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The Effects of Oxygen on Selectivity: The Reactions of 2-Propanethiolate on Oxygen-Covered Rh(111)

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Abstract: The selective oxidation of 2-propanethiolate on oxygen-covered Rh(111) was studied using temperature programmed reaction and high resolution electron energy loss spectroscopy. On Rh(111)-p(2×1)-O, reaction is proposed to proceed through carbon–sulfur bond breakage, affording 2-propyl, followed by rapid β-hydrogen elimination to propene or oxygen addition to 2-propoxide. The 2-propoxide immediately reacts to form acetone or combustion products. The selectivities for the different products depend strongly on the oxygen coverage. Oxygen influences the product distributions by (1) passivating the rhodium surface with respect to nonselective decomposition, (2) scavenging surface hydrogen so as to inhibit propane formation at high oxygen coverages, and (3) reacting with 2-propyl to form 2-propoxide. The observed addition of oxygen to 2-propyl is very promising in light of great industrial interest in selective alkane oxidation, which is generally thought to proceed via alkyl radicals.

Introduction

The reactivity of transition metal surfaces can be modified dramatically via control of the coverages of surface species that may modify the electronic and steric properties of the surface. Rhodium surface chemistry, in particular, is modified in a rather unusual way by the addition of surface oxygen. Relatively high oxygen coverages, ~0.5 monolayers, lead to partial oxidation of olefins[1–4] and selective β-dehydrogenation of alkoxides on oxygen-covered Rh(111),[5] whereas combustion and indiscriminate dehydrogenation are favored at lower oxygen coverages. Generally, an increase in oxygen coverage leads to more combustion, as expected based on Le Chatelier's principle.[6–8] These phenomena have been attributed to the inhibition of carbon–hydrogen bond cleavage by oxygen on Rh(111); in contrast to other systems, oxygen on Rh(111) does not serve as a Brønsted base.

This investigation was motivated by a desire to determine if the unusual increase in partial oxidation and selective dehydrogenation for increasing oxygen coverages extended to thiols. Thiols are important in modeling desulfurization reactions, and rhodium sulfides are known to be extremely active for dibenzothiophene hydrodesulfurization.[9,10] We were particularly interested in whether sulfur removal could be combined with partial oxidation on oxygen-covered Rh(111).

Herein, we show that oxygen addition and β-hydride elimination are combined with sulfur removal in the reactions of 2-propanethiol and diisopropyl disulfide on oxygen-covered Rh(111). Propene is produced from desulfurization and selective β-hydride elimination from the resulting alkyl; acetone is formed from desulfurization followed by oxygen addition combined with subsequent β-hydrogen loss. Previously, we reported preliminary findings for Rh(111)-p(2×1)-O ($\theta_O = 0.5$) for which the selectivities for propene and acetone formation were 66% and 11%, respectively.[11] Both propene and acetone are evolved from the Rh(111)-p(2×1)-O surface at 375 K.

In this study, we examine the influence of the oxygen coverage on the product distributions of the 2-propanethiolate reaction on oxygen-covered Rh(111). A combination of chemical and spectroscopic studies demonstrates that 2-propanethiolate is the common intermediate that leads to hydrocarbon products and acetone. 2-Propanethiolate is synthesized on the surface from reaction of both 2-propanethiol and diisopropyl disulfide. Furthermore, the product distributions depend strongly on the initial oxygen coverage; partial oxidation and selective β-H elimination are enhanced at relatively high oxygen coverages. At lower oxygen coverages, there is extensive, indiscriminate dehydrogenation to produce $C_{(a)}$, CO, CO_2, H_2, and H_2O, as well as hydrogenolysis to produce propane. These data indicate that the unusual dependence of the product distribution on oxygen coverage on Rh is rather general and that oxygen coverage can be used to manipulate product distributions in a variety of reactions, including desulfurization.

Experimental Section

All experiments were performed in a stainless steel ultra-high-vacuum chamber with a base pressure below 1×10^{-10} Torr.[12] The chamber is equipped with a cylindrical mirror analyzer (PHI 15-155) for Auger electron spectroscopy, optics for low-energy electron diffraction (PHI 15-120), a computer-controlled quadrupole mass spectrometer (UTI-100C) for temperature-programmed reaction spectroscopy, and a computer-controlled LK2000-14-R electron spectrometer for high-resolution electron energy loss spectroscopy.

The preparation and routine cleaning procedures of the crystal have been described in detail elsewhere.[13] The (2×1) oxygen overlayer is prepared by exposing the crystal to dioxygen ($\Delta p \approx 3 \times 10^{-9}$ Torr) at 300 K to saturation (150 s) and annealing for 60 s at 300 K. A sharp (2×2) LEED pattern, believed to result from three domains of (2×1)

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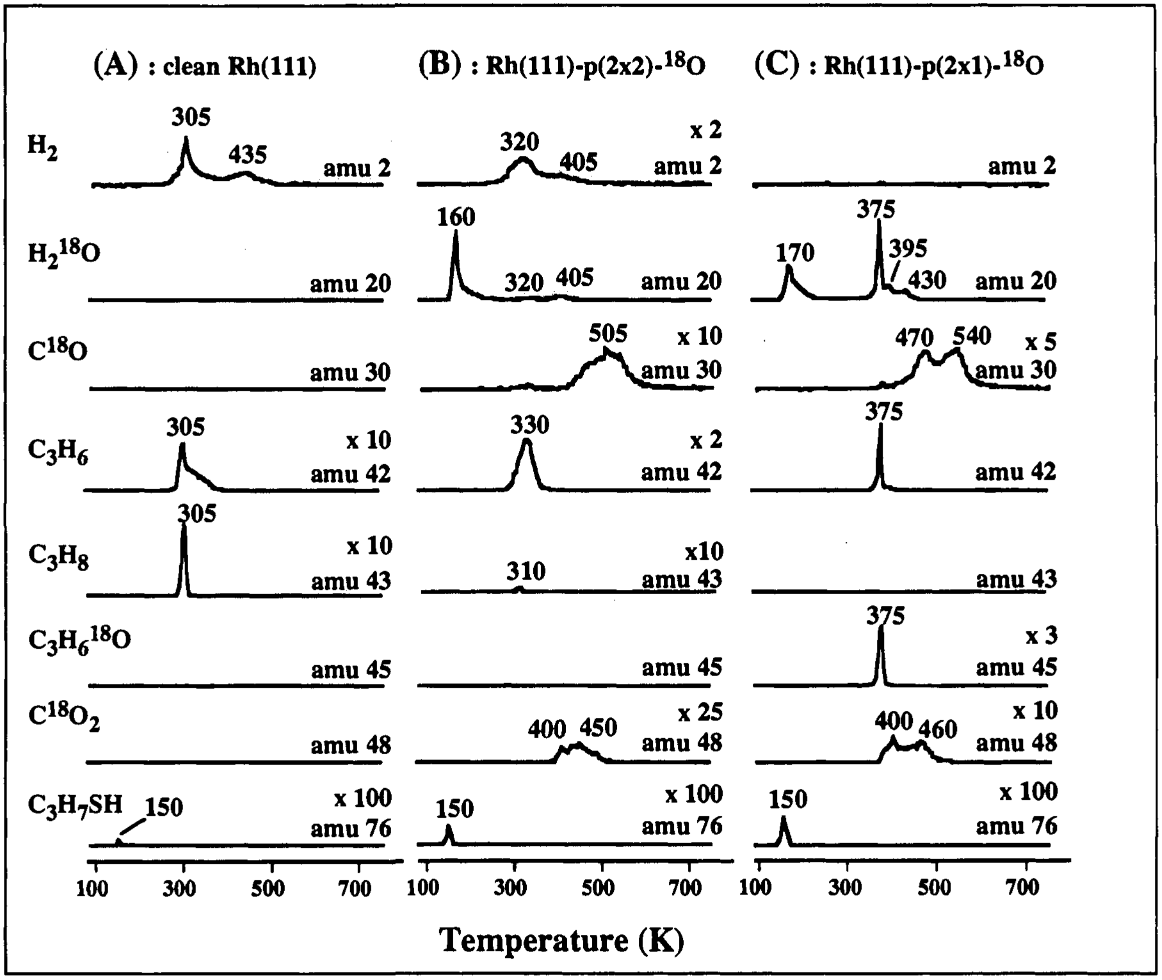

Figure 1. Temperature-programmed reaction spectra of 2-propanethiol multilayers on oxygen-covered Rh(111) as a function of initial oxygen coverage: (A) clean surface; (B) 0.25 monolayers (Rh(111)-p(2×2)-O); and (C) 0.5 monolayers (Rh(111)-p(2×1)-O). All data have been corrected for fragmentation from other products.

periodicity,[4,14] is obtained from a surface prepared in this fashion. The lower coverage oxygen overlayers are prepared by exposing the crystal to dioxygen ($\Delta p \approx 5 \times 10^{-10}$ Torr) at 300 K for varying times (3 to 190 s) followed by annealing at 300 K for 60 s. The oxygen coverages attained for specific dosing times are measured using temperature-programmed desorption yields of O_2; the (2×1) overlayer serves as a standard.[4] The $(\sqrt{3}\times\sqrt{3})$-S overlayer ($\theta_S = 0.33$), used as a standard in the determination of sulfur coverages, is prepared by exposing the crystal to H_2S ($\Delta p \approx 1 \times 10^{-9}$ Torr) at 200 K to saturation (150 s) and annealing for 60 s at 400 K to remove all hydrogen. A sharp $(\sqrt{3}\times\sqrt{3})$-R30° LEED pattern is observed after this procedure.

In the temperature-programmed reaction experiments, the crystal is radiatively heated to 750 K in line-of-site of an apertured mass spectrometer detector. Ten selected masses are monitored via computer-control of the mass spectrometer in a single experiment. The heating rate decreases monotonically from 9 K/s at 100 K to 6 K/s at 750 K, but it is highly reproducible from experiment to experiment. The crystal is negatively biased at −50 V to repel low-energy electrons that may induce non-thermal chemistry. Electron bombardment is used to heat the crystal in the range of 800−1500 K, in order to desorb surface oxygen, for example. These experiments were always performed subsequent to radiative heating to 750 K using the retarding bias on the crystal so that electron-induced effects are eliminated.

High-resolution electron energy loss data were all obtained at a crystal temperature of 100 K. The crystal was heated to the specified temperature, at the same rate as used in the temperature-programmed reaction, and allowed to cool to 100 K prior to data collection. The spectrometer operates at a primary energy of ≈3 eV, with a resolution of ≈55 cm^{-1} at a count rate of $\approx 5 \times 10^5$ counts per second for the elastic peak. All spectra shown are obtained for specular detection angles.

2-Propanethiol (Aldrich, 98%) and diisopropyl disulfide (Aldrich, 96%) were stored over molecular sieves and subjected to several freeze−pump−thaw cycles before each dose. H_2S (Matheson, C. P.), $^{16}O_2$ (Matheson, 99.99%), and $^{18}O_2$ (Cambridge Isotopes) were used as received. The purity of all reactants was regularly confirmed by mass spectrometry. Reactants are directly dosed onto the crystal, while it is positioned approximately 5 mm from the aperture of the doser. During dosing of reactants the pressure rise in the chamber is typically on the order of 2×10^{-11} Torr.

Results

Temperature-Programmed Reaction Studies. Acetone, propene, propane, CO_2, CO, H_2O, and H_2 are evolved into the gas-phase during temperature programmed reaction of 2-propanethiol on oxygen-covered Rh(111) (Figure 1). The product distribution depends strongly on the initial oxygen coverage (Figure 2).[15] On the clean surface, 84 ± 5% of the thiolates that react decompose to dihydrogen and surface carbon.[16] Dihydrogen evolves in peaks at 305 and 435 K (Figure 1A). The remaining thiolates form propane and propene at 305 K.

Upon the introduction of a small amount of oxygen to the surface ($\theta_O \approx 0.10$), CO and H_2O are also formed from

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(15) In Figure 2 the data have been corrected for the low-temperature removal of oxygen in the reaction of 2-propanethiol. The figure shows the yields in the reaction of 2-propanethiol as a function of the actual oxygen coverage at the reaction temperature, which is ≈0.1 monolayers less than the initial oxygen coverage. The oxygen coverage was corrected based on measured sulfur coverages and assuming that 2 thiols remove one oxygen as H_2O. Hence, the maximum attainable oxygen coverage at the reaction temperature in the reaction of 2-propanethiol on Rh(111) is 0.4, since 0.1 monolayers of oxygen are removed as water at 170 K, in the reaction with 0.2 monolayers of 2-propanethiol.

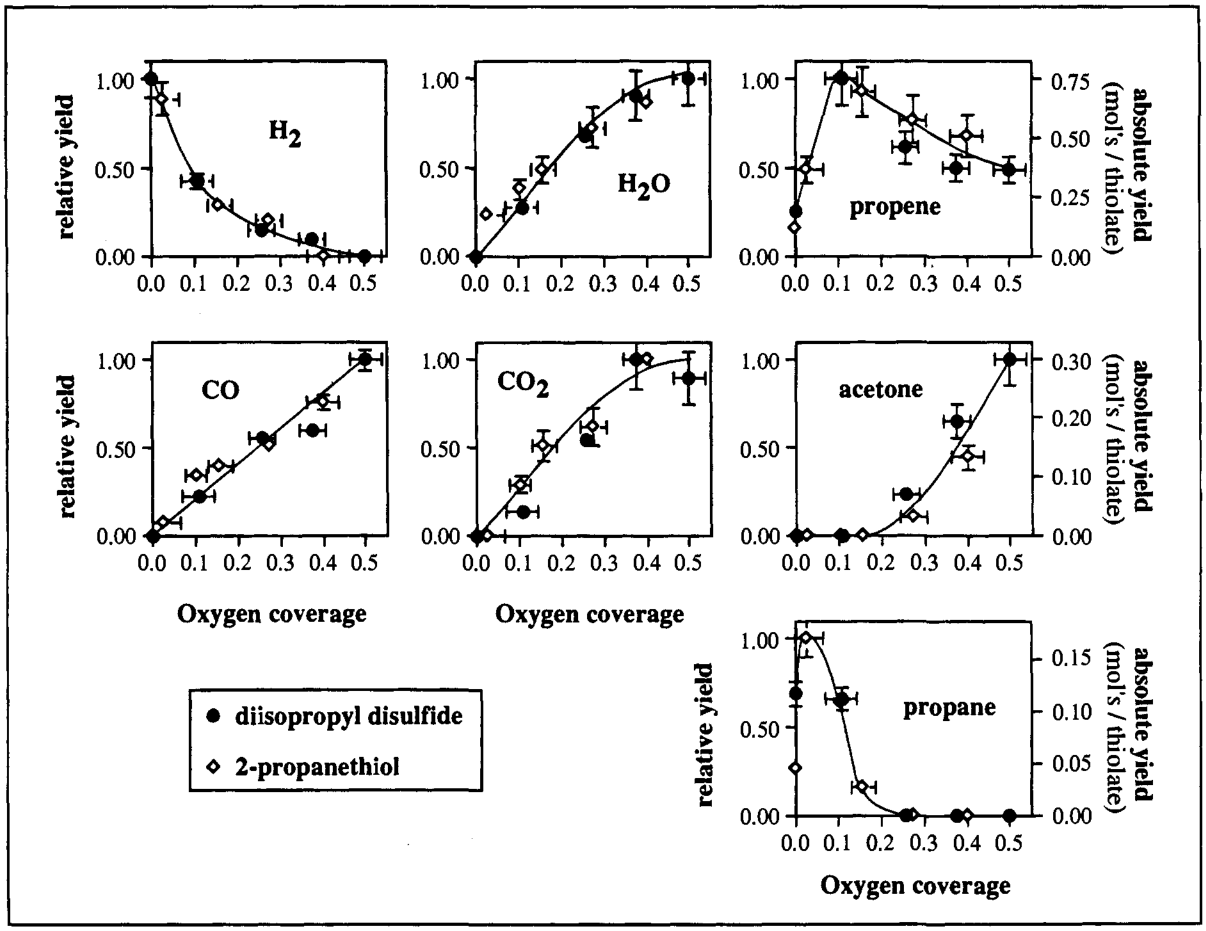

Figure 2. Relative and absolute[16,17] product yields versus oxygen coverage for the reaction of saturation exposures of 2-propanethiol and diisopropyl disulfide. The yields are plotted against the oxygen coverage at the reaction temperature.[15,16] The H_2O yield plotted for the reaction of 2-propanethiol includes only the H_2O formed in the decomposition of the 2-propanethiolate intermediate, not the H_2O formed at low temperature from the sulfhydryl hydrogen.

2-propanethiol reaction. Water evolves in three peaks, at 170, 310, and 410 K, and CO in a broad feature, ranging from 400 to 550 K. Carbon dioxide evolution is first observed between 400 and 500 K for an initial oxygen coverage of 0.2 monolayers. The yields of CO, CO_2, and H_2O increase monotonically with increasing oxygen coverage, as the yield of dihydrogen decreases (Figure 2). The CO_2:CO ratio increases as the oxygen coverage increases in the range of 0.1–0.5 monolayers. Surface carbon is formed for all oxygen coverages studied. The temperatures of CO and CO_2 evolution are nearly independent of the oxygen coverage, as are the water peaks around 170 and 410 K. The water evolution peak at 310 K shifts to higher temperatures for increasing oxygen coverages: 320 K on Rh(111)-p(2×2)-O and 375 K on Rh(111)-p(2×1)-O (Figure 1). The two dihydrogen peaks, at 305 and 435 K on the clean surface, shift to 320 and 405 K on Rh(111)-p(2×2)-O, ultimately coalescing to a single peak at 350 K for oxygen coverages above 0.45 monolayers. On the Rh(111)-p(2×1)-O surface no dihydrogen is formed (Figure 2).

The yields of propane and propene initially rise and later decrease as a function of the initial oxygen coverage (Figure 2). The propene yield is at maximum 74 ± 6%, on Rh(111)-p(2×2)-O, corresponding to an initial oxygen coverage of 0.25, from which it evolves at 330 K. In comparison, the selectivity is 11 ± 1% and the peak temperature is 305 K for the clean surface. The temperature of propene formation further increases upon increasing the oxygen coverage, to 375 K on Rh(111)-p(2×1)-O. Propane formation is at maximum for an initial oxygen coverage of 0.15, reaching a selectivity of 17 ± 5%. The temperature of propane evolution increases from 305 K on the clean surface to 310 K on Rh(111)-p(2×2)-O. No propane is formed for initial oxygen coverages above 0.3 monolayers. A maximum of one deuterium is incorporated into propane formed during reaction of 2-propanethiol in the presence of adsorbed deuterium; only d_0- and d_1-propane are detected.

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(16) Selectivities are calculated using product yields and Auger electron intensities. The water evolution at 170 K, in the reaction of 2-propanethiol on Rh(111)-p(2 × 1)-O, is ascribed to a stoichiometric formation of OH following sulfur–hydrogen bond breakage. Given the saturation thiolate coverage of 0.20 monolayers, according to Auger measurements,[19] the peak at 170 K must correspond to 0.10 molecules of water per rhodium atom in the reaction on Rh(111)-p(2×1)-^{18}O. All hydrogen formed during reaction on this surface evolves as water (Figure 1C), so the integrated intensity at 20 amu in temperature-programmed reaction spectroscopy is used to determine the total amount of water formed per 2-propanethiolate on Rh-(111)-p(2×1)-^{18}O. Propene and acetone each account for 0.5 equiv of water; 3.5 equiv are formed during nonselective reaction to CO and CO_2. The selectivities for propene and acetone formation and nonselective decomposition are estimated as 66%, 11%, and 23%, respectively, using these calculations, the measured thiolate coverage (0.20),[19] and the measured acetone yield of 0.022 molecules per rhodium atom.[17] The CO and CO_2 yields are estimated based on 30 and 48 amu intensities for the reaction on Rh(111)-p(2×1)-^{18}O. Accordingly, 0.036 molecules of CO_2, 0.066 molecules of CO, and 0.036 surface carbon atoms are formed in nonselective decomposition on Rh(111)-p(2×1)-O, since no oxygen is left on the surface after reaction up to 750 K. The yields of acetone, propene, CO, CO_2, and water are determined by comparing the integrated mass spectrometer signal intensities of 45, 42, 30, 48, and 20 amu, respectively, to those measured for reaction on Rh(111)-p(2×1)-^{18}O. The yield of propane is estimated by comparing the integrated mass spectrometer intensity at 43 amu to that of 42 amu (propene), corrected for their respective mass spectrometer intensities. The errors are based on the standard deviation in the mass spectrometer intensities in sets of five identical experiments. Although the errors quoted in the text are sometimes relatively large, due to propagation of errors in calculations, the signal intensities in the temperature-programmed reaction experiments were highly reproducible, with standard deviations below 10%.

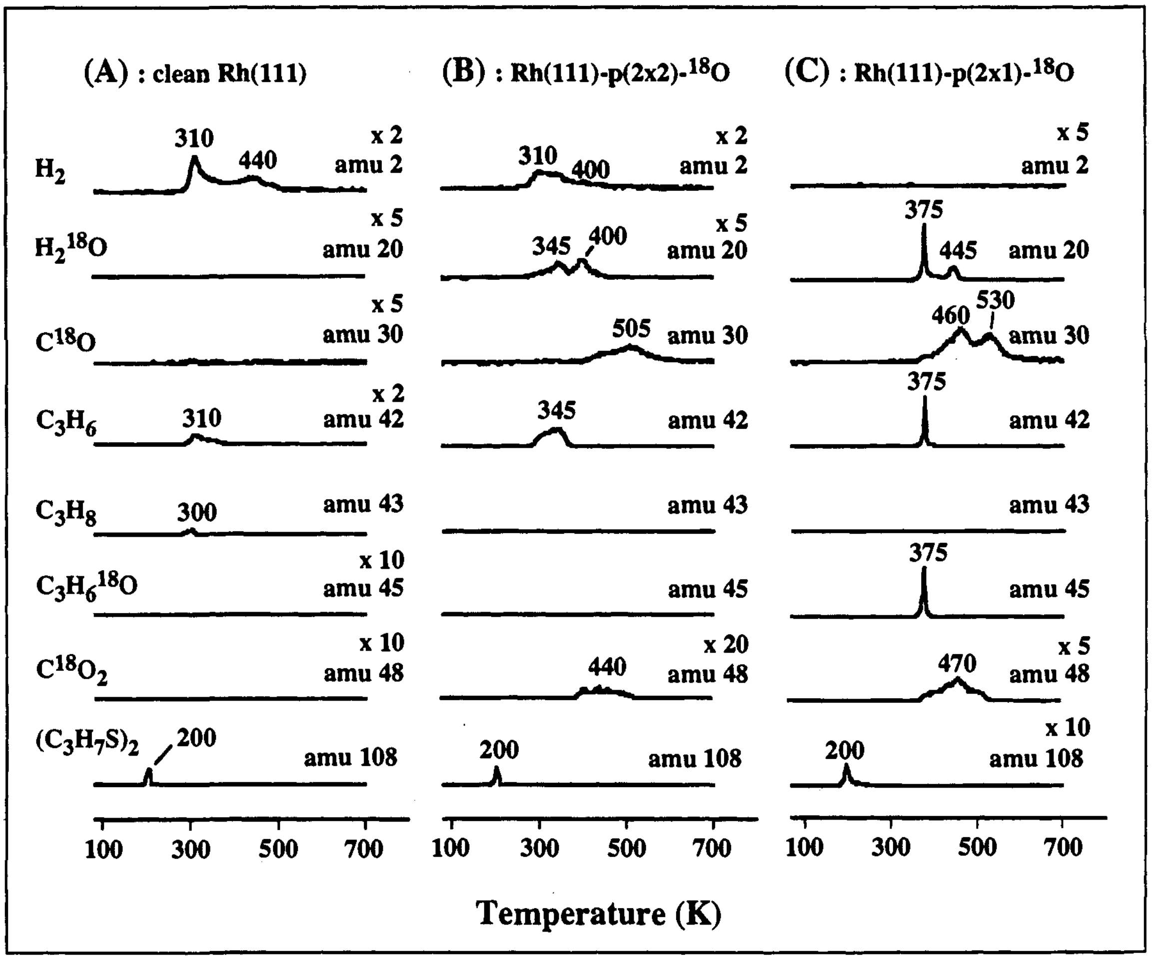

Figure 3. Temperature-programmed reaction data for diisopropyl disulfide as a function of initial oxygen coverage: (A) clean surface; (B) Rh(111)-p(2×2)-O, $\theta_O = 0.25$; and, (C) Rh(111)-p(2×1)-O, θ_O=0.50.

These results clearly indicate that propane is formed via thiolate hydrogenolysis, not propene hydrogenation.

Acetone is first evolved at a coverage of 0.3 monolayers of oxygen. As the oxygen coverage increases the acetone yield also rises, reaching a maximum at the maximum attainable oxygen coverage, 0.5 monolayers. The maximum selectivity for acetone formation is 11 ± 4%, corresponding to 0.022 ± 0.003 molecules per Rh atom.[17] The temperature of acetone evolution increases from 355 K for an oxygen coverage of 0.3 monolayers to 375 K on Rh(111)-p(2×1)-O.

Diisopropyl disulfide, $((CH_3)_2C(H)S)_2$, was also investigated to test for the effect of the sulfhydryl hydrogen on reactivity. The same products, with similar distributions, are produced during temperature-programmed reaction of diisopropyl disulfide as for 2-propanethiol on oxygen-covered Rh(111) (Figure 3). For example, on clean Rh(111) decomposition to gaseous H_2 and surface carbon is the dominant pathway, accounting for 80 ± 6% of the reaction; propene and propane are the only other products. On the Rh(111)-p(2×1)-O surface, with oxygen coverage of 0.5 monolayers at the reaction temperature, acetone (selectivity 30 ± 7%) and propene (selectivity 47 ± 8%) are produced, along with water, carbon monoxide and carbon dioxide. No oxygen is detected subsequent to reaction of diisopropyl disulfide on Rh(111)-p(2×1)-O up to 750 K. The primary difference compared to 2-propanethiol reaction is the absence of the water peak at 170 K, providing strong evidence that this peak originates from sulfur−hydrogen bond breakage in 2-propanethiol, followed by reaction with surface oxygen to produce water. There are also differences in product distributions for any given initial oxygen coverage, which can be accounted for by the higher oxygen coverage at the reaction temperature (Figure 2) since no oxygen is lost by water formation at 170 K in the disulfide reaction.[15]

The product distributions in the reaction of diisopropyl disulfide have an analogous dependence on oxygen-covered Rh(111) as that described above for 2-propanethiol (Figure 2). The only difference is that in the formation of 2-propanethiolate from diisopropyl disulfide, no oxygen is removed as water below 200 K.[15] As a consequence, the maximum oxygen coverage at the reaction temperature is 0.1 monolayers higher than in the reaction of 2-propanethiol, namely 0.5 monolayers. Accordingly, the yields of acetone, water, and CO are higher, where the yield of propene is lower than for reaction of 2-propanethiol on Rh(111)-p(2×1)-O (Figure 2).

Products were identified based on quantitative analysis of the fragmentation patterns measured during temperature-programmed reaction. Extensive surveys of masses between 2 and 120 amu were performed in order to identify the ions produced during temperature programmed reaction.[18] Comparison of the ion distributions for products formed from reaction on ^{16}O- and ^{18}O-overlayers is used to distinguish the contributions of oxygen-containing products from hydrocarbons. For example, acetone and propene are both formed in peaks with indistinguishable line shapes and peak temperatures (375 K) during the reaction

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[17] An estimated 0.022 ± 0.003 molecules of acetone are formed in the temperature-programmed reaction of a saturation coverage of 2-propanethiol on Rh(111)-p(2×1)-O. The integrated signal intensity at 58 amu is compared to that in the reaction of a saturation coverage of 2-propanol on Rh(111)-p(2×1)-O, which is known to yield 0.17 molecules of acetone per rhodium atom.[5]

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Table 1. Fragmentation Patterns for the Reaction Products of 2-Propanethiol on Rh(111)-p(2×1)-O

	intensity at *m/e*												
molecule	15	27	28	29	31	41	42	43	45	57	58	60	76
acetone[a]	59	13	18	3		3	15	100			10		
2-propanol[a]	36	30	8	22	5	12	7	43	100		1		
2-propanethiol[a]	37	81	20	13		100	28	94	3		2		16
propene[a]	5	55	31	2		100	53						
propane[a]	7	47	100	93		11	1	17					
propanal[b]		35	63	100		1	1	2		16	65		
propene oxide[b]		63	100	68	30	1	3	33		2	43		
allyl alcohol[b]		20	12	40	30	7	1	1		100	27		
methyl vinyl ether[b]					55			63			100		
^{16}O-product	18	57	29	1		100	56	21			2		
^{18}O-product						100	53	1	15			2	
^{16}O-product − (acetone spectrum scaled to 58 amu signal)	6	54	25	1		100	53	1					

[a] Measured in our laboratory spectrometer. [b] Taken from literature.[31]

of 2-propanethiol on Rh(111)-p(2×1)-O (Figure 1). The highest mass fragment in this peak is 58 amu for reaction on Rh(111)-p(2×1)-^{16}O and 60 amu for Rh(111)-p(2×1)-^{18}O (Table 1). The shift in the highest masses for the two different isotopes of oxygen clearly indicates that there is an oxygen-containing product with C_3H_6O stoichiometry. The ratios of the two major fragments of acetone-^{16}O, 43 and 58 amu, and acetone-^{18}O, 45 and 60 amu, for the 375 K product peak are the same as that measured for an authentic sample of acetone-^{16}O, within experimental error. All other C_3H_6O isomers are ruled out as products based on their respective fragmentation patterns (Table 1). Propanal and propene oxide can be excluded as products based on the low signal intensity at 29 amu. The lack of signal at 57 and 31 amu eliminates allyl alcohol and methyl vinyl ether, respectively. Acetone alone cannot account for the entire observed ion-intensity distribution in the 375 K peak derived from reaction on the Rh(111)-p(2×1)-O surface, however. In particular, the intensities of the 27, 41, and 42 amu signals relative to the parent are too high. The residual pattern subsequent to subtraction of the acetone spectrum is virtually identical to that of propene, identifying it as a second product (Table 1). No propane is formed on the Rh(111)-p(2×1)-O surface based on the absence of signal at 29 and 43 amu after subtraction of the contributions from acetone and propene. Water, which also evolves in the same peak during reaction on the (2×1)-O surface, is identified from the parent ions, 18 and 20 amu, for the ^{16}O- and ^{18}O-labeled surfaces, respectively. Carbon dioxide and CO are both also identified based on their parent ions, 44 and 28 amu on Rh(111)-p(2×1)-^{16}O and 48 and 30 amu for Rh(111)-p(2×1)-^{18}O. The CO and CO_2 peaks have different maxima and lines hapes and are, therefore, easily distinguished from other products. Dihydrogen is also identified based on its parent ion, 2 amu, which does not overlap with other fragmentation patterns. Similar analyses were performed for lower oxygen coverage, except that propane formation also needed to be included. Propane is identified by the intensity at 29 and 43 amu after subtraction of the contributions from acetone and propene.

The maximum amount of 2-propanethiol that reacts was determined to be 0.25 ± 0.02 molecules per rhodium atom on clean Rh(111), 0.21 ± 0.02 on Rh(111)-p(2×2)-O and 0.20 ± 0.02 on Rh(111)-p(2×1)-O, using Auger electron spectroscopy.[19] Similarly, 0.08 ± 0.01 molecules of diisopropyl disulfide react per rhodium atom on Rh(111)-p(2×1)-O, corresponding to ~0.16 sulfur atoms remaining on the surface after reaction to 750 K, similar to the 2-propanethiol case. On the clean surface, 0.11 ± 0.01 molecules (0.22 sulfur atoms) are deposited from the disulfide at saturation. The saturation exposure is defined as the minimum exposure required for molecular desorption. The 150 K 2-propanethiol and 200 K disulfide peak intensities increase indefinitely with increasing exposure and are essentially independent of the initial oxygen coverage, indicating that they are due to sublimation of multilayers. The yields of the reaction products are also a maximum at the minimum exposure required for multilayer sublimation.

High-Resolution Electron Energy Loss Investigations. 2-Propanethiol forms the 2-propanethiolate intermediate upon adsorption at 100 K for all oxygen coverages studied, including clean Rh(111), based on high resolution electron energy loss data (Figure 4, Table 2). Thiolate formation is inferred from the vibrational data for 2-propanethiol on Rh(111)-p(2×1)-O, based on the absence of the S−H torsion and S−H stretch modes (Figure 4Aii). These modes are respectively observed at 280 and 2530 cm^{-1} in the spectrum of condensed 2-propanethiol at 100 K (Figure 4Ai). The positions of the remaining peaks are the same for a monolayer and multilayers of 2-propanethiol, within experimental error, indicating that the hydrocarbon skeleton remains intact while the S−H bond is cleaved. The only significant difference for the monolayer is a peak at 435 cm^{-1}, which is assigned to the rhodium−molecule stretch mode. The peak at 555 cm^{-1} is due to the Rh−O stretch, based on comparison to the spectrum of the freshly-prepared Rh(111)-p(2×1)-O surface.

Diisopropyl disulfide adsorbs intact on oxygen-covered Rh-(111) at 100 K (Figure 4). Intact sulfur−sulfur bonds are indicated by the loss at 540 cm^{-1}, based on comparison to the spectrum of condensed diisopropyl disulfide. This loss is not resolved in the spectrum of a monolayer coverage of diisopropyl disulfide at 100 K, due to the intense Rh−O stretching loss at 545 cm^{-1}. The formation of the thiolate would be signified, however, by the appearance of a peak near 435 cm^{-1}, due to the Rh−thiolate stretch. The absence of this loss in spectra collected after heating up to 200 K indicates that no thiolate formation occurs below this temperature. On Rh(111)-p(2×1)-O, the sulfur−sulfur bond breaks between 200 and 250 K, based on the appearance of the peak at 420 cm^{-1}. The spectrum collected after heating to 250 K is nearly identical to that obtained following 2-propanethiol reaction. Similar data were obtained for both the thiol and disulfide over the entire range of oxygen coverages; the clean surface and oxygen coverages

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(19) The intensity of the sulfur (LMM) Auger peak at 152 eV, relative to the Rh (MNN) peak at 302 eV, is compared to the relative intensity for Rh(111)-($\sqrt{3}\times\sqrt{3}$)-S, with known coverage 0.33, in order to estimate the amount of sulfur deposited during reaction. The sulfur coverage calculated this way is an upper limit because the presence of surface carbon can decrease the Rh (MNN) intensity by shielding, thus increasing the relative intensity of the sulfur peak. The linear relationship between dosing time and relative sulfur peak intensity for submonolayer coverages suggests that this effect is minimal, however.

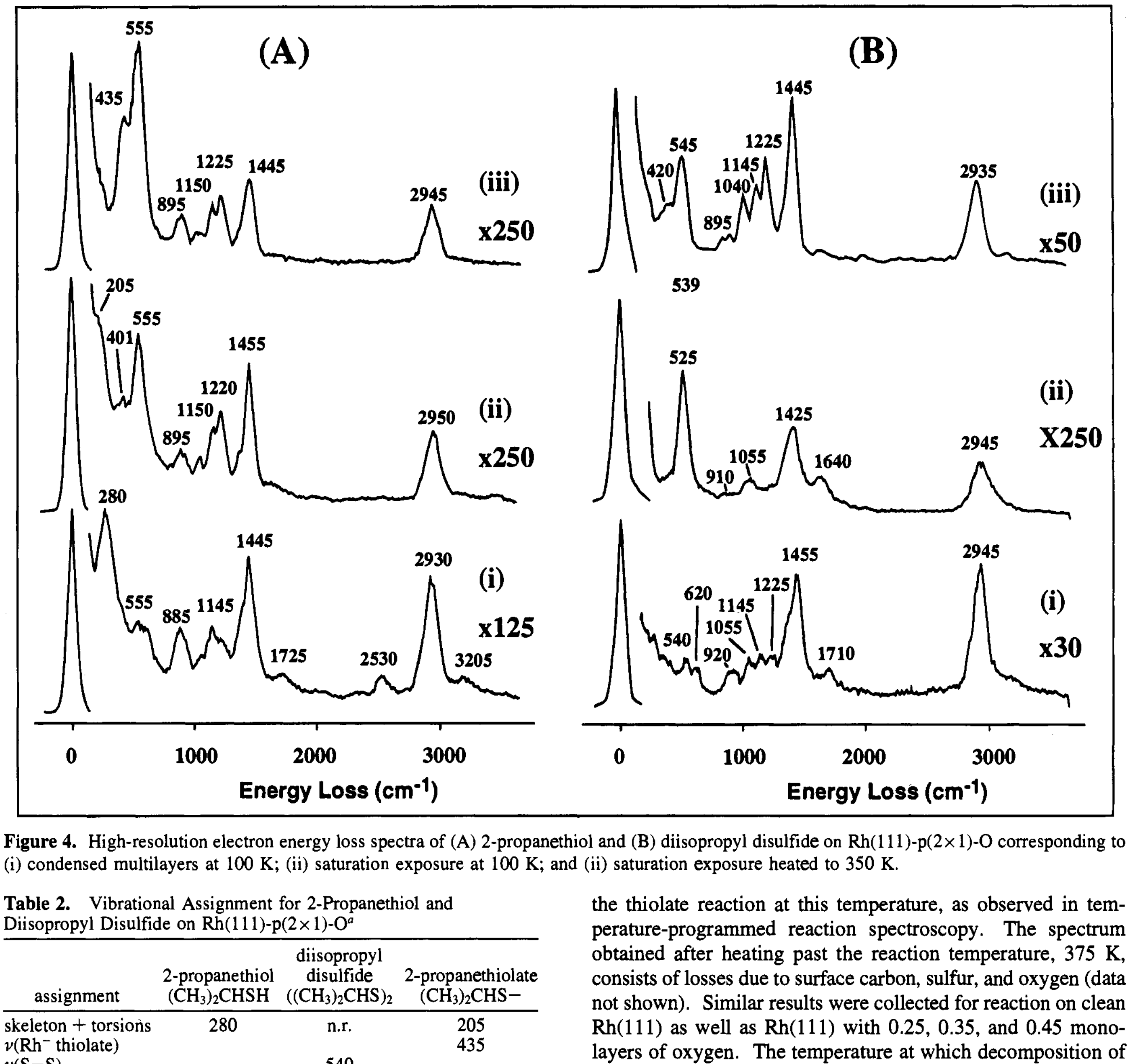

Figure 4. High-resolution electron energy loss spectra of (A) 2-propanethiol and (B) diisopropyl disulfide on Rh(111)-p(2×1)-O corresponding to (i) condensed multilayers at 100 K; (ii) saturation exposure at 100 K; and (ii) saturation exposure heated to 350 K.

Table 2. Vibrational Assignment for 2-Propanethiol and Diisopropyl Disulfide on Rh(111)-p(2×1)-O[a]

assignment	2-propanethiol $(CH_3)_2CHSH$	diisopropyl disulfide $((CH_3)_2CHS)_2$	2-propanethiolate $(CH_3)_2CHS-$
skeleton + torsions	280	n.r.	205
$\nu(Rh^-$ thiolate)			435
$\nu(S-S)$		540	
$\nu(Rh-O)$	555	n.r.	555
$\nu(C-S)$	620	620	n.r.
$\nu(C-C)$	885	920	895
$\varrho(CH_3)$	1055	1055	1050
$\varrho(CH_3) + \nu(C-C)$	1145	1145	1150
$\delta(CH)$	1220	1225	1220
$\delta_s(CH_3)$	1390	n.r.	1380
$\delta_a(CH_3)$	1445	1455	1455
combination	1725	1710	
$\nu(S-H)$	2530		
$\nu(C-H)$	2930	2945	2950
combination	3205		

[a] Assignments are based on comparison to IR data.[32-35]

of 0.25, 0.35, 0.45, and 0.5 were specifically studied (data not shown). The temperature of sulfur–sulfur bond cleavage in the disulfide decreases with decreasing oxygen coverage. Thiolate formation occurs below 180 K on the clean surface.

The adsorbed 2-propanethiolate intermediates remain intact up to 350 K, the temperature where reaction commences, on Rh(111)-p(2×1)-O, based on the fact that the vibrational spectrum is essentially unchanged upon heating (Figure 4Aiii, 4Biii). The spectrum drastically changes as the temperature approaches 375 K, in that all losses assigned to the thiolate rapidly decrease in intensity. These data are consistent with the thiolate reaction at this temperature, as observed in temperature-programmed reaction spectroscopy. The spectrum obtained after heating past the reaction temperature, 375 K, consists of losses due to surface carbon, sulfur, and oxygen (data not shown). Similar results were collected for reaction on clean Rh(111) as well as Rh(111) with 0.25, 0.35, and 0.45 monolayers of oxygen. The temperature at which decomposition of the 2-propanethiolate intermediate commences decreases with decreasing oxygen coverage, from 350 K on Rh(111)-p(2×1)-O to 250 K on the clean Rh(111) surface.

Discussion

The proposed mechanism for 2-propanethiol and diisopropyl disulfide reaction on oxygen-covered Rh(111) is consistent with all of our data (Figure 5). Both reactants form the 2-propanethiolate intermediate below 250 K, as indicated by vibrational and temperature-programmed reaction data. Specifically, the absence of modes associated with the S–H bond in the high-resolution electron energy loss spectrum obtained following 2-propanethiol adsorption at 100 K is compelling evidence for thiolate formation at this temperature. The disulfide bond in diisopropyl disulfide cleaves between 200 and 250 K on Rh(111)-p(2×1)-O, affording two 2-propanethiolates. The correspondence in the vibrational spectra of $((CH_3)_2HCS)_2$ and $(CH_3)_2HCSH$ at 250 K is supporting evidence for thiolate formation. The evolution of water in the range of 160–170 K during the reaction of 2-propanethiol, but not for diisopropyl disulfide, on oxygen-covered Rh(111) is further evidence for S–H bond cleavage in the thiol at low surface temperature. The 170 K water formation probably proceeds via adsorbed OH

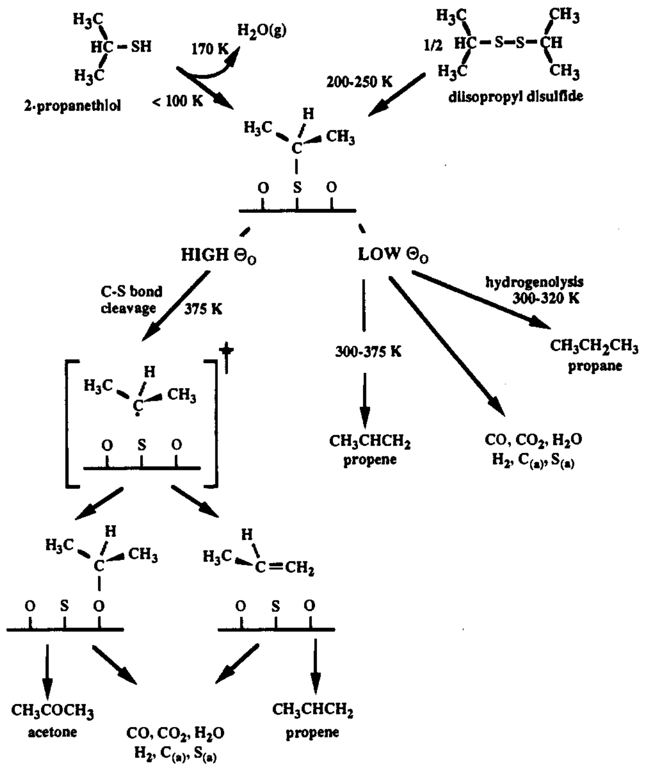

Figure 5. Proposed mechanism for the reaction of 2-propanethiolate on oxygen-covered Rh(111).

formed by reaction of the sulfhydryl hydrogen with surface oxygen. Hydroxyls are known to react with hydrogen and other hydroxyls to form water on Rh(111) at low temperatures, leading to water evolution between 160 and 220 K,[20] whereas coadsorbed hydrogen and oxygen mainly form H_2 on Rh(111).[21] Notably, the yield of H_2 from the 2-propanethiol reaction decreases dramatically with initial oxygen coverage even though the thiolate coverage is relatively constant. The adsorbed 2-propanethiolate remains intact up to the temperature of product evolution, based on the similarity of the high-resolution electron energy loss spectra obtained as layers of 2-propanethiol or diisopropyl disulfide are heated above 250 K.

The correspondence of the peak temperatures and line shapes for propene, acetone, and water for thiolate reaction on Rh(111)-p(2×1)-O is a strong indication that all three are formed from a common rate-determining step. The rate-determining step is proposed to be homolytic C–S bond cleavage to afford the 2-propyl radical. The radical would thereafter undergo competing β-hydrogen elimination and oxygen addition affording propene and 2-propoxide, respectively. Subsequent, rapid β-H elimination in the 2-propoxide would yield acetone. Water would be concurrently formed from reaction of surface oxygen with the hydrogen eliminated from both the radical and the propoxide. Both propene and acetone would rapidly desorb from the surface above 300 K.[4,22] 2-Propoxide is known to undergo selective β-hydrogen elimination to acetone and water at ~265 K on Rh(111)-p(2×1)-O;[5] thus, an analogous reaction would be rapid at 375 K, the thiolate reaction temperature.

The proposed radical mechanism is supported by preliminary studies of 2-butanethiol, ethyl iodide, and 2-propyl iodide.[23,24] In these studies, the reaction temperature correlates with the C–X (X = I or S) bond strengths. Both 2-butanethiol and 2-propanethiol produce their respective olefins and ketones in peaks at 375 with indistinguishable line shapes. The C–S bond strengths of the two secondary thiols are essentially the same, 70.5 kcal/mol,[25] accounting for their identical reactivity. Based on careful analysis of the leading edge of the evolution of acetone, the activation energy for C–S bond breakage in 2-propanethiolate on Rh(111)-p(2×1)-O at saturation coverage is estimated to be 29 kcal/mol.[26] In comparison, 2-propyl iodide reacts similarly to 2-propanethiolate, producing acetone, propene, and water at 335 K during temperature-programmed reaction on Rh(111)-p(2×1)-O.[24] Acetaldehyde, ethene, and H_2O are formed at 365 K from ethyl iodide reaction on Rh(111)-p(2×1)-O. Again, the peak temperatures correlate with the relative bond strengths. The C–I bond strength in 2-propyl iodide is 54.3 kcal/mol[25] compared to an estimated activation energy of 17 kcal/mol for reaction on Rh(111)-p(2×1)-O, based on leading edge analysis.[26] The difference in C–X bond enthalpies in the gas phase is ≈16 kcal/mol, compared to a ≈12 kcal/mol difference in the reaction barriers for the surface reactions. The excellent correlation between reactivity and C–X bond strength lends credibility to the radical mechanism. Furthermore, alkyl iodides are known to readily produce alkyl groups on a variety of transition metal surfaces.[27] While these studies provide compelling evidence for the proposed radical mechanism, heterolytic C–S bond cleavage, forming a cation, may lead to similar results. This issue will be addressed by future investigations of thiols with alkyl groups that may undergo rearrangement reactions.

Several other plausible mechanisms for the thiolate reactions can be ruled out based on our data. For example, acetone could be formed from propene oxidation rather than 2-propoxide dehydrogenation. Although propene has been shown to undergo partial oxidation on Rh(111)-p(2×1)-O,[4] the acetone yields from 2-propanethiol or diisopropyl disulfide are considerably higher, making this an unlikely mechanism. Furthermore, no acetone formation is detected during propene exposure to Rh(111)-p(2×1)-O maintained at 375 K, whereas acetone is readily detected during 2-propanethiol dosing under identical conditions. Direct nucleophilic attack of the 2-carbon of the thiolate by oxygen is also deemed unlikely because C–S and C–O bond cleavage would have to be accompanied by hydrogen rearrangement to produce propene, the major product, while C–S and C–H bond breaking would be required for acetone production. This mechanism would most certainly result in dramatically different kinetics for propene and acetone formation since the relatively stronger C–O bond would only be broken along the path to propene formation.

The most striking aspect of this work is that partial oxidation can be coupled with desulfurization of 2-propanethiolate on oxygen-covered Rh(111) at high oxygen coverages. Olefin elimination is also an important reaction pathway for 2-propanethiolate on oxygen-covered Rh(111). Surprisingly, more complete oxidation, including combustion to CO_2, is important at lower oxygen coverages than required for partial oxidation to acetone. The observation of partial oxidation at high oxygen coverages is similar to trends observed for olefins,[1-4] suggesting that it is a rather general effect.

The changes in the product distributions are explained by three effects of oxygen coverage: (1) inhibition of C–H bond breaking; (2) retardation of C–S bond breaking; and, (3) increase in the probability for oxygen addition to the nascent 2-propyl radical. Careful examination of the peak shapes of

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the evolution of propene and acetone for reaction on oxygen-covered Rh(111) shows that above 0.4 monolayers of oxygen, propene and acetone evolve with identical peak shapes. For oxygen coverages below 0.40 monolayers, however, the leading edges of propene and acetone evolution are no longer identical, although the peak temperature and the falling edge remain the same. Propene formation starts approximately 20 K lower than acetone formation on Rh(111) with 0.30 monolayers of oxygen. The temperature required for this reaction pathway to propene formation decreases with decreasing oxygen coverage, reaching 300 K on clean Rh(111). These observations and temperature-dependent vibrational data suggest that the temperature required for C−S bond breaking decreases with decreasing oxygen coverage and that C−S bond breaking is no longer the rate-limiting step for acetone formation for oxygen coverages below 0.4 monolayers.

The relative yields of acetone and propene exhibit a dependence on oxygen coverage that is consistent with the proposed mechanism. The acetone yield increases while the amount of propene decreases with increasing oxygen coverage (Figure 2). The formation of CO and CO_2 can also be attributed, in part, to decomposition of the 2-propoxide. Around 300 K oxygen attacks 2-propoxide, yielding a carboxylate species based on preliminary vibrational studies.[23] This carboxylate species subsequently forms acetone, evolving at 320 K, or CO and CO_2, around 550 and 450 K, respectively.

The enhancement of partial oxidation for higher oxygen coverages is attributed in part to the inhibition of C−H bond activation by oxygen on Rh(111). Clean Rh(111) is extremely effective in activating C−H bonds, as illustrated by the predominance of nonselective dehydrogenation of 2-propanethiolate (Figures 1−3). Indeed, a variety of hydrocarbons and oxygenates are facilely dehydrogenated on clean Rh(111).[4,28−30] Oxygen inhibits dehydrogenation processes for these classes of molecules[4,5,29] as well as for 2-propanethiolate on Rh(111). At low oxygen coverages, the inhibition of nonselective C−H bond activation is signified by the increase in the yields of propene and propane (Figure 2). Propane formation is limited by the availability of surface hydrogen, which decreases with increasing oxygen coverage, as more hydrogen leaves the surface at low temperatures as water. The extent of nonselective dehydrogenation is mainly indicated by the amount of H_2 production, which decreases monotonically with initial oxygen coverage, reaching zero for a coverage of 0.5 monolayers of oxygen. Most of the water produced is due to either reaction of the sulfhydryl hydrogen with surface oxygen or selective β-C−H elimination which accompanies propene and acetone formation, as discussed above. Even though the total decomposition of the hydrocarbon skeleton becomes less important for higher oxygen coverage, the yields of CO and CO_2 increase, as more oxygen becomes available for the combustion of formed carbon. Furthermore, both propene and 2-propoxide partially decompose, forming CO and CO_2 between 400 and 600 K.[4,5]

Conclusion

Acetone, propene, propane, and combustion products are formed in the reaction of 2-propanethiol and diisopropyl disulfide on oxygen-covered Rh(111). Both reactants form 2-propanethiolate below 250 K. The reaction is proposed to proceed through carbon−sulfur bond cleavage in 2-propanethiolate, forming 2-propyl, followed by fast β-hydrogen elimination to propene, hydrogen addition to propane or oxygen addition to 2-propoxide. Subsequent fast β-hydrogen elimination in 2-propoxide yields acetone. Decomposition reactions to $S_{(a)}$, H_2, H_2O, $C_{(a)}$, CO, and CO_2 are competing pathways. The selectivities for different pathways change dramatically as a function of the oxygen coverage. Oxygen influences the reaction in four ways. Firstly, oxygen inhibits non-selective carbon−hydrogen bond cleavage by the rhodium surface. As a consequence the selectivity for nonselective decomposition decreases, whereas the bond-selective reaction pathways increase, as a function of the oxygen coverage. In addition, oxygen lowers the availability of hydrogen on the surface, by removing it as water at low temperatures. Propane formation, depending on the availability of hydrogen, is consequently not observed at higher oxygen coverages. Thirdly, oxygen retards C−S bond breaking. Lastly, oxygen directly adds to 2-propyl, forming 2-propoxide. This addition and the subsequent formation of acetone only occur at high oxygen coverages ($\theta_O = 0.3-0.5$), where the probability of oxygen addition and the barrier for C-S bond breaking are highest.

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