greater electron demand than the charge in **3**. In other words, the lone pairs on fluorine mitigate the electron demand in the α-fluoro primary cation relative to the β-fluoro secondary cation. This is consistent with the view that monofluorination at a cationic center provides π-conjugative electron donation that outweighs the σ-withdrawing effect.[9]

Conclusions

The use of isotopic (^{2}H, ^{13}C) double labeling in neutral product studies of gas-phase ion chemistry has here been demonstrated for the first time. Analysis of fluorine-containing products by ^{19}F NMR reveals the position and extent of isotopic label in the reaction mixture, since the breadth of the fluorine chemical shift scale permits resolution of every isotopomeric product. The formal equivalent of $CH_3CDFCH_2^+$ rearranges by deuteride shift, methyl shift, or fluorine shift in the proportions 1.9:1:0.45. In ion-neutral complexes, the ions formed by the latter two shifts (deuterated analogues of **3** and **4**) interconvert, signaling that these ions are of comparable stability (as predicted by SCF calculations at 6-31G**). As free ions, these cations rearrange extensively to the more stable 2-propyl cations on the millisecond timescale. In ion-neutral complexes, however, the lifetimes are so brief that no rearrangement to this global minimum (deuterated **1**, which is also the ion formed by initial deuteride shift) can be detected. From the proportions of recovered neutral products, we can extract approximate values of conformational equilibrium constants, branching ratios, and isotope effects. The scope and range of isotopic double labeling are thus exemplified.

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Supplementary Material Available: Tables of Cartesian coordinates for the 6-31G** optimized geometry of *skew*-**3** and SCF normal modes for **1**, **3**, **4**, and **7** and a figure of the proton NMR of **6a** (2 pages). Ordering information is given on any current masthead page.

Partial Oxidation without Allylic C-H Bond Activation: The Conversion of Propene to Acetone on Rh(111)-p(2×1)-O

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Abstract: Propene is selectively oxidized to acetone by adsorbed atomic oxygen below 290 K on Rh(111)-p(2×1)-O (θ_O = 0.5) under ultrahigh vacuum conditions. The selectivity for acetone production over combustion is high, although the absolute yield is low, ~0.02 acetone molecules per Rh atom, because a large fraction of the propene desorbs prior to oxygen addition. An oxametallacycle, formed by a direct addition of oxygen to the 2-carbon, is proposed to be the intermediate that results in acetone formation. Isotopic labeling experiments demonstrate that the C-H bond at the 2-position of the carbon chain is selectively broken and transferred to the 1-position during acetone formation. This is supportive evidence for oxygen addition prior to dehydrogenation, since oxygen addition to the 2-carbon would decrease the C-H bond strength at the 2-carbon. Propene oxidation is dramatically different from reactions on Ag. Significantly, the allylic hydrogens of the propene are not activated during the oxidation. Furthermore, the ketone, not the epoxide or aldehyde, is formed on Rh. An important role of the surface oxygen is the inhibition of C-H bond activation. On clean Rh(111), propylidyne is formed. Propylidyne is totally oxidized into CO, CO_2, and H_2O when coadsorbed with oxygen. The inhibition of dehydrogenation allows oxygen addition to compete favorably with dehydrogenation on surfaces with oxygen coverages greater than 0.45 monolayers. For lower oxygen coverages, only combustion products are formed.

Introduction

The selective oxidation of hydrocarbons is an area of immense industrial importance because heterogeneous oxidation processes provide both large-scale petrochemical commodities and precursors for many specialty chemicals.[1] For example, the selective epoxidation of ethylene over silver-based catalysts is a large-scale process,[2] so that extensive efforts to understand the catalytic reaction mechanism have been made.[3]

It is well known that ethylene can be selectively epoxidized with oxygen adsorbed on Ag, whereas propene is mainly converted to carbon dioxide and water.[4] Indeed, under ultrahigh vacuum conditions, propene combusts to carbon dioxide and water on Ag(110).[5] The nonselective oxidation of propene on silver is largely attributed to the high acidity of the allylic protons. Norbornene and styrene, which contain no allylic protons, are oxidized to their respective epoxides by oxygen chemisorbed on Ag(110)[6] and Ag(111),[7] supporting the proposal that gas-phase acidity dictates oxidation selectivity on Ag. Because of the high reactivity of allylic protons on Ag, selective oxidation of propene is difficult.

Herein, we report that propene is selectively oxidized to acetone by oxygen chemisorbed on Rh(111)-p(2×1)-O. Surprisingly, allylic C-H bond activation does not occur in the propene oxidation to acetone. As a result, the product distribution and kinetics for propene oxidation are similar to those previously reported for styrene, which contains no allylic protons. Styrene is oxidized to acetophenone on Rh(111)-p(2×1)-O.[8,9] Indeed, we have widely observed that alkenes are oxidized to their corresponding methyl ketones on Rh(111)-p(2×1)-O.[10]

Furthermore, we have shown that an oxygen coverage of 0.5 is required for partial oxidation. Although the interactions of

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oxygen with the Rh(111) surface have been extensively studied under ultrahigh vacuum conditions,[11-20] there is a disagreement about the oxygen coverage associated with the (2×2) LEED pattern. Dynamic LEED studies of a Rh(111)-(2×2)-O surface were most consistent with an oxygen coverage of 0.25 and oxygen occupying the 3-fold hollow sites.[17] However, the angular distribution of rhodium atoms ejected by ion bombardment is attributed to an oxygen coverage of 0.50 monolayers.[20]

In this paper, we reconcile the reported differences in oxygen coverage for the (2×2) overlayers. We have observed a (2×2) LEED pattern for oxygen coverages of both 0.25 and 0.50 on Rh(111). The coverage of 0.25 is ascribed to the true p(2×2)-O overlayer, whereas the LEED pattern for 0.50 monolayers is attributed to three domains of p(2×1)-O. The Rh(111)-p(2×1)-O, not the p(2×2)-O surface, induces partial oxidation. All lower oxygen coverages including the 0.25 monolayer p(2×2)-O, lead to combustion.

Experimental Section

Experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure of ~1 × 10^{-10} Torr, described in detail previously.[21] The chamber is equipped with electron optics for retarding field Auger electron spectroscopy and low-energy electron diffraction, an X-ray photoelectron spectrometer, and a quadrupole mass spectrometer mounted in a differentially pumped liquid nitrogen cooled cryoshield. The entrance aperture to the mass spectrometer was ~0.1 in., comparable to the crystal diameter of 0.25 in., and the sample-shield separation was ~0.1 in. This geometry minimized angular effects while optimizing the detection of gases originating from the Rh surface. The mass spectrometer housing was liquid nitrogen cooled during data acquisition to achieve a lower background pressure and a higher pumping speed in the mass spectrometer chamber. Several experiments were performed with the mass spectrometer shield at room temperature. The data obtained were qualitatively the same with or without cooling, demonstrating that the observed reactions did not occur on the walls of the mass spectrometer shield. The signal intensity was ~3-5 times higher and the temperature resolution somewhat degraded when experiments were performed with the shield at room temperature.

The preparation and cleaning of Rh(111) have been described previously.[22] The surface composition was monitored by Auger electron and X-ray photoelectron spectroscopies and low-energy electron diffraction (LEED). Temperature-programmed reaction of adsorbed oxygen was also used to confirm that the surface was pure. Surface carbon and oxygen combine to CO and CO_2 in the range of 400-800 K. Subsurface carbon reacts with surface oxygen to produce CO above 1000 K.[15] No CO is produced during temperature-programmed reaction of oxygen on the freshly prepared Rh(111) surface, confirming its purity.

The Rh(111)-p(2×1)-O surface was prepared by exposing clean Rh(111) to dioxygen for 2 min at 300 K. The reservoir pressure was 1 Torr and chamber pressure 5 × 10^{-9} Torr during dioxygen adsorption. Oxygen overlayers with lower coverages were made by dosing dioxygen at 300 K for 30-300 s using a reservoir pressure of 100 mTorr during which the chamber pressure was 4 × 10^{-10} Torr. The Rh(111)-p(2×2)-O overlayer required a 60-s dose.

Propene (CP) and dioxygen (research purity) were obtained from Matheson, propene-d_6 (99% d), propene-*3,3,3*-d_3 (99% d) and $^{18}O_2$ (99.5%) were obtained from Cambridge Isotope Laboratories, and propene-*1,1*-d_2 (98% d) was obtained from MSD. All samples of propene were trapped into glass bottles with liquid nitrogen, and subjected to several freeze-pump-thaw cycles before each day of experimentation. Sample purities were confirmed by using mass spectrometry. The propene-*3,3,3*-d_3 sample initially contained a significant amount of CD_4 and C_2H_4, and was purified by low-temperature vacuum distillation. Equimolar mixtures of propene isotopes were prepared directly in the dosing line by mixing equal pressures of the two propene isotopes. The mixture composition was measured with the mass spectrometer during dosing.

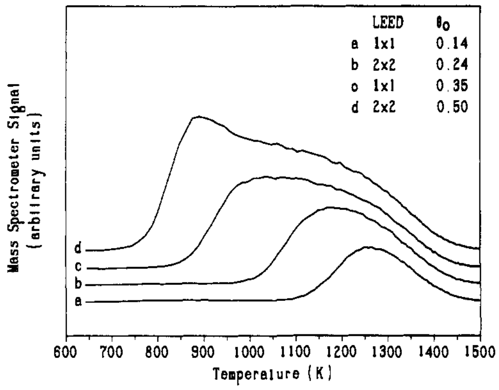

Figure 1. Temperature-programmed desorption of oxygen on Rh(111). The coverages are 0.14, 0.24, 0.35, and 0.50 monolayers, respectively, based on O(1s) XPS intensities (Table I). The heating rate varied between 50 K/s at 650 K and 15 K/s at 1500 K.

Table I. Oxygen Coverage Determination Using LEED and XPS

adsorbate	oxygen	oxygen	carbon monoxide	sulfur
LEED pattern	(2 × 2)	(2 × 2)	(2 × 2)	($\sqrt{3} \times \sqrt{3}$)-R30°
XPS counts[a]	O(1s) 9800	O(1s) 4900	O(1s) 14900	S(2p) 3880
sensitivity[24]	2.93	2.93	2.93	1.68
O_2 desorption	1.00	0.48		
coverage	0.50 ± 0.02	0.25 ± 0.02	0.75	0.33

[a] The O(1s) and S(2p) data were collected for 10 min, and the peak area was determined by using software supplied with the spectrometer.

All samples were dosed through a leak valve with a directed doser separated from the crystal by ~0.1 in. The size of the crystal was comparable to the diameter of the doser exit, ~0.25 in., so that the gas flux was uniform across the crystal face. The exposures are reported in units of time and are referenced to the time required to achieve saturation exposure while maintaining the pressure in the reactant reservoir, the leak valve position, and the distance between crystal and doser constant. During adsorption of propene, the pressure increase was <1 × 10^{-10} Torr. The time required for saturation was ~20 s, indicating a flux equivalent to a local pressure of >5 × 10^{-8} Torr in the vicinity of the crystal. Saturation exposure is defined as the minimum time required to produce the maximum yield of products during temperature-programmed reaction. The crystal temperature was maintained below 130 K during adsorption unless otherwise noted.

Reaction products were monitored with an UTI-100C mass spectrometer interfaced to an IBM PC. Two programs were employed to monitor gaseous products.[23] A broad search for reaction products was performed in which more than 100 masses were monitored. In order to achieve better temperature resolution and signal-to-noise ratio, up to 10 selected products were monitored in separate experiments. The heating rate during temperature-programmed reaction was approximately constant at 10 K/s.

Results

Ordered Oxygen Overlayers. A sharp (2×2) LEED pattern was observed for two different oxygen coverages that differed by a factor of 2. The (2×2) LEED pattern for the higher oxygen coverage was observed following exposure of clean Rh(111) to dioxygen for 2 min using a capillary doser located ~0.5 in. from the sample. The doser reservoir pressure was 1 Torr, and the sample temperature was 300 K, and subsequently cooled to 120 K. During O_2 dosing, the chamber pressure was ~5 × 10^{-9} Torr. Larger oxygen exposures did not increase the amount of adsorption

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Table II. Mass Spectra Fragmentation Pattern for the Reaction Products of Propene on Rh(111)-p(2 × 2)-O and for Selected Samples

	mass/charge ratio (intensity)									
molecule	60	58	57	45	43	31	29	28	27	15
oxidation product[a]		17			100					44
^{18}O product	17			100						44
acetone[a]		17	1		100	1	5	13	9	40
propene oxide[a]		32	4		29	28	78	100	74	26
propanal[b]		64	17		1	1	100	60	30	
allyl alcohol[b]		24	100		1	30	38	10	16	
methyl vinyl ether[b]		100			63	55				

[a] Measured in our laboratory spectrometer. [b] Taken from the literature.[28]

at 300 K on the basis of temperature-programmed desorption experiments. Molecular oxygen was produced via atom recombination in the range of 800–1400 K (Figure 1d). The (2×2) LEED pattern for the saturation oxygen on Rh(111) persists up to ~500 K, at which point it disorders to produce a (1×1) LEED pattern. The (2×2) pattern reappears upon cooling to below 300 K.

A (2×2) LEED pattern was also observed for half the saturation coverage of oxygen. Exposure of Rh(111) to O_2 at 300 K for 60 s using a reservoir pressure of 100 mTorr and subsequent cooling to 120 K afforded a (2×2) LEED pattern and 50% of the amount of O_2 in temperature-programmed desorption (Table I). The background pressure was 4×10^{-10} Torr during the oxygen adsorption. In this case, the (2×2) LEED pattern disorders upon heating to ~290 K and O_2 is formed between 1000 and 1400 K (Figure 1b), similar to earlier LEED studies.[12] No other ordered overlayers were observed.

The oxygen coverages associated with the two (2×2) LEED patterns differ by a factor of 2, based on the relative O_2 yields in temperature-programmed desorption (Figure 1 and Table I). These temperature-programmed desorption data are in good agreement with those previously reported.[14] Coadsorption of ^{16}O and ^{18}O yields the three isotopes of O_2 in statistical ratios over the entire high-temperature range.

The absolute oxygen coverages were estimated to be 0.5 and 0.25, by using X-ray photoelectron data summarized in Table I. The O(1s) photoelectron intensities from the two ordered (2×2) overlayers are compared with the O(1s) intensity of a Rh(111)-(2×2)-CO overlayer having a CO coverage of 0.75 monolayers,[25,26] and the S(2p) intensity of a Rh(111)-($\sqrt{3}\times\sqrt{3}$)-R30°-S overlayer, which has a known sulfur coverage of 0.33 monolayers.[18,27]

The true p(2×2)-O overlayer should have an oxygen coverage of 0.25 and probably corresponds to the structure proposed on the basis of LEED calculations. The 2×2 LEED pattern for $\theta_O = 0.50$ is, therefore, most likely due to three domains of 2×1 periodicity. Dynamic LEED studies are needed to define the structure in detail, however. Hence, we will refer to the surface with an oxygen coverage of 0.50 as Rh(111)-p(2×1)-O.

Oxidation Reactions of Propene on Rh(111)-p(2×1)-O. Propene is selectively oxidized to acetone at 290 K by oxygen chemisorbed on Rh(111)-p(2×1)-O (Figure 2). Propene desorption and combustion to CO, CO_2, and H_2O are competing processes. Temperature-programmed reaction data for a saturation exposure of propene on an ^{18}O-labeled Rh(111)-p(2×1)-O are shown. Saturation is defined as the minimum exposure required for the maximum product yield including propene. The data show the most intense ion for each product.

Water, carbon monoxide, and carbon dioxide are all formed in the range of 350–550 K, the range where surface carbon and oxygen recombine and where CO desorbs. Small amounts of water are also evolved at 250 K. In addition, propene desorbs at 240, 190, and 170 K. No dihydrogen is detected from propene reaction on Rh(111)-p(2×1)-O.

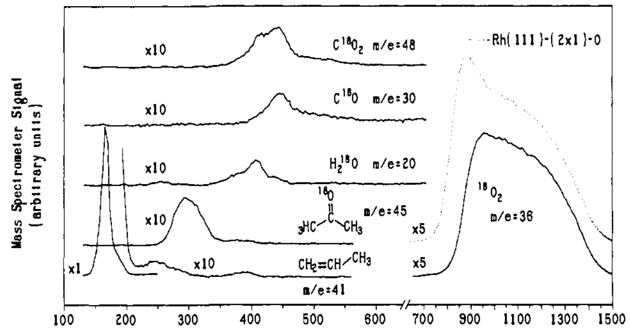

Figure 2. Reactions of propene on Rh(111)-p(2×1)-^{18}O. A saturation amount of propene was adsorbed at 130 K. The heating rate was approximately constant at 10 K/s below 700 K and decreased almost linearly from ~30 K/s above 700 K.

No residual carbon is detected in Auger electron spectra obtained following temperature-programmed reaction of propene to 700 K. A substantial amount of oxygen remains on the surface, 0.43 ± 0.01 monolayers, which recombines between 900 and 1400 K in a broad peak, similar to the O_2 production from the freshly prepared Rh(111)-p(2×1)-O (Figure 2). No CO is produced above 600 K, confirming that there is no residual carbon.

The oxidation product was unequivocally identified as acetone on the basis of qualitative and quantitative aspects of mass spectral data (Table II). All ions up to $m/e = 80$ were monitored in initial experiments, and the highest ion detected was $m/e = 58$, assigned as the parent ion. A single oxygen atom is added to the product because $m/e = 60$ ($(CH_3)_2C^{18}O$) but *not* $m/e = 58$ or $m/e = 62$ is detected for the product of propene oxidation on Rh(111)-p(2×1)-^{18}O. Furthermore, the fragmentation pattern of the 290 K product quantitatively agrees with that measured for an authentic acetone sample (Table II). Acetone has three distinct fragment ions: $m/e = 58$, the acetone molecular ion, $m/e = 43$ (CH_3CO^+), and $m/e = 15$ ($CH_3{}^+$). The relative intensities of these ions are approximately 0.17:1.00:0.40 for the product peak and the acetone sample. Consistently, the ratio of $(CH_3)_2C^{18}O^+$ ($m/e = 60$), $CH_3C^{18}O^+$ ($m/e = 45$), and $CH_3{}^+$ ($m/e = 15$) is 0.17:1.00:0.44 when reaction occurs on the ^{18}O-labeled surface.

All other possible oxidation products with C_3H_6O stoichiometry are excluded on the basis of qualitative differences in their mass spectra and that of the product (Table II).[28] The mass spectrum of propene oxide contains intense fragments in the range $m/e = 26–31$, but none of these ions are detected in the product peak. Propanal is excluded because its mass spectrum contains very little $m/e = 43$, which is the most intense ion in the product spectrum. Furthermore, the most intense fragment ion in the mass spectrum of propanal, $m/e = 29$, is absent for the product. Allyl alcohol is excluded because its most intense ion is $m/e = 57$, which is absent in the product.

Acetone is formed for all exposures of propene on Rh(111)-p(2×1)-O. At low exposures (1 s, ~0.05 of saturation) acetone is evolved in a peak centered at 320 K, and no propene desorbs.

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At intermediate exposures (0.15 saturation), propene desorption commences at 190 K. Concomitantly, the acetone yield increases and the peak temperature for its evolution shifts to 310 K. For propene exposures above 0.5 saturation, a second propene peak is observed at 170 K with an unresolved shoulder at 190 K. The acetone yield also increases up to exposures of 0.5 sautration, and its peak temperature shifts to 290 K. The maximum acetone yield is ~2.7 times greater than for 0.05 of saturation. For all exposures, CO and CO_2 are evolved at 450 K and water is formed in a peak centered at 400 K. Small amounts of water are also evolved at ~260 K. The relative yields of acetone and CO plus CO_2 are essentially independent of exposure, based on the relative intensities of their respective temperature-programmed reaction peaks.

The maximum coverage of propene on Rh(111)-p(2×1)-O at 130 K is estimated to be ~0.22 monolayers, on the basis of the relative intensities of the C(1s) and O(1s) peaks in X-ray photoelectron spectra. The propene coverage depends on the adsorption temperature. For example, the propene coverage is estimated to be ~0.04 for a surface temperature of 200 K after dosing for 60 s, equivalent to saturation at 130 K. The yields of all oxidation products are essentially the same for adsorption temperatures of 130 and 200 K. These data are consistent with the observed desorption of weakly bound propene and indicate that the probability for oxygen addition is not increased significantly by an increase in adsorption temperature.

Sequential adsorption experiments provide additional evidence that weakly bound propene is not oxidized. Adsorption of 0.04 monolayers of propene-d_0 at 200 K followed by adsorption of a saturation amount of propene-d_6 at 120 K yields only acetone-d_0 during temperature-programmed reaction. Furthermore, only propene-d_0 desorbs at 240 K and only propene-d_6 at 170 K, suggesting that the higher temperature adsorption state leads to propene oxidation and that it does not interchange with more weakly bound propene.

Approximately 0.01 CO molecules are formed per Rh atom from combustion of propene. This estimate is based on the relative CO yields for propene combustion and for desorption from Rh(111)-($\sqrt{3}\times\sqrt{3}$)R30°-CO ($\theta_{CO} = 0.33$) and (2×2)-CO ($\theta_{CO} = 0.75$).[25,26] Similarly, the acetone yield is estimated to be ~0.02 molecules per Rh atom.[29] The CO_2 and H_2O yields are of the same magnitude as CO. Thus, the total conversion[30] to all oxidation products is ~10% for adsorption at 130 K or ~50% for 200 K.

Although the absolute yield of acetone is small, we have strong evidence that oxidation does *not* occur only at defects or impurities in the oxygen overlayer. The ratio of acetone-^{16}O and -^{18}O produced from propene oxidation is the same as the ^{16}O:^{18}O ratio on a p(2×1)-O overlayer made by sequential adsorption of $^{16}O_2$ and $^{18}O_2$. Sequential adsorption of $^{16}O_2$ and $^{18}O_2$ at 300 K should result in different populations of oxygen isotopes in perfect and defect sites, since they should have different binding energies. If oxidation is promoted exclusively at minority sites, the ^{16}O:^{18}O ratio of the acetone products would not reflect the ratio of ^{16}O:^{18}O on the surface. For example, the ratio of acetone-^{16}O to -^{18}O evolved from Rh(111)-p(2×1)-O with an ^{16}O:^{18}O of 0.32 ± 0.03 is 0.28 ± 0.03. The isotopic distribution of the combustion products also reflected the relative oxygen coverage. The ratios of all oxygen isotopes were constant over the entire temperature range for O_2 production. The mixed oxygen overlayer was prepared by first adsorbing $^{16}O_2$ followed by $^{18}O_2$, and the ratios were measured by temperature-programmed reaction. Analogous experiments were performed for other oxygen overlayers prepared by first adsorbing $^{18}O_2$ followed by $^{16}O_2$.

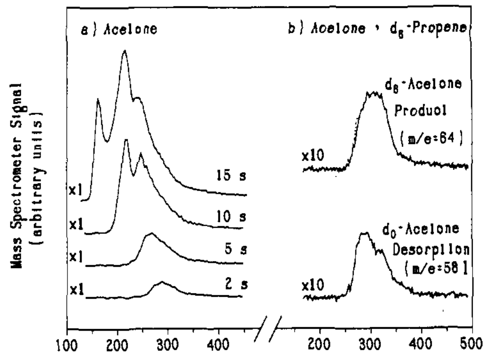

Figure 3. (a) Acetone desorption from Rh(111)-p(2×1)-O. (b) Acetone isotopes desorption from a reaction of coadsorbed [d_6]propene (approximately saturated) and [d_0]acetone (~0.1 saturation) on Rh(111)-(2×1)-O.

Selective deuteration of the propene was used to probe the details of hydrogen transfer during propene oxidation. Some intermolecular hydrogen transfer occurs during the course of propene oxidation. Temperature-programmed reaction of an equimolar mixture of propene-d_6 and propene-d_0 on Rh(111)-p-(2×1)-O yields acetone-d_6, -d_5, -d_1, and -d_0 with similar kinetics in a ratio of 1.9:0.8:0.1:1.0.[31] No acetone-d_4, -d_3, or -d_2 was formed. These data indicate that, at most, one C–H bond is activated during acetone formation. Statistical exchange would yield nearly equal amounts of the four acetone isotopes since only a small isotope effect is observed for reaction of propene-d_0 vs -d_6.

In contrast, allylic protons are *not* activated during acetone formation. Only CD_3COCH_3 is produced from reaction of $CD_3CH{=}CH_2$ on Rh(111)-p(2×1)-O. Furthermore, temperature-programmed reaction of an equimolar mixture of $CD_3CH{=}CH_2$ and $CH_3CH{=}CH_2$ yields only $(CH_3)_2CO$ and CD_3COCH_3.[31] Thus, neither intra- nor intermolecular transfer of allylic protons occurs during propene oxidation to acetone.

Methylene C–H bonds are also not broken during acetone formation. Selective oxidation of propene-*1,1*-d_2 yields only acetone-d_2. Reaction of an equimolar mixture of propene-d_0 and -*1,1*-d_2 ($CH_3CH{=}CD_2$) on Rh(111)-p(2×1)-O yields only acetone-d_0 and -d_2. Only m/e = 58 and 60 amu, corresponding to acetone-d_0 and -d_2, are detected; no 59 amu acetone-d_1 is detected.

Taken together, the selective isotopic labeling experiments show that the C–H bond at the 2-position is selectively broken during the formation of acetone. The nonstatistical exchange between propene-d_0 and -d_6 suggests that either both inter- and intramolecular proton transfer occurs or that dehydrogenation and hydrogenation occur rapidly compared to the rate of diffusion of hydrogen.

Acetone Desorption and Reactions. The rate of gaseous acetone evolution from propene oxidation is limited by desorption, not by reaction. Temperature-programmed reaction following exposure of propene-d_6 (~1.0 saturation) to Rh(111)-p(2×1)-O containing acetone-d_0 (0.1 saturation) produces acetone-d_0 and -d_6 with similar kinetics and yields (Figure 3b). The leading edge of the acetone-d_6 and -d_0 peaks are indistinguishable, and no H–D exchange products were detected, indicating that the initial rate of acetone evolution is controlled by desorption.

Acetone primarily desorbs from Rh(111)-p(2×1)-O (Figure 3a). No dehydrogenation or combustion is detected although there is a minor amount of oxygen exchange with the surface.

At low exposures (2 s, ~0.1 saturation), acetone desorbs in a single peak at 290 K that shifts to lower temperature as a function of exposure. At high exposures (>10 s, ~0.5 saturation),

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(29) A correction factor of 1.7 for acetone (m/e = 43) mass spectrometer detection sensitivity is used. The correction includes fragmentation, ionization efficiency, multiplier gain, and quadrupole transmission using the method suggested by *UTI-100C Operating and Service Manual*; UTI: Milpitas, CA, 1981. A systematic error may result from the inaccuracy of the assumptions for quantitative mass spectral analysis and from the differences in pumping speed for different molecules in the mass spectrometer chamber. This possible error (up to ~50%), however, will not alter the major conclusions of this paper.

(30) Defined as (number of propene molecules that react)/(total number of propene molecules adsorbed).

(31) All acetone products were monitored at their parent molecular ions. The ratios are obtained after correction for natural abundance and fragmentation in the mass spectrometer. The relative intensities of (parent − 1):(parent):(parent + 1) for [d_0]acetone are ~6:100:4 in our mass spectrometer.

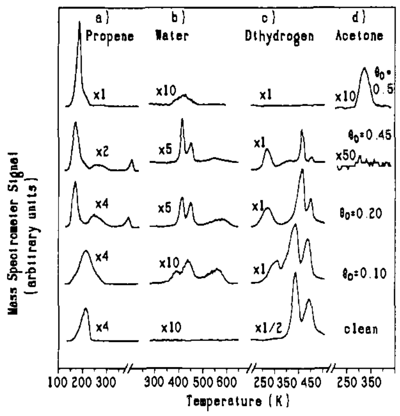

Figure 4. Reactions of propene on oxygen-precovered Rh(111). The initial oxygen coverages are 0.0, 0.10, 0.20, 0.45, and 0.50 monolayers.

a second acetone desorption peak is observed at 220 K. Multilayer sublimation is observed at 160 K (Figure 3a). A leading-edge analysis of the 160 K peak yields a heat of desorption of 45 kJ/mol, in good agreement with the heat of sublimation of 43.8 kJ/mol, calculated by using thermodynamic data.[32]

A small amount of oxygen is exchanged with the surface. A minor amount of acetone-^{18}O (5%, ~0.016 molecules per Rh atom) is produced at 310 K, coincident with a tail in the acetone-^{16}O peak. The amount of acetone-^{18}O formed from oxygen exchange with the surface *increases* substantially (0.05 molecules/Rh) for *lower* ^{18}O coverages ($\theta_O = 0.40$).

Although no combustion is induced on the full Rh(111)-p(2×1)-O surface, carbon monoxide, carbon dioxide, and water are produced from acetone reaction for initial oxygen coverages below 0.50 monolayers. Vibrational studies of acetone on Rh(111)-p(2×2)-O, presumed to have an oxygen coverage of 0.25, obtained at 300 K have suggested the presence of surface acetate, CH_3COO, which presumably leads to combustion products.[33] Our observation of some oxygen exchange between the surface and acetone suggests that $(CH_3)_2COO$ may be present, and the highest temperature peak of acetone desorption at 290 K is attributed, in part, to the decomposition of $(CH_3)_2COO$ species. Temperature-programmed desorption and reaction of acetone on Rh(111)-p(2×1)-O ($\theta_O = 0.5$) are slightly different from previous studies on Rh(111)-p(2×2)-O, presumably due to the oxygen coverage difference.[33]

Dependence of Propene Reactivity on Oxygen Coverage. Propene is oxidized to acetone only for oxygen coverages on the order of 0.50 monolayers, not at lower oxygen coverages. Furthermore, propene is not oxidized by water or hydroxyl formed from $H_2{}^{18}O$ on Rh(111)-p(2×1)-O. Only acetone-^{16}O is formed during temperature-programmed reaction of propene coadsorbed with $H_2{}^{18}O$. Previous studies suggested that hydrogen-bonded OH is present when water is adsorbed on oxygen-precovered Rh(111).[34] Our data demonstrate that the oxygen overlayer serves as the oxidant and that the oxygen inhibits C–H bond activation.

On clean Rh(111), propene irreversibly decomposes to H_2 and adsorbed carbon via propylidyne.[35] Desorption of propene competes with propylidyne formation at 220 K. The propylidyne decomposes to ethylidyne and CH_2, which eventually yield dihydrogen in peaks at 390 and 450 K and in a tail extending to 700 K (Figure 4).

Propylidyne reacts with oxygen to produce combustion products but not acetone. Oxygen adsorbed on Rh(111) following synthesis of surface propylidyne yields H_2 at 260 and 380 K, and CO, CO_2, and H_2O at 400–600 K (data not shown). Propylidyne was formed by adsorbing propene (~0.5 saturation) at 120 K followed by rapid heating to ~270 K. Oxygen was exposed to the surface for ~2 min after cooling to 120 K. Temperature-programmed reaction data for propylidyne (~0.5 saturation) and oxygen is similar to that for propene on Rh(111) precovered with ~0.3 monolayers of oxygen.

The presence of even low coverages of oxygen ($\theta_O = 0.10$) alters the propene desorption kinetics as is evidenced by a broadening of the propene desorption peak near 200 K (Figure 4). Furthermore, the amount of propene desorption is increased by ~35%. In addition, gaseous water is evolved in three peaks at 380, 440, and 550 K and a new dihydrogen evolution peak is observed at 300 K. Carbon monoxide and carbon dioxide are also evolved between 450 and 650 K, but no acetone is formed.

For oxygen coverages in the range of 0.2–0.45, three propene peaks are observed at 170, 250, and 390 K. In addition, minor amounts of propane are formed at ~200 K at intermediate oxygen coverages (not shown). Water is evolved in two narrow peaks of 410 and 450 K and in a broad peak centered at 550 K. Dihydrogen is evolved in peaks at 260, 410, and 450 K with a tail extending to 700 K. The two higher temperature dihydrogen peaks are coincident with water evolution, suggesting they are produced from a common intermediate. The yield of water relative to dihydrogen at 410 and 450 K increases with the increasing oxygen coverage.

The total amount of propene that reacts on Rh(111) decreases as a function of oxygen coverage. The combined dihydrogen and water yield decreases while propene desorption increases as the oxygen coverage is increased. The yields of combustion products reach a maximum at an oxygen coverage of ~0.25. The yields of CO, CO_2, and H_2O are approximately 10, 3, and 1.5 larger for an oxygen coverage of 0.25 compared to the 0.5 monolayer Rh(111)-p(2×1)-O surface. Small amounts of carbon remain following temperature-programmed reaction of saturation amounts of propene up to 800 K on surfaces precovered with less than 0.40 monolayers of oxygen. These data suggest that intermediate oxygen coverages permit significant amounts of C–H bond breaking while providing an adequate supply of oxygen for combustion.

Although no reversible activation of the allylic C–H bonds occurs on the full Rh(111)-p(2×1)-O overlayer, they react extensively on surfaces with lower oxygen coverages. For example, reaction of $CD_3CH{=}CH_2$ on Rh(111) with 0.30 monolayers of oxygen produces propene-d_3 in peaks at 170, 220, and 380 K, propene-d_6 and -d_5 at 220 and 380 K, and [d$_4$]propene at 180, 220, and 380 K. All isotopes of dihydrogen are also evolved. The leading edge and the peak temperature for D_2 (T_p = 230 K) evolution are lower than for H_2 (T_p = 240 K). On clean Rh(111), H_2 is evolved at 358 and 424 K, and D_2 is evolved at 378 and 442 K from propene-d_3 reaction. Exchange is also observed during reaction of $CH_3CH{=}CD_2$ on Rh(111) ($\theta_O = 0.3$): propene-d_2, -d_3, -d_4, and -d_5 are evolved at 220 and 380 K. H_2 is evolved in peaks at 230, 380, and 420 K, but D_2 desorption is not observed below 350 K during temperature-programmed reaction of $CH_3CH{=}CD_2$ on Rh(111), $\theta_O = 0.3$. These data suggest that the allylic C–H(D) bonds are broken first on Rh(111) with oxygen coverages below 0.45.

Discussion

The selective oxidation of propene by oxygen on Rh(111)-p(2×1)-O is an unprecedented reaction. In contrast to other heterogeneous partial oxidation reactions, allylic C–H bonds are not activated, the ketone is selectively formed, and high oxygen coverages favor partial oxidation while low oxygen coverages favor combustion and dehydrogenation. Although the absolute yield is small, the unique features of this reaction warrant careful consideration.

We propose that surface oxygen directly adds to the 2-carbon to form the metallacycle **1** containing one or more Rh centers. This intermediate represents the most direct route for oxygen

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(32) The heat of sublimation of acetone is calculated from the heat of fusion (5.7 kJ/mol), heat of vaporization (32 kJ/mol), and heat capacities (126 J/mol for liquid and 75 J/mol for gaseous acetone). All data are taken from the *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Lide, D. R., Eds.; CRC Press: Boca Raton, 1989.

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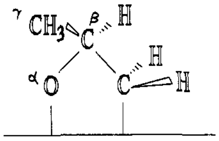
addition and acetone formation. Spectroscopic studies are planned to identify the intermediate.



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In order to form acetone from the proposed oxametallacycle intermediate **1**, transfer of hydrogen is necessary. The most direct pathway would be selective dehydrogenation of the 2-carbon, which is β to the metal and α to oxygen. Acetone would be formed by hydrogenation of the 1-carbon following β-hydrogen elimination.

β-Hydrogen elimination from an oxygen-containing intermediate is expected to be most facile because the electronegative oxygen atom stabilizes the product of homolytic dehydrogenation of the carbon bound to oxygen.[36] Indeed, the preference for β-hydrogen elimination has been demonstrated in several cases,[37,38] including the elimination of acetone from 2-propoxide.[39]

Our isotopic labeling experiments confirm the expectation that the C–H bond at the 2-position is selectively cleaved to form acetone. There is no H–D exchange during the reaction of $CD_3CH{=}CH_2$ or $CH_3CH{=}CD_2$ on Rh(111)-p(2×1)-O, demonstrating that neither the allylic nor methylenic C–H bonds are broken during acetone formation. Therefore, the 2-C–H bond must be broken and the hydrogen transferred to the 1-carbon to yield acetone. The selectivity for dehydrogenation of the 2-carbon is a strong evidence for the proposed oxygen addition prior to dehydrogenation. Without oxygen addition, dehydrogenation at the 2-position would not be favored; rather, allylic C–H bond activation is anticipated. Indeed, preference for allylic C–H bond activation is observed on the clean surface and for lower oxygen coverages where acetone is not formed. These data further support the assertion that oxygen addition precedes hydrogen migration and demonstrate the importance of inhibiting propene reaction on clean Rh sites.

The transfer of hydrogen to the 1-carbon may be either an intramolecular 2,1-shift or intermolecular transfer of hydrogen via the surface. The hydrogen migration is, at least in part, surface mediated, since reaction of an equimolar mixture of propene-d_6 and -d_0 on Rh(111)-p(2×1)-O produces acetone-d_6, -d_5, -d_1, and -d_0, but not acetone-d_4, -d_3, and -d_2. The ratio of acetone-d_6, -d_5, -d_1, and -d_0 is not statistical, however, suggesting that either the hydrogen remains in the vicinity of the propene from which it was originally removed or that there is also some intramolecular hydrogen shift. Direct intermolecular hydrogen transfer is unlikely since the coverage of the intermediate is sufficiently low that nearest-neighbor interactions are unlikely.

Intermediate **1** is analogous to those proposed for olefin oxidation by transition-metal oxo complexes,[40-48] for isobutylene oxide formation from *tert*-butyl alcohol on Ag(110)+O,[36] and for norbornene and styrene oxidation on Ag.[49] The oxidation of alkenes by chromyl chloride, CrO_2Cl_2, is proposed to proceed by alkene coordination to the chromium atom, followed by a [2+2] cycloaddition of the alkene to the oxo–chromium bond to form a four-membered metallacycle intermediate. The subsequent reaction of the metallacycle yields corresponding epoxide and chlorohydrins.[40] An oxametallacyclobutane, formed by olefin addition to an Ir oxo complex, has been structurally characterized.[41] Similarly, oxametallacyclobutane $[ClCrO_2C_2H_2]^+$ is proposed to form during the gas-phase reaction of $[ClCrO_2]^+$ with ethylene,[45] and ferraoxetane ($FeOC_2H_4$) is formed in the reaction of atomic iron with ethylene oxide in low-temperature matrices.[46] Although previously proposed, oxametallacycle intermediates have not been identified on Ag or in other heterogeneous systems.

Other intermediates that were considered and excluded for selective oxidation of propene on Rh(111)-p(2×1)-O are propene oxide, propylidyne, and π-allyl. Propene oxide is excluded because propene oxide does *not* react on Rh(111)-p(2×1)-O; instead, it molecularly desorbs from the surface without isomerization or decomposition.[50] Since no propene oxide is formed from propene oxidation, it is excluded as an intermediate product. Propylidyne is excluded because it is *not* selectively oxidized when coadsorbed with oxygen; CO, CO_2, and H_2O are the only oxidation products. π-Allyl is excluded since allylic protons are not activated in the reaction of $H_2C{=}CHCD_3$ to produce acetone. If π-allyl were formed and subsequently oxidized, acetone-d_2 should be produced from $H_2C{=}CHCD_3$, but none is detected. This is in contrast to metal oxides and Rh/Al_2O_3 catalysts where π-allyl intermediates have been proposed for propene oxidation.[51,52]

A cationic intermediate, $[\text{-RhOCH}_2\text{CH}^+\text{CH}_3]$, formed by the direct attack of surface oxygen to the C═C double, has been proposed for the selective oxidation of olefins promoted by a Rh–O_2 complex supported on alumina.[53] In this case, alkenes are oxidized to ketones and aldehydes with a nearly 100% selectivity with respect to combustion. Such a cationic intermediate is not likely for propene oxidation to acetone on the Rh(111)-p(2×1)-O. The relative stability of the primary and secondary cations would favor aaldehyde over ketone formation, yet no propanal is formed from propene oxidation on Rh(111)-p(2×1)-O. Future experiments will specifically investigate the oxidation of olefins that would undergo skeletal rearrangements if a cationic intermediate is formed to address this possibility.

The oxidation of alkenes is qualitatively different on Ag and Rh even though a similar oxametallacycle has been proposed as the reaction intermediate on both surfaces. Most striking is the difference in the reactivity of allylic protons. On Rh(111)-p(2×1)-O, no allylic protons are cleaved prior to acetone formation. The inhibition of allylic C–H bond breaking by oxygen on Rh(111)-p(2×1)-O is essential for partial oxidation. In contrast, allylic C–H bonds are facilely abstracted by oxygen on Ag, resulting in propene combustion and *not* partial oxidation. The difference in the lability of allylic C–H bonds in the two cases is most certaintly due to differences in the nature of the oxygen overlayer. On Rh(111), oxygen inhibits dehydrogenation, whereas oxygen promotes allylic C–H bond breaking via an acid–base reaction on Ag(110).[5] Theoretical studies are necessary to understand the difference in oxygen bonding to these two surfaces.

Even without allylic protons, the oxidation reactions that are promoted by Ag and Rh(111)-p(2×1)-O are significantly different. Styrene and norbornene, which have no allylic protons, are epoxidized on silver.[6,7] In contrast, styrene is oxidized to acetophenone on Rh(111)-p(2×1)-O in a reaction directly analogous

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[50] Propene oxide only desorbs from Rh(111)-p(2×1)-O in peaks at 250, 195, and 160 K without any isomerization to acetone. These data were obtained in separate experiments.

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to propene oxidation.[9] The similarity of propene and styrene oxidation on Rh(111)-p(2×1)-O underscores the fact that allylic protons do not control alkene oxidation on Rh.

Since ketones are more thermodynamically stable than epoxides, ketones should be formed as long as there is a kinetically favorable pathway. Therefore, epoxidation must be kinetically favorable on Ag. Since hydrogen transfer is necessary for ketone but not for epoxide formation, the difference between Ag and Rh must be related to their ability to promote processes leading to the hydrogen transfer. Interestingly, β C–H bond cleavage occurs at ~300 K for adsorbed alkoxides, such as methoxide, on Ag(110) in a process analogous to that proposed here for Rh(111)-p(2×1)-O. It is conceivable that epoxide formation competes with β-elimination on Ag but that the β-elimination leads to combustion since Ag does not readily promote hydrogenation.

Another unusual aspect of the oxidation behavior on Rh(111) is that *selective* oxidation only occurs at relatively high oxygen coverage, $\theta_O \approx 0.5$. At lower oxygen coverages, combustion to CO, CO_2, and H_2O occurs. Oxygen-rich conditions are generally expected to favor combustion, contrary to our observations. We attribute this result to the role that oxygen plays as an inhibitor of C–H bond breaking. We propose that propylidyne is formed from propene reaction more rapidly than oxygen can add, for oxygen coverages below 0.45. Since propylidyne is oxidized to CO, CO_2, and water, its formation precludes acetone formation. At high oxygen coverages, dehydrogenation is completely blocked, so that dehydrogenation is not induced at low temperature and oxygen may be directly added to the intact olefin.

Because of the small absolute yield of acetone, the possible role of defects or domain boundaries in the oxygen overlayer cannot be entirely ruled out. Our data for mixed oxygen overlayers are strong evidence that the oxidation reaction is a characteristic of the extended surface. Rapid equilibration among different surface sites would also yield the same results, however. Experiments on stepped Rh surfaces are planned to address this point. Nevertheless, the unique oxidation behavior is of interest whether it occurs on the extended surface or at minority sites.

We propose that the dense oxygen overlayer ($\theta_O = 0.5$) is a key in favoring selective oxidation of propene. On the basis of a scale model of the oxygen overlayer, there is barely sufficient space for the propene to coordinate to Rh across the C=C bond. Once coordinated, the olefinic carbons are in proximity to one or more oxygen atoms. As a result, addition of oxygen to the 2-carbon can occur without significant displacement of the oxygen. This is important since the oxygen atoms are rather strongly bound (Rh–O bond energy 102 kcal/mol[14]) and do not become mobile on the surface until temperatures exceed 500 K, well above the temperature where oxidation occurs. Furthermore, the density of the p(2×1)-O overlayer does not allow for C–H–metal interactions that would lead to C–H bond breaking processes. Since oxygen does not promote dehydrogenation, this accounts for the inhibition of dehydrogenation on this surface.

The oxygen may also affect the coordination of the olefin to the surface, either via electronic effects or by forcing the olefin away from the surface because of repulsive steric interactions. Weakening of the bonding of ethylene to metal surfaces by coadsorbed oxygen has been documented. For example, on Pt(111), chemisorbed oxygen was found to alter the ethylene di-σ-bonded to π-bonded ratio.[54,55] Spectroscopic studies are planned to probe the adsorption of propene as a function of oxygen coverage to probe for differences in coordination that may account for the unusual reactivity at high oxygen coverages.

The unusual reactivity of Rh(111)-p(2×1)-O suggests that oxygen plays dramatically different roles on various transition-metal surfaces and that this role strongly depends on the oxygen coverage. Theoretical studies comparing oxygen bonding on Rh and Ag are planned to address this point. These differences are clearly important in alkene oxidation and may also result in unusual chemistry on other surfaces.

Conclusion

Propene is selectively oxidized by adsorbed atomic oxygen to acetone on Rh(111)-p(2×1)-O ($\theta_O = 0.5$). Desorption and combustion are competing processes. An oxametallacycle formed by a direct addition of oxygen to the 2-carbon is proposed to be the intermediate that leads to acetone formation via an intermolecular hydrogen 2,1-shift. Selective isotopic labeling experiments demonstrate that the C–H bond at the 2-position is selectively broken during acetone formation. This is supporting evidence for oxygen addition to the 2-carbon prior to dehydrogenation. This oxidation chemistry is unique in that allylic C–H bonds are not activated during the formation of acetone. Oxygen inhibits allylic C–H bond breaking so that oxygen addition competes favorably with dehydrogenation. Partial oxidation is favored for oxygen coverages greater than 0.45 monolayers while combustion is favored at lower oxygen coverages. This is attributed to the fact that propylidyne, formed on clean Rh(111) sites, undergoes combustion when coadsorbed with oxygen. At high oxygen coverages, the interaction of the C–H bond with the rhodium surface is obstructed by the oxygen.

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Registry No. $CH_3CH{=}CH_2$, 115-07-1; $(CH_3)_2C^{18}O^+$, 67-64-1; Rh, 7440-16-6.

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