

Selectivity in Hydrogenation Catalysis with Unsaturated Aldehydes: Parallel versus Sequential Steps

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Abstract

A high-flux molecular beam setup has been used to characterize the kinetics of the steady-state catalytic hydrogenation of unsaturated aldehydes, specifically of crotonaldehyde, promoted by platinum surfaces under single-collision conditions. Surprisingly, in addition to the hydrogenation of the individual single bonds, to yield the saturated aldehyde and the unsaturated alcohol, the formation of the saturated alcohol, the product of the hydrogenation of both C=C and C=O bonds, was detected as well. This indicates that the dual hydrogenation reaction is a primary pathway, and not the result of a secondary hydrogenation of the other products as commonly assumed. Moreover, an increase in the partial pressure of the reactant was found to shift the reaction selectivity from the saturated alcohol to the saturated aldehyde without significantly affecting the selectivity toward the production of the unsaturated alcohol. We explain these observations by proposing a mechanism involving the parallel formation of several monohydrogenated intermediates on the surface.

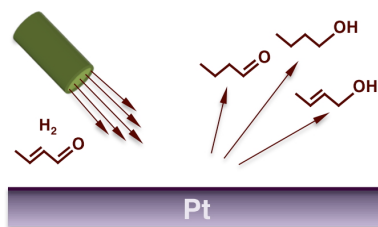


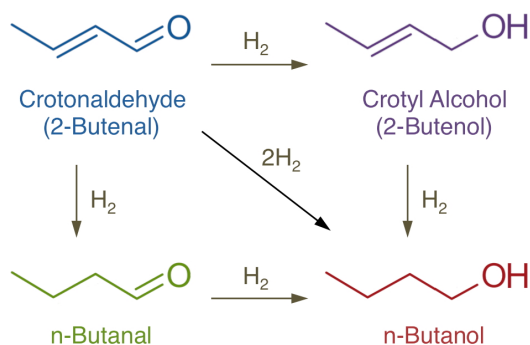
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One of the major challenges in heterogeneous catalysis is the creation of highly selective processes.¹⁻³ Although catalysis was originally conceived as a way to increase reaction rates, it is selectivity that has become the most important criterion in the design of many modern catalysts. Selective catalysts require lower amounts of feedstocks, avoid the need for subsequent separation steps, and minimize the generation of (potentially polluting) byproducts. The attainment of selectivity in heterogeneous catalysis requires the preparation of solids containing a large number of well-defined sites designed for the promotion of a particular reaction.

Selectivity is particularly difficult to control in hydrogenation processes with unsaturated organic molecules, as the surface of the catalyst in those cases, typically transition metal nanoparticles dispersed on a high-surface-area support, tends to be covered with strongly bonded carbonaceous deposits.⁴⁻⁶ Those carbon-containing layers modify the behavior of the surface, and can affect the adsorption mode of the reactants as well as the uptake and activation of hydrogen.^{7,8} This is particularly critical if the molecule to be hydrogenated contains two or more unsaturations, as the initial adsorption mode may define the selectivity of their conversion.⁹

One of the simplest and most studied cases of hydrogenation selectivity involves conjugated unsaturated aldehydes such as acrolein, (2-propenal), crotonaldehyde (2-butenal), prenal (3-methyl-2-butenal), and cinnamaldehyde (3-phenyl-2-butenal). With those, the selective hydrogenation of C=O bonds is usually the desired pathway, because the resulting allyl alcohols are valuable intermediates for the manufacturing of perfumes and pharmaceuticals.¹⁰⁻¹² Unfortunately, the thermodynamic drive is toward the hydrogenation of the C=C bond instead, to

produce the corresponding saturated aldehyde or even, ultimately, the associated saturated alcohol^{13,14}. Selectivity toward the production of the unsaturated alcohol must therefore be controlled kinetically. Here we focus on the hydrogenation of crotonaldehyde, promoted by platinum surfaces. The corresponding reaction network is shown in Scheme 1. Single hydrogenation of either the C=O or the C=C bond leads to the formation of crotyl alcohol (2-butenol) or n-butanal, respectively, and further hydrogenation of the second unsaturation leads to the production of n-butanol. Two questions regarding selectivity can be identified in this case: (1) what controls the formation of crotyl alcohol (the desired product)?; and (2) can deeper hydrogenation to n-butanol be avoided?



Scheme 1. Reaction network for the hydrogenation of crotonaldehyde.

The answers to these questions hinge on the details of the mechanism of these reactions. Regarding the second question in particular, it is generally assumed that full hydrogenation is a two step process involving the formation of the half-hydrogenated intermediate products (crotyl alcohol and n-butanal), but this does not need to be the case; the addition of all four hydrogen atoms, to yield n-butanol, can in fact take place on intermediate species adsorbed on the surface before any product is released to the gas (or liquid) phase. This issue is usually not easy to

resolve, as it may be difficult to separate primary from secondary products in these hydrogenation processes. By carrying out catalytic experiments under a single collision regime, we here address this question head on.

The experiments reported in this manuscript were carried out by using an effusive but collimated molecular beam directed at a model platinum surface under a well-controlled ultrahigh vacuum (UHV) environment.¹⁵ It is in general difficult to sustain catalytic hydrogenation reactions under vacuum, but we have recently developed a high-flux beam setup that affords this type of studies.¹⁶⁻¹⁹ Our arrangement is based on a single capillary tube capable of delivering fluxes equivalent to pressures in the mTorr to Torr range on the surface, and on using mass

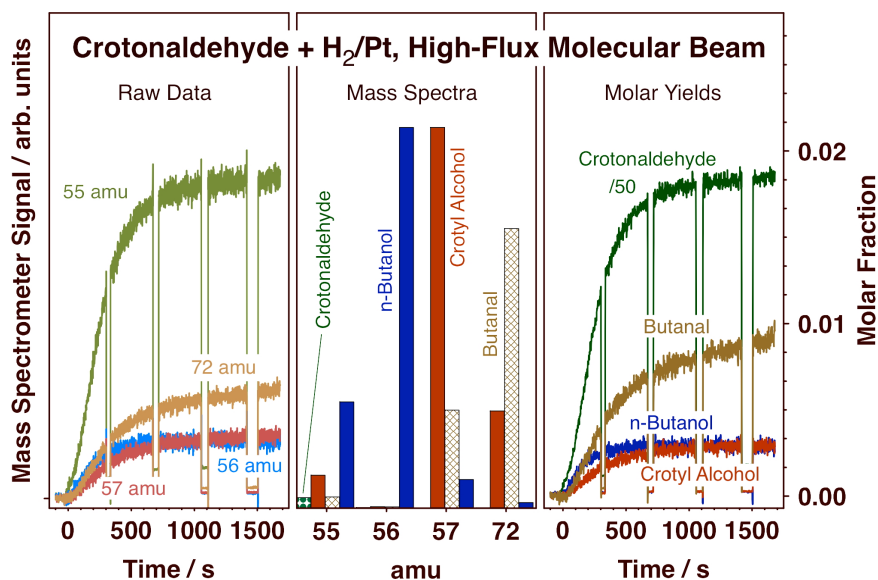


Figure 1. Kinetics of crotonaldehyde hydrogenation promoted by a Pt surface at room temperature (300 K), measured with our high-flux molecular beam setup. The raw data, shown in the left panel as mass spectrometry signals vs. time, can be converted, using the cracking patterns in the center panel, to turnover frequencies (TOFs), or, as shown in the right panel, molar fractions. It is clear that a steady-state catalytic regime can be reached for this reaction. The selectivity of formation of all primary products can also be calculated from these data.

spectrometry for the detection of the reactants and products. Data from a typical run for the room-temperature (300 K) hydrogenation of crotonaldehyde promoted by a polycrystalline Pt disk, obtained with that setup, are reported in Figure 1. The choice of a polycrystalline disk as the substrate (instead of a single crystal, as often done in UHV surface-science experiments) was made to better mimic the surfaces of realistic supported catalysts. The crotonaldehyde + H₂ mixed beam used here was estimated to provide fluxes equivalent to partial pressures for the two reactants of about 4 μ Torr and 1 mTor, respectively. The evolution of both the reactant and the products were followed over time by mass spectrometry, by choosing appropriate masses (55, 56, 57, and 72 amu in Figure 1), to measure the corresponding partial pressures. The beam was interrupted periodically ($t \sim 300, 650, 1050$, and 1420 s in this example) using a blocking flag to check on the background pressures.

A few general observations are worth highlighting from these results. First, a steady-state catalytic regime can certainly be reached using this beam setup, as seen by the leveling off of most of the reported traces after less than 1000 s of reaction (the values for crotyl alcohol and butanal partial pressures keep increasing because those compounds are sticky and cannot be pumped fast enough from the UHV chamber). Second, accurate reaction rates can be measured with our setup by following the partial pressures of the appropriate compounds (the two are proportional to each other); in this figure the conversion is reported in molar fractions to highlight the efficiency of the reaction (Figure 1, right panel), but that can be converted into absolute turnover frequencies (TOFs) after appropriate calibration;¹⁷ the total TOF in this case is about 0.06 ML/s (1 ML = 1 crotonaldehyde molecule converted per Pt surface atom). Third, catalysis is corroborated by the large turnover numbers (TONs) possible; in this example the

TON reaches a value close to 10 crotonaldehyde molecules converted in total per platinum surface atom after 1500 s of reaction, at which point the reaction rates still show no signs of deviating from the initial steady-state values. Finally, all relevant products can be uniquely identified and followed after proper deconvolution of the raw data (Figure 1, left panel), which was done using the mass-spectrometer cracking patterns of the molecules involved (Figure 1, center panel) and a well-established deconvolution process.²⁰ This affords an accurate measurement of reaction selectivities. In the case of the example in Figure 1, the evolution of all the main products (n-butanal, crotyl alcohol, and n-butanol) is clearly seen, with a selectivity toward the unsaturated (crotyl) alcohol of close to 20%. Other masses were monitored, but no other major products (CO, propene, butene) were detected.

The latter observation, that is, the selective hydrogenation of our reactant without any accompanying decomposition steps, is particularly relevant to the uniqueness of the setup used in these studies, because previous temperature programmed desorption (TPD) research with unsaturated aldehydes on hydrogen-predosed Pt(111) surfaces has not only failed to identify the production of hydrogenation products (the saturated aldehyde or the unsaturated or saturated alcohols), but has also detected decomposition products instead, CO and propene in the case of crotonaldehyde.²¹ This discrepancy highlights the different chemical regimes probed by the two approaches. In TPD, the temperature of the surface is ramped as the experiment proceeds, and that promotes the desorption of adsorbates.^{20,22} It is difficult to reproduce steady-state hydrogenation conditions that way, even if the surface is predosed with H₂ before adding the reactant, because the adsorbed atomic hydrogen recombines and desorbs at relatively low temperatures; it has not been possible, to the best of our knowledge, to mimic steady-state

hydrogenation conditions, maintaining high hydrogen surface coverages at the temperature of the conversion of the organic reactant, using such transient experiment.^{5,9,15,23-32} Our high-flux molecular beam arrangement, on the other hand, provides the means to sustain high hydrogen surface coverages as the catalytic conversion takes place, in an steady-state regime.^{16,20} Such conditions not only promote hydrogenation reactions, but also inhibit decomposition pathways, in part at least because the adsorbed hydrogen also promotes weaker (π -bonded rather than di- σ) adsorption of the reactants.^{27,33-35}

In the experiment reported in Figure 1 a gas mixture with both crotonaldehyde and molecular hydrogen was prepared in the gas manifold and fed together as a single beam to the solid sample in the UHV chamber. Alternatively, kinetic runs could be carried out by using a pure H₂ beam and by feeding the crotonaldehyde into the background environment via a leak valve, in order to better control and vary its partial pressure; we have shown previously that the two types of experiments are equivalent once the efficiency enhancement afforded by the directionality of the beam is taken into account.¹⁹ The data obtained from a kinetic characterization of the dependence of the TOFs of all of the products on the pressure of the reactant (P_{CrotAld}) are reported in Figure 2. The left panel displays the raw results, whereas the right panel reports the calculated selectivities and total conversions. Again, several lessons can be learned from this information. First, there is a clear positive dependence of the TOFs on crotonaldehyde pressure. However, that dependence is not linear, but rather shows an asymptotic behavior. We interpret this trend as reflecting a reaction rate limited by the coverage of crotonaldehyde on the Pt surface, which can be described by a Langmuir isotherm ($\theta = K \cdot P / [1 + K \cdot P]$). The solid (blue) line provided for the total TOFs in the left panel of Figure 2 is the result of such fit, with a

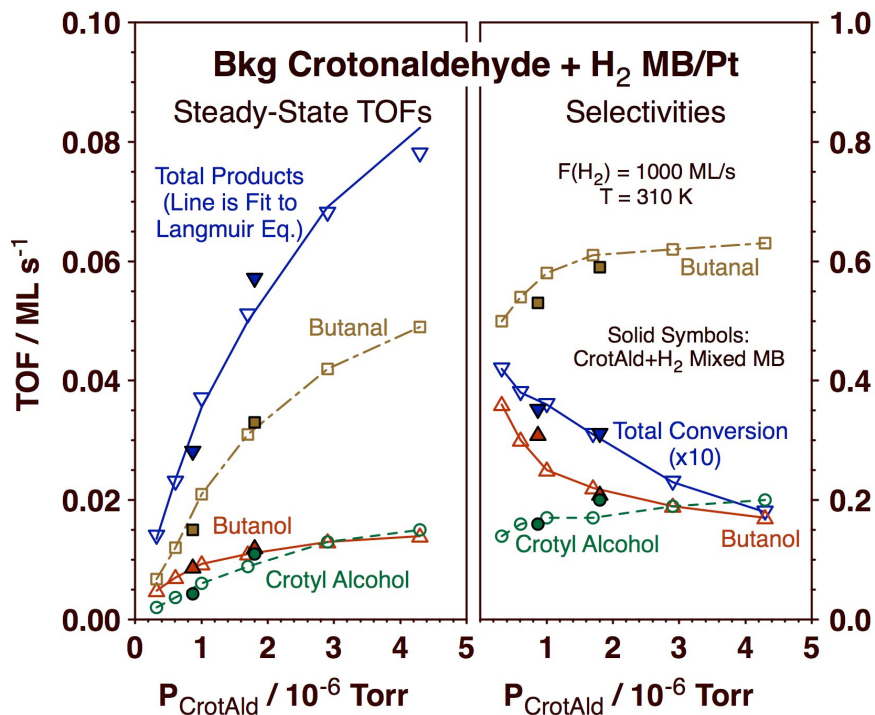


Figure 2. Left: Steady-state TOFs for all three main products resulting from hydrogenation of crotonaldehyde on a Pt polycrystalline surface. Right: total conversion, as a fraction of the reactant's impinging frequency on the surface, and selectivities for each of the products. Both sets of data are reported as a function of the pressure of crotonaldehyde (P_{CrotAld} , introduced in the UHV chamber via a leak valve) while keeping the H₂ molecular-beam (MB) flux constant at 1000 ML/s. The behavior of the total conversion rate can be explained by assuming Langmuir isothermal adsorption, as indicated by the fit provided by the solid blue line for the TOF of the total products (left panel). In terms of selectivity, the main trend is a shift from n-butanol to n-butanal production as the crotonaldehyde pressure is increased.

maximum total TOF of 0.14 ML/s and an equilibrium constant K for crotonaldehyde adsorption (in the presence of the hydrogen beam) of $3.3 \times 10^5 \text{ Torr}^{-1}$. The latter number implies that the crotonaldehyde coverage in these reactions is a measurable fraction of its monolayer saturation coverage: half saturation is obtained at $P_{\text{CrotAld}} = 1/K = 3 \times 10^{-6} \text{ Torr}$.

In order to quantify the influence of the flux of molecular hydrogen on the kinetics of

crotonaldehyde conversion, a number of additional experiments were carried out using crotonaldehyde + H₂ mixed molecular beams of different compositions and total fluxes. The data are summarized in Table 1. Because the final composition of the beams is difficult to control (it must be determined by mass spectrometry during the experiment, as it differs from the original composition because of differences in diffusion rate between the two reactants through the leak valve), it was not easy to carry out a systematic study in this case. Nevertheless, it became clear from the data that the hydrogen flux does not exert a significant influence on the rate of reaction under our experimental conditions. To highlight this conclusion, we provide in Table 1 a comparison between the TOFs measured experimentally (third column) and those calculated for a nominal H₂ flux of 1000 ML s⁻¹ using the Langmuir isothermal equation introduced above, with TOF_{max} = 0.14 ML/s and K = 3.3 × 10⁵ Torr⁻¹ (TOF_{calc}, fourth column). A least-square fit yields a molecular hydrogen order of about n = 0.5, but the differences between the experimental and calculated TOF values are within our experimental error (approximately 10%), so a TOF order of n = 0 in hydrogen flux can also be considered acceptable. A value of n = 1, on the other hand, falls outside the boundaries of our uncertainty. In any case, under the reaction conditions used here, namely, in a large excess of hydrogen in the molecular beams, the expectation is that the platinum surface is always saturated with hydrogen atoms during the

Table 1. Kinetic data for the conversion of crotonaldehyde from crotonaldehyde + H₂ mixed molecular beams on Pt.

F _{H₂} / ML s ⁻¹	F _{CrotAld} / ML s ⁻¹	TOF / ML s ⁻¹	TOF _{calc} ^a / ML s ⁻¹	S _{CrotAld}	S _{ButAld}	S _{ButAld}
600	0.60	0.021	0.023	0.19	0.57	0.24
1000	0.90	0.028	0.031	0.16	0.53	0.31
1270	1.80	0.057	0.053	0.20	0.59	0.21

^a Calculated using the Langmuir isotherm equation from Figure 2, assuming F_{H₂} = 1000 ML s⁻¹ (see text).

steady-state hydrogenation reactions,^{17,19} and that therefore the hydrogen pressure does not affect their kinetics.⁸ It should be noted that the adsorbed hydrogen on the surface does not necessarily block crotonaldehyde adsorption; it has been determined, that, in general, coadsorbed hydrogen modifies the adsorption mode and the adsorption strength, but not the adsorption coverage, of unsaturated hydrocarbons.^{27,36,37} Presumably, atomic hydrogen chemisorbs on nesting sites (three-fold hollow sites on the (111) planes), leaving the surface metal atoms still accessible for bonding with hydrocarbons. In our case, it appears that the crotonaldehyde catalytic conversion occurs under conditions of hydrogen surface saturation and of moderate to high crotonaldehyde coverages.

Several additional observations can be indicated from the data in the right panel of Figure 2. For one, the total conversion, in terms of reaction probability, decreases with increasing P_{CrotAld} . Of course, the reactivity (TOF) goes up in absolute terms, but it does so in a less than linear way. This, again, is a reflection of the Langmuir-type behavior associated with the crotonaldehyde adsorption, which asymptotically approaches monolayer saturation. In terms of selectivity, the main trend is a shift from n-butanol production (the full hydrogenation product) to n-butanal with increasing crotonaldehyde pressure; crotyl alcohol is less influenced by such change. At this point it should be noted that some n-butanol is always made in these reactions, even though catalysis here is probed under single-collision conditions (one of the main advantages of using molecular beams): n-butanol is actually a primary, not a secondary, product, as often assumed. That is one of the central issues we set up to answer in this study (as discussed in the introduction), and our results imply that the surface intermediates that form on the surface of the catalyst during the hydrogenation of unsaturated aldehydes must include species that survive

until all four hydrogen atoms are incorporated. Previous catalytic work has assumed that butanol is a secondary product, arising from hydrogenation of the primary products (the saturated aldehyde and/or the unsaturated alcohol), based on the observation of minimal if any saturated alcohol production at early conversion times. It should be indicated, however, that in some instances a small amount of the fully hydrogenated product has been observed even in the earliest measured sample, and that the lack of its formation at time zero has been claimed based on extrapolation of the data.³⁸⁻⁴⁰

We next speculate on how the trends reported here, specifically the formation of the saturated alcohol as a primary product and the shift in selectivity from the production of the saturated alcohol to the saturated aldehyde with increasing reactant pressure or flux, may be explained in terms of the mechanism of these reactions. For this purpose, we rely on the extensive surface-science and theoretical studies published in the past. The basics of our proposed mechanism are sketched in Figure 3. The unsaturated aldehyde hydrogenation reactions are likely to be initiated by the molecular adsorption of the reactant (crotonaldehyde) on the hydrogen-covered platinum surface. Density functional theory (DFT) calculations have indicated that di- σ bonded adsorbates resulting from rehybridization and bonding of either the C=C or the C=O bond (or both) to Pt surface atoms are quite stable,⁴¹⁻⁵¹ so those could be proposed as the starting point of these reactions. However, it is also well known from both experimental data^{9,27,35,52-54} and DFT calculations^{36,37,55} that, at least with olefins, π bonding becomes dominant as the surface is modified with adsorbed hydrogen atoms, and that it is the π intermediate that becomes hydrogenated during catalysis.^{5,27} In fact, the di- σ bonding that has been seen for crotonaldehyde on clean Pt(111) using sum-frequency generation (SFG) spectroscopy has been

shown to disappear upon the addition of hydrogen to the reaction mixture.⁴⁰ We here propose that the starting surface species in the catalytic hydrogenation of unsaturated aldehydes are the π bonded reactants (Figure 3, bottom right).

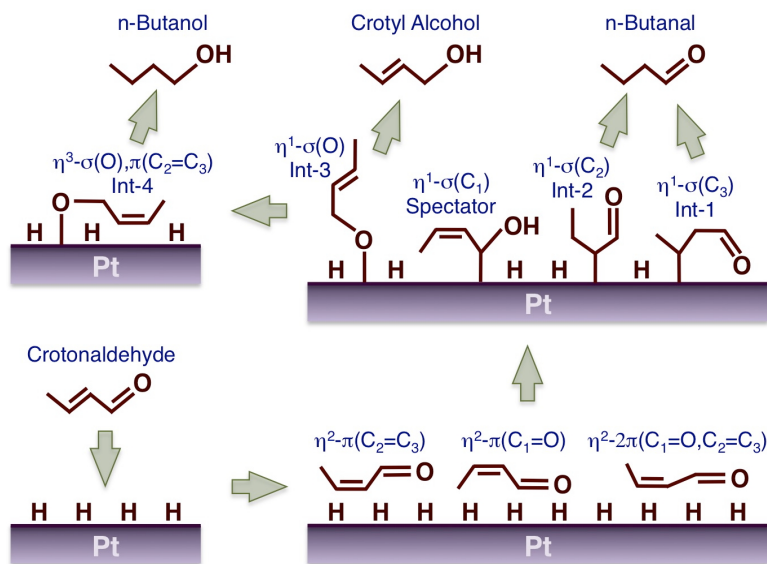


Figure 3. Mechanism proposed for the hydrogenation of crotonaldehyde on Pt surfaces to account for the production of n-butanol as a primary product and the trends seen in selectivity with increasing reactant pressure, namely, a shift from the saturated to the unsaturated alcohol.

Hydrogenation of the initial π -bonded adsorbates is likely to involve more than one surface intermediate.^{7,56} Typically, catalytic hydrogenations with transition-metal solid catalysts take place in a stepwise manner, via the incorporation of individual atomic hydrogen atoms,^{5,17,18,26,57-59} and this so-called Horiuti-Polanyi mechanism leads, in the case of unsaturated aldehydes, to the possible formation of four intermediates, as shown in Figure 3 (top right).⁶⁰ H addition to the C=C bond yields two possible intermediates: a $\eta^1\text{-}\sigma(\text{C}_3)$ 1-(2-oxoethyl)ethyl species (**Int-1**), and a $\eta^1\text{-}\sigma(\text{C}_2)$ 1-(oxomethyl)propyl adsorbate (**Int-2**). Both of those species are likely to form during crotonaldehyde activation, as suggested by the infrared spectroscopy detection of a free

C=O group in the surface species formed from thermal activation of crotonaldehyde on Pt(111) single crystal surfaces²¹ and during crotonaldehyde hydrogenation on Pt/SiO₂,³⁹ and can easily incorporate a second hydrogen atom to produce n-butanal. In parallel, the $\eta^2\text{-}\pi(\text{C}_1=\text{O})$ surface precursor can add hydrogen atoms either at the oxygen or carbon (C₁) ends of the C=O bond. The first reaction yields a $\eta^1\text{-}\sigma(\text{C}_1)$ 1-hydroxo-2-butenyl adsorbate, a species analogous to that suggested, based on reflection-absorption infrared spectroscopy (RAIRS) data, for acrolein on a Pd model catalyst. Such surface species was deemed to be only a spectator,⁶¹⁻⁶³ and we suggest that the same may be the case on Pt as well.

The last possibility is H addition to the C₁ carbon atom, to produce a $\eta^1\text{-}\sigma(\text{O})$ 2-butenoxy species (**Int-3**). We envision that intermediate undergoing two competing subsequent steps, to account for the changes in selectivity seen with changing crotonaldehyde partial pressure in the reaction mixture. Under high pressures, which leads to high surface coverages of the organic species, a standing-up adsorption geometry may be favored (as is the case with many other surface adsorbates),⁶⁴ and subsequent conversion is likely to involve hydrogen addition to the oxygen atom to produce crotyl alcohol. At lower pressures, which result in lower adsorbate coverages, more room may be available on the surface for additional coordination. We propose that, under those circumstances, a new $\eta^3\text{-}\sigma(\text{O}),\pi(\text{C}_2=\text{C}_3)$ 2-butenoxy species (**Int-4**) may form, and hydrogenation of the C=C double bond (to form a $\eta^1\text{-}\sigma(\text{O})$ 2-butoxy intermediate) may take precedent over the oxo-hydrogenation step; the end result in this case is the production of n-butanol. DFT calculations have provided evidence for the particular stability of this type of η^3 adsorbed species on clean platinum surfaces,⁴⁷ and also for a change in mechanism with coverage.⁶⁵ Overall, the mechanism proposed in Figure 3 accounts for the main experimental

observations of this work, and is also consistent with most of the reported details of these systems extracted from surface-science experiments and quantum mechanics calculations.

Experimental Section

The molecular-beam kinetic measurements were carried out in a UHV apparatus described in previous publications.^{16,66} A polished 1 cm in diameter polycrystalline Pt disk approximately 1 mm in thickness was used as the catalyst after cleaning using oxygen and, occasionally, sputtering treatments. The central element of our instrument is a gas doser, made out of a single capillary 150 μm in diameter and 1.2 cm in length, used to generate the collimated high-flux effusive molecular beams required to sustain steady-state catalytic conversions. In some experiments the reaction mixture was premixed in a calibrated volume placed behind the leak valve used to set the beam flux, which was quantified by following the drop in pressure in the backing volume versus time using a MKS Baratron capacitance manometer. The beam fluxes are reported in units of ML/s (monolayers per second, assuming a Pt surface density of 1.5×10^{15} Pt sites/ cm^2). A UTI 100C quadrupole mass spectrometer interfaced to a personal computer was used to follow the partial-pressure data during the kinetic runs.

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