estimates described below. Molecularly adsorbed butanol undergoes quasi-equilibrated C–H activation (4.3) to form \( \text{CH}_3\text{CH}_2\text{CH}^*\text{OH} \), which then reacts in an irreversible step with \( \text{H}^* \) with concerted O–H formation and C–O cleavage to form vicinal \( \text{H}_2\text{O}^* \) and \( \text{CH}_3\text{CH}_2\text{CH}^* \) (4.4). The corresponding rate equation is

\[
\frac{r}{[L]} = \frac{\beta([\text{BuOH}])}{(1 + K_{\text{CO}}(\text{CO}))^2}
\]

with \( \beta \) given by

\[
\beta = K_{\text{BuOH}}K_{\text{CH}}K_{\text{C–O}}
\]

Molecularly adsorbed propanol can react directly with a vicinal vacant site by cleaving its C–O bond and forming \( \text{CH}_3\text{CH}_2\text{CH}_2^* \) and \( \text{OH}^* \) (Step 16). This direct activation would lead to rates with the functional form of eq 6, but with a different chemical meaning of \( \beta \). The intrinsic activation barrier for this step (\( \Delta H_{act,16} = 171 \text{ kJ mol}^{-1} \)) is much larger than for cleaving the O–H bond in 1-butanol to form propoxyl (\( \text{CH}_3\text{CH}_2\text{CH}_2^* \)) and \( \text{H}^* \) (Step 17, \( \Delta H_{act,17} = 73 \text{ kJ mol}^{-1} \)) or for cleaving the C–H bond in 1-butanol at the O-bound C atom to give hydroxypropyl species (\( \text{CH}_3\text{CH}_2\text{CH}^*\text{OH} \)) and \( \text{H}^* \) (Step 18, \( \Delta H_{act,18} = 83 \text{ kJ mol}^{-1} \)). Thus, C–H and O–H activation steps occur before the C–O bond cleaves on Ir surfaces.

The reaction network in Scheme 5 includes six different C–O activation steps (Steps 16, 19, 21, 22, 25, and 26). Out of the six C–O activation routes, there are two pathways (Steps 16 and 21) involving transition states that contain eight H atoms and would lead to rates that are unaffected by \( \text{H}_2 \) pressure, as observed experimentally (Figure 2). C–O cleavage is mediated in molecularly adsorbed propanol (via reaction with a vicinal * in Step 16 in the first route and in \( \text{CH}_3\text{CH}_2\text{CH}^*\text{OH} \) species with parameters defined in Scheme 4. Regressing all rate data to the functional form of eq 6 shows that the elementary steps in Scheme 4 accurately describes the measured C–O cleavage rates at all 1-butanol, \( \text{H}_2 \), and \( \text{CO} \) pressures (Figure 3). The parameter \( \beta \) in eq 7 is \( 6.0 \pm 0.59 \times 10^{-7} \text{ kPa}^{-1} \text{s}^{-1} \) at 523 K; the \( K_{\text{CO}} \) value was slightly smaller for C–O hydrogenolysis (0.47 ± 0.06 kPa\(^{-1}\)) than for decarbonylation (0.63 ± 0.02 kPa\(^{-1}\)). The variance in \( K_{\text{CO}} \) values and the relationship between the types of sites involved in each reaction are discussed in Section 3.5.

Scheme 5 shows possible pathways and the corresponding enthalpic barriers for C–O hydrogenolysis of 1-propanol.

\[\begin{align*}
\text{Scheme 4. Proposed Sequence of Steps and Intermediates in C–O Hydrogenolysis of 1-Butanol on Ir Clusters}^2 \hfill \\
(4.1) & \quad \text{H}_2 + 2^* \leftrightarrow 2^* \text{H}^* \quad K_{\text{H}} \\
(4.2) & \quad \text{C}_2\text{H}_5\text{CH}_2\text{OH} + \text{C}_2\text{H}_5\text{CH}_2\text{OH}^* \leftrightarrow \text{C}_2\text{H}_5\text{CH}_2\text{CHO} \quad K_{\text{BuOH}} \hfill \\
(4.3) & \quad \text{C}_2\text{H}_5\text{CH}_2\text{CHO} + \text{C}_2\text{H}_5\text{CH}_2\text{CHO}^* + \text{H}^* \quad K_{\text{C}} \\
(4.4) & \quad \text{C}_2\text{H}_5\text{CH}_2\text{CHO} + \text{C}_2\text{H}_5\text{CH}_2\text{CHO}^* + \text{H}_2\text{O}^* \quad K_{\text{C–O}} \hfill \\
(4.5) & \quad \text{C}_2\text{H}_5\text{CHO} + \text{C}_2\text{H}_5\text{CH}_2\text{CHO}^* \leftrightarrow \text{C}_2\text{H}_5\text{CH}_2\text{CHO} + \text{C}_2\text{H}_5\text{CH}_2\text{CHO}^* \quad K_{\text{C–O}} \hfill \\
(4.6) & \quad \text{H}_2\text{O} + \text{H}_2\text{O}^* \quad K_{\text{HO}} \\
\end{align*}\]

\[\begin{align*}
\text{Scheme 5. DFT-Derived Effective Enthalpy Barriers (} \Delta H^2 \text{, black, bold font), Intrinsic Activation Enthalpies (} \Delta H_{act, in} \text{, blue, italic font), and Reaction Enthalpies (} \Delta H_{rxn, red} \text{ for Propanol C–O Hydrogenolysis Pathways}^a \hfill \\
\end{align*}\]
(via reaction with an additional H*) in Step 21 in the second route. The $\Delta H^R$ value for H*-assisted CH$_3$CH$_2$CH*OH activation ($\Delta H^R = 74$ kJ mol$^{-1}$) is much smaller, however, than for direct C=O activation in molecularly adsorbed propanol (Step 16, $\Delta H^R = 171$ kJ mol$^{-1}$), leading to a very small contribution from Step 16, as can be determined from the ratio of these two steps:

$$\frac{r_{16}}{r_{21}} = \frac{A_{16}e^{-\Delta H_{16}^R/RT}}{A_{21}}$$

(8)

with an exponential term much smaller than unity ($2.1 \times 10^{-10}$ at 523 K). These results indicate that C=O hydrogenolysis of alkanol-alkanal reactants proceeds predominantly via H*-assisted C=O activation in CH$_3$CH$_2$CH*OH species. The C=O bond in propanol weakens upon formation of a C-M bond during C-H activation to form CH$_3$CH$_2$CH*OH; a vicinal H* then interacts with the lone pair in the O atom to assist the cleavage of the C=O bond. This mechanism is consistent with the independence of C=O hydrogenolysis rates on H$_2$ pressure (Figure 2).

The other four C=O activation routes in Scheme 5 (via Steps 19, 22, 24, or 25) involve kinetically relevant transition states with fewer H atoms than alkanol reactants and would thus lead to C=O hydrogenolysis rates that would decrease as H$_2$ pressure increases, in contrast with experiments (Figure 2). Nevertheless, we consider such steps in detail in the SI (Section S7) for completeness and to confirm that these theoretical treatments can indeed rule out such sequences of elementary steps based on their activation free energies, in addition to comparisons with experiments. DFT-predicted effective free energy barriers confirm that H*-assisted activation of CH$_3$CH$_2$CH*OH is preferred over all other C=O activation routes. H*-assisted C=O activation proceeds with lower intrinsic enthalpy barriers than unassisted C=O activation in ring opening hydrogenolysis of heterocyclic oxygenates, but was not considered for C=O activation in alkanol reactants in previous work, which only considered "unassisted" C=O cleavage reactions.  

### 3.5. Effects of Ir Cluster Size on Decarbonylation and C=O Hydrogenolysis Turnover Rates

C=O hydrogenolysis turnover rates increased by a factor of 30 with increasing cluster size (0.7-7 nm), while C-C hydrogenolysis turnover rates decreased about 5-fold (Figure 7a) at conditions (1 kPa CO) that lead to significant CO* coverages (based on regressed $K_{CO}$ values in Sections 3.2 and 3.4), which implicates the preferential involvement of exposed atoms of different coordination in these two reactions. C=O hydrogenolysis occurs preferentially on exposed atoms with high coordination that prevail on low-index planes and larger clusters, while lower-coordination atoms appear to favor C=C hydrogenolysis, despite C=C hydrogenolysis rates of alkanes occurring preferentially on higher-coordinated atoms. The ratio of C=O to C=C hydrogenolysis rates increases with increasing CO pressure (Figure 7b; 0.7 nm Ir clusters), suggesting that C=O hydrogenolysis occurs on atoms that bind CO* more weakly than atoms involved in C=C hydrogenolysis, consistent with CO* binding energies that are weaker on low-index metal planes than on corner and edge atoms.

These effects of Ir cluster size on decarbonylation and C=O hydrogenolysis turnover rates reflect the effects of surface coordination on the lumped rate constants $\alpha$ (eq 2) and $\beta$ (eq 6) for decarbonylation and C=O hydrogenolysis, respectively, and the CO adsorption constants ($K_{CO}$). The lumped rate constants depend upon the free energies of surface-bound transition states ($G_{CH_3}$ for decarbonylation or $G_{C=O}$ for C=O hydrogenolysis) and gas-phase species (see Section S8 (SI) for more details). Bond-order conservation considerations would suggest that low-coordination atoms bind all adsorbed species (including transition states) more strongly, thus C=O and C=C hydrogenolysis rates would be higher on smaller clusters, but only at conditions of low CO* coverages, for which $\alpha$ and $\beta$ solely determine turnover rates, but not for the turnover rates reported in Figure 7a measured at conditions (1 kPa CO) that lead to significant CO* coverages. At high CO* coverages, it is the relative effects of coordination on $\alpha$ or $\beta$, and on $K_{CO}$ (and thus on $G^*_{CH_3}$ or $G^*_{C=O}$ and $G_{CO*}$) that determine their preference for atoms with a given coordination (see Section S8 (SI) for more details). Higher decarbonylation turnover rates on smaller particles indicate that low coordination atoms favor the binding
of its kinetically relevant transition state over the two CO* species that must be removed to bind it, while the opposite is the case for C–O hydrogenolysis reactions on Ir clusters. These considerations are illustrated by a reaction coordinate in Figure S16 and can be related to the differences in the binding strength of the two transition states. The kinetically relevant transition state for decarbonylation has two C–M bonds (of 204 and 232 pm) and one H–M bond (163 pm) (Figure 8a), whereas the transition state for C–O hydrogenolysis contains just one C–M bond (213 pm) and one H–M bond (183 pm) (Figure 8b). The number and lengths of the bonds each kinetically relevant transition state forms to the surface than the transition state for C–O hydrogenolysis, which proceeds via activation of the C–O bond by vicinal H* instead of metal-atom insertion into a C–H bond, as in decarbonylation.

The $K_{CO}$ values regressed from eqs 2 and 6 for decarbonylation (0.63 ± 0.02 kPa$^{-1}$) and C–O hydrogenolysis (0.47 ± 0.06 kPa$^{-1}$) suggest that coverages are 0.3–0.4 ML at 1 kPa CO and 523 K on Ir clusters (0.7 nm), indicating that the observed size effects reflect the stabilization of transition states and CO* on crowded surfaces. In fact, CO* coverages are likely to be even higher because the Langmuir–Hinshelwood formalism used to derive eqs 2 and 6 assume that rate and equilibrium constants ($\alpha$ and $K_{CO}$ in eq 2) remain unchanged as CO* coverages increase. Yet, CO* species impose repulsive forces on vicinal CO* or transition states, rendering such species less stable, as confirmed by theoretical treatments.$^{53,55}$ Such CO* coverage effects would cause the $\alpha$ and $K_{CO}$ parameters in the rate equation (eq 2) to become smaller as CO* coverages increase with increasing CO pressure and thus invalidate the assumptions underlying the derivation of these Langmuir–Hinshelwood rate equations. If increasing CO* coverages decrease $\Delta G_{ads,CO}$ values (and thus $K_{CO}$) more than they decrease $\Delta G_{dec-C}$ (and thus $\alpha$, eq 3), $K_{CO}$ would be underestimated by eqs 2 and 6, indicating that actual CO* coverages are closer to 1 ML than those reported above (0.4 ML). Thus, the expectation for high CO* coverages suggests that the kinetically relevant transition state for decarbonylation has a smaller “footprint” on the catalyst surface than a pair of coadsorbed CO* species, partially due to the intact C–C bond of the transition state (whereas a pair of coadsorbed CO* species are not covalently bound to one another). These speculations also reveal the difficulties of applying Langmuir–Hinshelwood based rate equations to systems with strong coadsorbate interactions that may confound kinetic analyses and lead to inconsistencies between coverages determined by kinetics, spectroscopy data, and theory.

3.6. Comparisons of 1-Butanol Turnover Rates and Selectivities on Pt, Ru, Ir, and Cu. Decarbonylation consumes less H$_2$ stoichiometrically than C–O hydrogenolysis, making the former a seemingly attractive deoxygenation route. Decarbonylation, however, forms CO molecules that strongly inhibit both deoxygenation routes. We consider in this section C–O hydrogenolysis selectivities on Ru, Pt, and Cu metal surfaces. Decarbonylation rates were 10–100 times higher than C–O hydrogenolysis rates on Ru/SiO$_2$ (0.6 nm), Pt/SiO$_2$ (0.7 nm), and Ir/SiO$_2$ (0.7 nm) (Figure 9b), indicating that decarbonylation is the main decomposition pathway on Group VIII metals.$^{15,17}$ CO strongly inhibited decarbonylation and C–O hydrogenolysis rates on Pt and Ru (Figure 9a) as on Ir.

![Figure 8](image1.png)

**Figure 8.** Structures for the kinetically relevant transition states for (A) decarbonylation (Step 2.6 of Scheme 2) and (B) C–O hydrogenolysis (Step 4.4 of Scheme 4). Notable bond distances shown in pm.

![Figure 9](image2.png)

**Figure 9.** (a) Effect of CO (generated from 1-butanol/butanal conversion) pressure on decarbonylation turnover rates. (b) Effect of 1-butanol/butanal pool conversion on decarbonylation/C–O hydrogenolysis rate ratio on 1 wt % Ir/SiO$_2$ (0.7 nm, ◆), 1 wt % Pt/SiO$_2$ (0.7 nm, ▲), and 0.5 wt % Ru/SiO$_2$ (0.6 nm, ■) (483 K, 2 MPa H$_2$, 5 kPa 1-butanol). Dashed lines represent trends.
which is reflected by decreasing turnover rates with increasing CO pressure (with increasing 1-butanol/butanal pool conversion). Such inhibition is expected from large CO* binding energies on these metals (−166 kJ mol⁻¹ on Ir(111), −129 kJ mol⁻¹ on Pt(111), −162 kJ mol⁻¹ on Ru(0001) calculated in this work for isolated CO*). Similar considerations lead us to conclude that strong CO inhibition effects will also prevail on Rh, Ni, and Pd catalysts (CO binding energies: −153 kJ mol⁻¹ on Rh(111), −119 kJ mol⁻¹ on Ni(111), and −104 kJ mol⁻¹ on Pd(111), as calculated by DFT).

CO* species formed from decarbonylation can undergo secondary reactions with H₂ to form CH₄. The CH₄/C₃H₈ ratio in the products represents the fraction of CO* that undergoes secondary methanation reactions, which increases with increasing conversion (Figure 10b). CH₄/C₃H₈ ratios were much larger on Ru than on Ir or Pt (483 K, 5 kPa 1-butanol, 2 MPa H₂, Figure 10b); such higher CH₄ selectivities are consistent with methanation turnover rates that are ∼10-fold higher on Ru than on Pt and Ir clusters. Surfaces that scavenge CO* via reactions with hydrogen to form CH₄ will decrease CO pressures and CO* coverages, thus decreasing CO-inhibition effects (Figure 10a). Methanation, as the CO scavenging route, however, gives rise to H₂ consumption stoichiometries

\[ \text{C}_3\text{H}_7\text{CH}_2\text{OH} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{C}_3\text{H}_8 + \text{H}_2\text{O} \]  \hspace{1cm} (9)

that are even higher than for C–O hydrogenolysis

\[ \text{C}_3\text{H}_7\text{CH}_2\text{OH} + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{O} \]  \hspace{1cm} (10)

Thus, strategies that combine decarbonylation with methanation are more H₂-intensive than C–O hydrogenolysis, a reaction that altogether avoids CO formation and thus its strong inhibition effects.
Measured decarbonylation turnover rates on Cu/SiO₂ (5.0 nm) were >100 times lower than on Ir (0.7 or 7.1 nm) and Ru (0.6 nm) clusters at 523 K and Pt clusters (0.7 nm) at 483 K (Figure 11a). The lower decarbonylation turnover rates on Cu may reflect the required formation of two M–C bonds at the transition state (on Ir, Figure 8A) that mediate this reaction and the weak nature of such bonds at Cu surfaces; C* binding energies (BEₐ−) are significantly lower on Cu(111) (−438 kJ mol⁻¹) than on Ru(0001) (−698 kJ mol⁻¹), Ir(111) (−688 kJ mol⁻¹) or Pt(111) (−685 kJ mol⁻¹). These low C–C hydrogenolysis rates also appear to reflect the much weaker binding of CO* on Cu (111) (−46 kJ mol⁻¹) than on Ru (0001), Ir (111), or Pt (111) (−162 kJ mol⁻¹, −166 kJ mol⁻¹, −129 kJ mol⁻¹, respectively). C–O hydrogenolysis rates, on the other hand, vary much less with changing metal composition than those of decarbonylation. The very low decarbonylation rates on Cu in turn lead to high C–O hydrogenolysis selectivities (ratios of C–O to C–C hydrogenolysis >15, Figure 11b). This correlation is plausible given that the C–C cleavage transition state (on Ir, Figure 8A) involves two C–M bonds, while the C–O cleavage transition state includes only one (on Ir, Figure 8B). These C–C cleavage transition states thus become much less stable than C–O cleavage transition states (which may have an additional M–O bond depending on the mechanism) on surfaces that bind C* weakly, as on Cu surfaces, in comparison to Ir, Pt, or Ru surfaces. This leads to lower concentrations of the C–C cleavage transition states compared to that of C–O cleavage and consequently to higher C–O hydrogenolysis selectivities on Cu.

Among the metals examined here, only Cu selectively catalyzes C–O hydrogenolysis. C–O hydrogenolysis preserves valuable C atoms in the products and avoids strong inhibition by CO*, making it the preferred route for deoxygenation of alkanol/alkanal mixtures. Other Group IX metals (Ag and Au) also bind C* weakly (BEₐ−: −282 kJ mol⁻¹ and −382 kJ mol⁻¹ on Ag (111) and Au (111)) compared to Cu (111) (BEₐ−: −438 kJ mol⁻¹) or Group VIII metals (Ru, Rh, Pd, Os, Ir, and Pt) (BEₐ−: −616 to −702 kJ mol⁻¹) and thus are expected to exhibit low C–C cleavage rates. Their significantly weaker M–C bonds on terrace sites are also expected to lead to low C–O hydrogenolysis turnover rates, however, requiring the presence of low-coordination surface atoms that prevail on small Ag and Au clusters to achieve high C–O hydrogenolysis selectivities.

4. CONCLUSIONS

Decarbonylation is the main decomposition pathway of 1-butanol on Group VIII metals, such as Ir, Pt, and Ru. The main product of decarbonylation, CO, is a strong inhibitor, resulting in decreasing turnover rates with alkanol/alkanal pool conversion. Analyses of decarbonylation turnover rates indicate that at the reaction conditions used in this study (1–5 kPa 1-butanol, 1–3 MPa H₂, and 1–10 kPa CO at 523 K), Ir clusters are covered with chemisorbed CO* species, and the kinetically relevant transition state has three fewer H atoms than 1-butanol. These kinetic data, combined with DFT calculations of reaction and activation enthalpies across a series of RCHO*, RCOH*, and RCO* intermediates (R = CH₃CH₂CH₂CH₃, CH₃CH₂C), indicate that C–C cleavage proceeds in CH₃C=CH₂C=O intermediates following the kinetically relevant C–H activation of CH₃CH₂C=O* to form CH₃CH2CHO*. C–C hydrogenolysis in 1-butanol/butanal occurs only at the C–C bond vicinal to the O atom because the C≡O double bond in RCO* significantly weakens the adjacent C–C bond. DFT calculations demonstrate that C–O hydrogenolysis proceeds through an H*-assisted C–O activation of the CH₃CH₂CHOH* intermediate, leading to rates proportional to alkanol pressure and independent of H₂ pressure, consistent with experimental measurements. C–O hydrogenolysis turnover rates become comparable to decarbonylation rates as the cluster size of Ir is increased from 0.7 to 7 nm because C–O hydrogenolysis preferentially takes place on high-coordination Ir sites due to strongly adsorbed CO* blocking corner/edge sites. The use of large metal clusters, however, is inefficient as the majority of the precious metal is inaccessible. CO inhibition can instead be alleviated by coupling decarbonylation with methanation on metals such as Ru. Methanation, however, has a higher H₂ requirement than C–O hydrogenolysis. Group VIII metals are not ideal deoxygenation catalysts if C–C activations and H₂ consumption need to be minimized. Cu, on the other hand, is unique in its ability to catalyze C–O hydrogenolysis selectively over C–C hydrogenolysis because of weak binding of C* and CO*. This is crucial for the conversion of many biomass-derived intermediates with alkanol/alkanal functionalities to chemicals and fuels.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05361.

Methodological details, figures containing DFT-derived structures for all calculations herein, and further discussions of ruled-out C–O hydrogenolysis mechanisms, particle size effects, and the low coverages of H* on Ir surfaces (PDF)

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Notes

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