

Kinetic Control of Surface Reactions: Regioselectivity in the Reaction of 2-Methylcyclopropylmethanol on Mo(110)–(6×1)–O[†]

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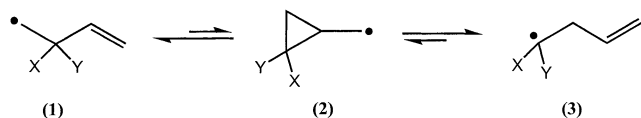
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The reactions of a diastereomeric mixture of 2-methylcyclopropylmethanol are investigated on oxygen-modified Mo(110) as a means of probing the influence of lifetime and stability of hydrocarbon radicals formed in a surface reaction on selectivity. 2-Methylcyclopropylmethanol forms 2-methylcyclopropylmethoxide at ~250 K. The C–O bond of 2-methylcyclopropylmethoxide subsequently breaks near 350 K, yielding the (2-methylcyclopropyl)methyl radical. The (2-methylcyclopropyl)methyl radical can undergo fast rearrangement to two different linear C₅ homoallyl radical species. The two different ring-opening pathways are due to the asymmetric methyl substitution of the cyclopropyl unit. Only one pathway results in a surface-bound product: adsorbed 4-penten-2-oxide is formed via rearrangement to 4-penten-2-yl radical and subsequent trapping on surface oxygen. The 4-penten-2-oxide is identified by comparison of infrared and temperature-programmed reaction data for the reaction product to analogous data for the reference compound. Evolution of C₅ hydrocarbons competes with trapping at 350 K. Careful analysis of temperature-programmed reaction data indicates that 3-methyl-1-butene, 2-methyl-1,3-butadiene, and 1,2-dimethylcyclopropane contribute to the 410 K product. However, the close resemblance of the fragmentation patterns for all C₅ hydrocarbons renders quantitative analysis impossible. At elevated temperatures the C–O bond of 4-penten-2-oxide breaks and C₅ hydrocarbon evolution sets in. 1-Pentene and 1,3-pentadiene, as well as propene, are formed in a ratio of 20:70:10 at ~520 K. Above 900 K CO is formed from recombination of adsorbed carbon and oxygen. Our results are discussed in the context of relative reaction rates for different pathways available to hydrocarbon radicals and their relation to product selectivity.

Introduction

The importance of radicals in synthetic organic chemistry has increased tremendously over the past few years. While some years ago their use was restricted to a few, very specific functional group transformation reactions, they are now used routinely in the synthesis of various complex organic molecules. Of special interest has been the development of radical rearrangement reactions¹ and their kinetic analyses.^{2–4} One important class of radical rearrangement reactions is the so-called homoallyl–homoallyl radical rearrangement (Scheme 1).^{5–7} It has been applied in the synthesis of several complex natural products.^{8–10}

SCHEME 1



Briefly, homoallyl radical, **1**, reacts via the cyclopropylmethyl radical, **2**, to homoallyl radical, **3**. During rearrangement the relative positions of the radical and the double bond do not change, but a 1,2-vinyl shift occurs, i.e., the X,Y-substituted carbon center shifts by one carbon atom. Radical-trapping studies⁶ show that in the case of X = H and Y = CH₃ the rate constant, *k_c*, for the cyclization step **1** → **2** is about 3 orders of

magnitude slower than both ring opening steps **2** → **1** and **2** → **3**. However, the rate constant for one of the possible ring-opening steps, **2** → **3**, is four times faster than the other, **2** → **1**. Thus, despite the fact that the **1** → **2** step is slow, **3** is formed, because it is the thermodynamic product.

Radicals are also very important in many surface processes such as C–C coupling, etching, dehydrogenation, and hydrogenation reactions. In an ongoing effort to develop tools for the detection of radicals and the determination of the radical lifetimes in the vicinity of surfaces, we have studied various radical-clock precursors and their reactivity on the oxygen-modified Mo(110) surface. Three different precursors (hydroxymethylcyclopropane,¹¹ bromomethylcyclopropane,¹² and cyclopropyl-methanethiol¹³) form a cyclopropylmethoxide intermediate on the O/Mo(110) surface. Adsorbed cyclopropylmethoxide subsequently undergoes homolytic C–O bond cleavage at ~350 K, yielding cyclopropylmethyl radical, **2** (X,Y = H) in the vicinity of the surface. Radical **2** (X,Y = H) rearranges to the ring-opened butenyl radical, **1** (X,Y = H), which either reacts with surface oxygen to form butenoxide or adds directly to the Mo surface to yield adsorbed butenyl. Butenoxide refers to the surface species in which the metal surface has replaced the hydroxyl hydrogen of the alcohol. The driving force for C–O bond formation of the ring-opened alkyl radical with oxygen on the surface is the higher C–O bond strength of the linear butenoxide species compared to cyclic cyclopropylmethoxide ($\Delta E = 1.2$ eV).^{14,15}

Detection of the rearranged species on the surface implies that (i) the radical remains in the vicinity of the surface after

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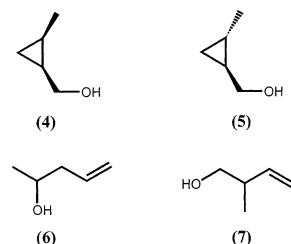
TABLE 1: Mass Fragmentation Patterns Obtained for Authentic Samples

| | <i>m/z</i> | 86 | 70 | 67 | 57 | 55 | 53 | 45 | 42 | 41 | 39 | 29 | 27 |
|------------------------------|------------|----|----|----|-----|----|-----|-----|-----|-----|----|----|----|
| 2-methylcyclopropylmethanol | 1 | 2 | 14 | 50 | 35 | 20 | 100 | 30 | 79 | 65 | 94 | 71 | |
| 4-penten-2-ol | 1 | 3 | 2 | 2 | 5 | 9 | 100 | 34 | 33 | 27 | 29 | 26 | |
| 2-methyl-4-buten-1-ol | 2 | 1 | 20 | 25 | 100 | 28 | 4 | | 80 | 62 | 89 | 70 | |
| 1-pentene | | 28 | 1 | | 66 | 8 | | 100 | 66 | 58 | 41 | 58 | |
| <i>trans</i> -1,3-pentadiene | | | | 75 | | 50 | | 24 | 51 | 100 | 11 | 60 | |
| 1,4-pentadiene | | | 64 | | | 45 | | 19 | 57 | 100 | 4 | 61 | |
| propene | | | | | | | | 59 | 100 | 84 | | 44 | |

C–O bond dissociation; (ii) the lifetime of the cyclic radical near the surface is sufficient for rearrangement to occur; and (iii) addition of the ring-opened radical to the surface is faster than dehydrogenation, hydrogenation, and desorption. This is in good agreement with the finding that saturated hydrocarbons undergo multiple collisions with metal surfaces upon adsorption, e.g., Pt(111).¹⁶ Assuming solution-phase rate constants,² the rearrangement time for the cyclopropylmethyl–butenyl rearrangement is estimated to be on the order of 2 ns.

Here we report our results for the cyclopropyl-homoallyl rearrangement of (2-methylcyclopropyl)methyl radical on oxygen-covered Mo(110). Studies of a diastereomeric mixture of 2-methylcyclopropylmethanol (**4** and **5**, Scheme 2) indicate that

SCHEME 2



surface-bound 2-methylcyclopropylmethoxide forms at 250 K and that the C–O bond of 2-methylcyclopropylmethoxide cleaves at 350 K, yielding the cyclic (2-methylcyclopropyl)methyl radical, **2** ($X = H$, $Y = CH_3$). Note the terms 2-methylcyclopropylmethanol and (2-methylcyclopropyl)methyl radical refer to the *diastereomeric* mixtures of reactants and cyclic radicals, respectively, unless specified otherwise. Subsequently, ring opening occurs, and *only* the 4-penten-2-yl radical **3** ($X = H$, $Y = CH_3$) is trapped as the 4-penten-2-oxide species on the surface. In contrast, the 2-methyl-4-butenyl radical is either hydrogenated or dehydrogenated to yield 3-methyl-1-butene and 2-methyl-1,3-butadiene, respectively. The 4-penten-2-oxide intermediate is stable up to ~ 480 K where the C–O bond breaks and a mixture of C_3 and C_5 hydrocarbons evolves.

Experimental Section

Infrared and temperature-programmed reaction experiments are performed in an ultrahigh vacuum chamber with a base pressure of $\leq 1 \times 10^{-10}$ Torr, described previously.^{17,18} The chamber is equipped with a UTI quadrupole mass spectrometer, low energy electron diffraction (LEED) optics, and an Auger spectrometer with a cylindrical mirror analyzer (Perkin-Elmer model 15-555). The infrared spectra are collected using a single-beam, clean-air purged Fourier transform infrared spectrometer (Nicolet, series 800) that is interfaced to our vacuum system. Spectra are averaged over 500 scans using an MCT detector at 4 cm^{-1} resolution; the scan time being approximately 3.5 min. The ratio of sample to background spectrum is taken to correct for variation in the infrared signal during data accumulation. The background spectrum is obtained with the crystal in the same position but after rapidly heating the crystal to 760 K to

remove molecular species and subsequent cooling to ~ 130 K. This procedure reveals only irreversible chemical transformations.

The crystal is positioned approximately 2 mm from the aperture (3 mm) of the mass spectrometer shield during the collection of temperature-programmed reaction data. The crystal is biased at -100 eV during temperature-programmed reaction to minimize reactions induced by electrons generated by the mass spectrometer. The mass spectrometer is computer interfaced, and data are collected with a program that allows collection of up to 16 separate ion intensity profiles during a single experiment. The heating rate is nearly constant with $dT/dt = (10 \pm 2)$ K/s between 110 and 760 K.

The Mo(110) crystal can be cooled to 100 K, heated to 760 K radiatively, or heated to 2300 K by electron bombardment. The Mo(110) surface is cleaned before each experiment by oxidation at 1200 K in 1×10^{-9} Torr of O_2 for 2 min. The crystal temperature is allowed to return to ~ 200 K and subsequently (three times) flashed to 2300 K to remove residual oxygen. No surface carbon or oxygen is detected in the Auger electron spectra of the surface recorded after cleaning.

Preparation and characterization of the oxygen overlayer ($\Theta_O = 0.67$ ML) used in this study have been outlined in detail previously.^{19,20} Briefly, the Mo(110) crystal is saturated with O_2 at 100 K. Subsequent heating of the surface to 500 K results in an overlayer with oxygen predominantly in low-symmetry, high-coordination sites.²¹ The coverage of this overlayer is $\Theta_O = 0.67$ monolayers (ML) determined by LEED²² and compared with the $O(KLL)/Mo(LMM)$ Auger ratio of an oxygen overlayer deposited by CH_3OH corresponding to 0.35 ML.²³

Oxygen (O_2 , 99.998% Matheson), D_2 (99.7% *d*, Matheson), $^{18}O_2$ (95–98% isotopic purity, Cambridge Isotope Labs), and 1,4-pentadiene (98+%, Lancaster) are used as received. D_2O (99.96% *d*, Sigma-Aldrich), 2-methylcyclopropylmethanol (98%, *cis/trans* mixture, Sigma-Aldrich), 4-penten-2-ol (99%, Sigma-Aldrich), 2-methyl-4-buten-1-ol (98%, Sigma-Aldrich), 1-pentene (Sigma-Aldrich), *cis*-2-pentene (Sigma-Aldrich), and *trans*-1,3-pentadiene (97%, Alfa-Aesar) are kept in glass bottles. All of these substances, except for D_2O are stored over molecular sieves and freeze-pumped-thawed three times at the beginning of each experimental day. Purities of all substances are routinely confirmed by mass spectrometry (Table 1).

Results

Temperature-Programmed Reaction Experiments. C_5 hydrocarbons are produced in two peaks centered at 410 and 520 K during temperature-programmed reaction (Figure 1a) of a diastereomeric 2-methylcyclopropylmethanol mixture on oxygen-covered Mo(110) ($\Theta = 0.67$ ML). The first product peak (410 K) is attributed to formation of a mixture of 1,2-dimethylcyclopropane, 3-methyl-1-butene, and 2-methyl-1,3-butadiene. The second product peak is identified as a 20:70:10 mixture of the linear hydrocarbons 1-pentene, 1,3-pentadiene, and propene based on quantitative comparison with mass

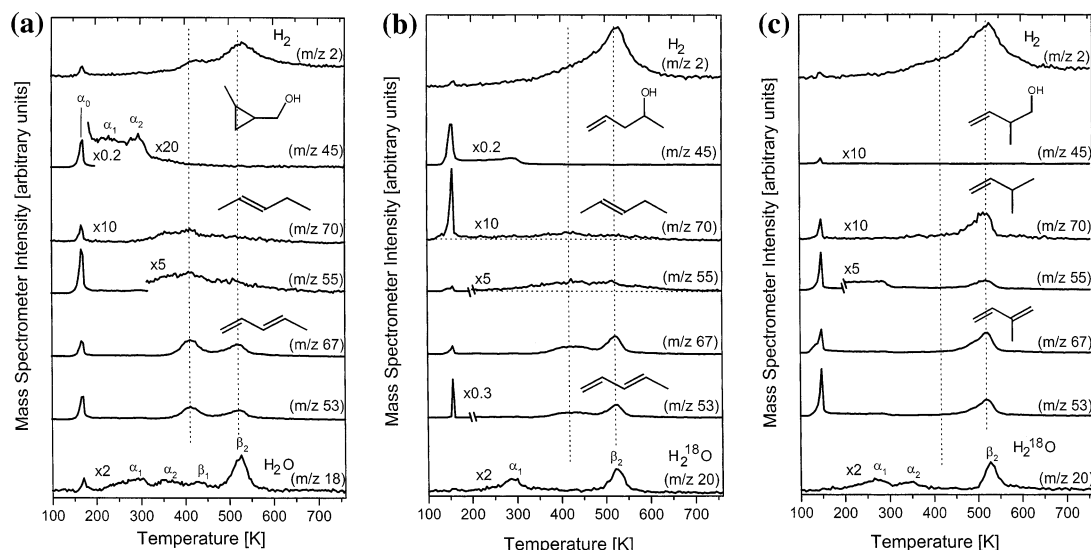


Figure 1. Temperature-programmed reaction spectra obtained after condensing multilayers of (a) a diastereomeric 2-methylcyclopropylmethanol mixture on ^{16}O -Mo(110); (b) 4-penten-2-ol; and (c) 2-methyl-4-buten-1-ol on ^{18}O -covered Mo(110) ($\Theta_0 = 0.67$ ML). (a) Traces for ions representative of cis/trans 2-methylcyclopropylmethanol ($m/z = 86, 45$), 1-pentene ($m/z = 70, 55$), 1,3-pentadiene ($m/z = 67, 53$), H_2O ($m/z = 18$), and dihydrogen ($m/z = 2$). (b) Traces for ions representative of 4-penten-2-ol ($m/z = 86, 45$), 1-pentene ($m/z = 70, 55$), 1,3-pentadiene ($m/z = 67, 53$), H_2^{18}O ($m/z = 20$), and dihydrogen ($m/z = 2$). (c) Traces for ions representative of 2-methyl-4-buten-1-ol ($m/z = 86, 55, 45$), 1-pentene ($m/z = 70, 55$), 1,3-pentadiene ($m/z = 67, 53$), H_2^{18}O ($m/z = 20$), and dihydrogen ($m/z = 2$). A constant heating rate of 10 ± 2 K/s is used between 100 and 760 K.

TABLE 2: Results of Temperature-Programmed Reaction Spectrometry Experimental Fragmentation Patterns for Samples on O-Modified Mo(110) ($\Theta_0 = 0.67$ ML)

| m/z | 86 | 70 | 67 | 57 | 55 | 53 | 45 | 42 | 41 | 39 | 29 | 27 |
|--|----|----|----|----|----|----|-----|----|----|-----|-----------------|-----------------|
| 2-Methylcyclopropylmethanol^a | | | | | | | | | | | | |
| molecular layer | 1 | 4 | 14 | 45 | 39 | 22 | 100 | 40 | 83 | 71 | 96 | 64 |
| 410 K peak (350–450K) | | 8 | 69 | | 24 | 52 | | 41 | 66 | 100 | 30 | 60 ^b |
| 520 K peak (450–600K) | | 5 | 58 | | 17 | 47 | | 38 | 76 | 100 | 27 | 58 ^b |
| 20:70:10 ratio of 1-pentene/ 1,3-pentadiene/propene | | 6 | 59 | | 15 | 41 | | 47 | 65 | 100 | 18 | 64 |
| 4-Penten-2-ol | | | | | | | | | | | | |
| molecular layer | 1 | 1 | 2 | 1 | 2 | 3 | 100 | 25 | 26 | 24 | 22 | 30 |
| 410 K peak (325–450K) | | 8 | 58 | | 20 | 47 | | 54 | 77 | 100 | 43 ^b | 61 ^b |
| 520 K peak (450–600K) | | 4 | 56 | | 13 | 48 | | 41 | 75 | 100 | 23 ^b | 56 ^b |
| 20:70:10 ratio of 1-pentene/ 1,3-pentadiene/propene | | 6 | 59 | | 15 | 41 | | 47 | 5 | 100 | 18 | 64 |
| 2-Methyl-4-buten-1-ol^c | | | | | | | | | | | | |
| molecular layer | 2 | 2 | 17 | 22 | 89 | 28 | 5 | | 81 | 69 | 100 | 69 |
| 520 K peak (450–600K) | | 9 | 58 | | 33 | 49 | | | 81 | 100 | 24 | 74 |
| 35:65 ratio of 3-methyl-1-butene/ 2-methyl-1,3-butadiene ^d | | 12 | 74 | | 43 | 57 | | | 36 | 100 | 11 | 79 |

^a Cis/trans mixture. ^b Baseline corrected. ^c High-temperature product evolution is observed as a single peak. ^d Using NIST mass spectra (Table 3).

spectrometric fragmentation patterns measured for the most intense masses of authentic samples (Table 2).

Intact 2-methylcyclopropylmethanol desorbs in three stages (α_0 – α_2) at 170, 230, and 290 K (Figure 1a) as indicated for the most abundant fragment mass ($m/z = 45$). The α_0 peak at 170 K does not saturate with increasing coverage, identifying this peak as sublimation of multilayers. The α_1 (230 K) and α_2 (290 K) peaks saturate before the multilayer peak appears and therefore are attributed to desorption of molecules bound to the surface. The α_2 peak reaches maximum intensity at 0.5 ML saturation, where saturation is defined as the exposure (integrated flux) for which multilayer desorption sets in. The multiplicity of molecular desorption peaks suggests that there are two adsorption states, which might arise from steric effects related to the methyl group at high coverages. Multiple desorption peaks have also been observed for other molecules on Mo(110), e.g., benzene.²⁴ Note that the α_1 and α_2 peaks cannot be attributed to desorption of the two stereoisomers, **4**

and **5** (Scheme 2), because the α_1 peak appears only at coverages where the α_2 peak is nearly saturated.

The 410 K peak is assigned to formation of C_5 hydrocarbons formed by C–O bond cleavage and subsequent dehydrogenation (m/z 67 and 53) and hydrogenation (m/z 70 and 55). However, definitive assignment of the products is hampered by the close resemblance of the fragmentation patterns for the various possible C_5 hydrocarbon products (Table 3) and by the lack of availability of 1,2-dimethyl- and methylenemethylcyclopropane samples. The overlapping evolution of hydrogenation (C_5H_{10}) and dehydrogenation (C_5H_8) products further complicates the analysis. Possible hydrocarbon products resulting from hydrogenation/dehydrogenation are (i) cyclic 1,2-dimethylcyclopropane/methylenemethylcyclopropane; (ii) linear 3-methyl-1-butene/2-methyl-1,3-butadiene; (iii) linear 1-pentene/1,3-pentadiene; and/or (iv) a mixture of any of these pairs (see below). Careful inspection of the m/z 70 and 55 traces shows intensity at temperatures as low as 320 K. This low-temperature tail is

TABLE 3: Mass Fragmentation Patterns for C₅ Hydrocarbons Taken from NIST²⁷

| <i>m/z</i> | 70 | 68 | 67 | 55 | 53 | 42 | 41 | 39 | 29 | 27 |
|---|----|-----|-----|-----|----|-----|----|----|----|----|
| Possible Hydrogenation Products — C ₅ H ₁₀ | | | | | | | | | | |
| 1,2 dimethylcyclopropane | 54 | | 2 | 100 | 10 | 45 | 42 | 40 | 32 | 35 |
| 1-pentene | 33 | | 2 | 61 | 6 | 100 | 50 | 44 | 28 | 39 |
| 3-methyl-1-butene | 28 | | 1 | 100 | 8 | 28 | 22 | 27 | 26 | 30 |
| Possible Dehydrogenation Products — C ₅ H ₈ | | | | | | | | | | |
| methylenemethylcyclopropane | 1 | 38 | 100 | 1 | 37 | 14 | 38 | 47 | 5 | 29 |
| 1,3-pentadiene | | 74 | 100 | | 54 | 11 | 38 | 56 | | 21 |
| 1,4-pentadiene | | 100 | 85 | | 57 | 19 | 43 | 57 | | 18 |
| 2-methyl-1,3-butadiene | | 64 | 100 | | 63 | 13 | 23 | 51 | | 22 |

attributed to 1,2-dimethylcyclopropane formation by comparison with data obtained from reaction of 2-methylcyclopropylmethanol on clean Mo(110).²⁵ Propene is identified as the C₃ fragment contributing to the 520 K peak by careful analysis of the residual intensity in the *m/z* 27, 39, 40, 41, and 42 traces obtained after correction for C₅ fragmentation. The fact that there is no residual intensity in *m/z* 29 excludes propane as a possible C₃-product, whereas the *m/z* 41 to *m/z* 42 ratio (>1) rules out cyclopropane formation (*m/z* 41:*m/z* 42 <1).

Water is formed in four peaks at 270, 350, 430, and 525 K denoted as α_1 , α_2 , β_1 , and β_2 (Figure 1a). The β water formation is observed at all coverages, whereas α_2 and α_1 appear at exposures above 0.33 and 1.0 times saturation, respectively. The α_1 (270 K) and α_2 (350 K) peaks arise exclusively from H-transfer to adsorbed oxygen and not from scission of the alkoxide C—O bond since only H₂¹⁸O is formed from reaction on ¹⁸O-labeled Mo(110) (data not shown). β -H₂O formation (430 and 525 K) incorporates oxygen originally bound to the surface and in the alkoxide, based on the detection of a 1:2 mixture of H₂¹⁶O and H₂¹⁸O during temperature-programmed reaction on ¹⁸O—Mo(110). Since the onset of the β_1 -H₂O peak at 430 K coincides with the maximum of the 410 K product peak, we propose that oxygen in the alkoxide is deposited on the surface prior to water formation.^{11–13} Similarly, the second high-temperature water peak (β_2) at 525 K also lags slightly behind the maximum of the 520 K product.

Deuterium labeling experiments (data not shown) indicate the involvement of surface hydroxyl groups (OH_a) in α_1 -H₂O formation and hydrogenation product evolution. The experiments are performed with an OD-precovered O/Mo(110) surface prepared as described previously.¹³ In brief, the 2/3 O ML overlayer is covered with multilayers of D₂O and subsequently heated to 300 K to remove multiple and molecular layers of adsorbed water. There is a broad water desorption feature (*m/z* 18, 19, and 20 in a 1:1.4:1 ratio) in the 275 to 500 K range, resulting from recombinant formation of water by surface hydroxyl groups and atomic hydrogen in temperature-programmed reaction following this preparation. Temperature-programmed reaction spectra obtained for this surface after exposure to 2-methylcyclopropylmethanol ($\Theta = 1/3$ ML) show additional water desorption peaks at 200 (H₂O molecular layer desorption)²⁶ and 245 K (α_1 -H₂O). In addition, the maximum of the broad feature is shifted to lower temperatures (~340 K) and its intensity in the *m/z* 18 and 19 traces is reduced by 45%, whereas the *m/z* 20 trace is reduced by 75%. The latter indicates that additional pathways, i.e., hydrogenation, lead to depletion of OD_a. This is further supported by observation of additional intensity over the 350–600 K range in the *m/z* 71 trace. Comparison with data from the undeuterated surface points to ca. 25% D₁ incorporation in the hydrogenation products. Interestingly, an increase in intensity is also detected in the *m/z* 69 trace. D₁ incorporation amounts to 6% in the dehydrogenation product. A similar 3% D₁ incorporation in the dehydrogenation

product (*m/z* 68) is observed for the 4-penten-2-ol precursor when reacted on the OD-precovered surface. This finding points to the existence of a partial H/D-exchange pathway. The fact that very similar amounts of D₁ incorporation in the dehydrogenation product are observed in the reaction of 2-methylcyclopropylmethanol and 4-penten-2-ol clearly shows that the H/D exchange is not coupled to the radical rearrangement.

Recombinant formation of CO from adsorbed oxygen (O_a) and carbon (C_a) is observed in the 850–1100 K temperature range (data not shown). Experiments on the ¹⁸O-labeled surface reveal that there is an increase in the amount of oxygen deposition from reaction with increasing dose. For example, the C¹⁸O/C¹⁶O is ~5:1 for the 15 s dose versus ~2:1 for the 4 min dose.

Temperature-programmed reaction studies of 4-penten-2-ol, **6**, and 2-methyl-4-buten-1-ol, **7**, were performed because they provide alternative routes to the two possible ring-opened products that could be formed after ring-opening of the (2-methylcyclopropyl)methyl radical (Scheme 2). In both cases, the corresponding alkoxides should form via O—H bond dissociation. Careful analysis of the temperature-programmed reaction spectrum for 4-penten-2-ol, **6**, indicates that 4-penten-2-oxide is the common intermediate formed in the 2-methylcyclopropylmethanol and 4-penten-2-ol reactions on O-covered Mo(110) (Figure 1b). Two product peaks are observed in the 350 to 600 K range. The fragmentation patterns for the products of 4-penten-2-ol reaction are the same within experimental error to those measured for the 520 K peak of 2-methylcyclopropylmethanol reaction (Table 2).

In contrast, the fragmentation patterns measured for hydrocarbons produced from reaction of 2-methyl-4-buten-1-ol, **7**, on oxygen-covered Mo(110) are qualitatively different than the other two cases; thus, 2-methyl-4-buten-1-oxide is excluded as the intermediate for the 520 K product evolution from 2-methylcyclopropylmethanol (Figure 1c). Most striking is the substantially higher intensity of *m/z* 70 for the product of 2-methyl-4-buten-1-ol formed at ~520 K (Figure 1). However, the fragmentation pattern of the 520 K product of 2-methyl-4-buten-1-ol reaction closely resembles that of the 410 K product of 2-methylcyclopropylmethanol reaction (Table 2). Therefore we propose that the 410 K peak in the 2-methylcyclopropylmethanol system and the 520 K peak in the 2-methyl-4-buten-1-ol system arise from the same radical intermediate. Definitive assignment of the products is hampered by the close resemblance of the fragmentation patterns for the C₅ hydrocarbons involved (Table 3). In analogy to 3-buten-1-ol,¹² the products evolved from the 2-methyl-4-butenoxide intermediate are 3-methyl-1-butene and 2-methyl-1,3-butadiene. Comparison with mass spectra from the NIST database²⁷ (Table 3) yields an estimate of 35:65 for the 3-methyl-1-butene/2-methyl-1,3-butadiene ratio in the 520 K peak of 2-methyl-4-buten-1-ol reaction.

Fourier Transform Infrared Spectroscopy. Infrared spectra provide evidence that 2-methylcyclopropylmethanol adsorbs

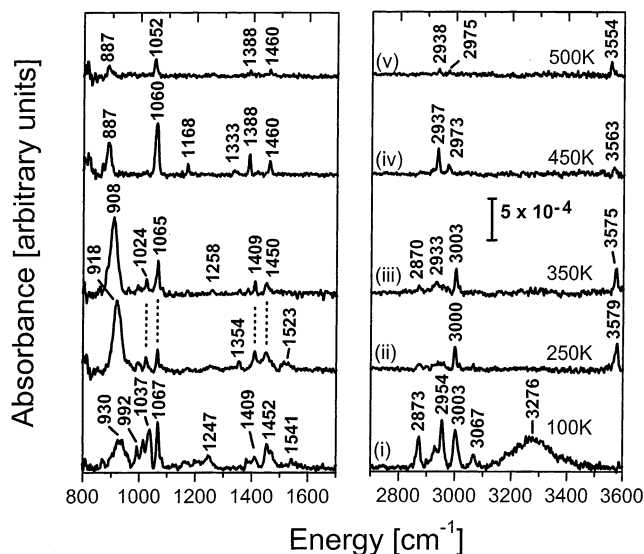


Figure 2. Reflection absorption infrared spectra of (i) condensed multilayers of 2-methylcyclopropylmethanol on O-modified Mo(110) ($\Theta_{\text{O}} = 0.67$ ML); and after heating of a saturation coverage to (ii) 250 K, (iii) 350 K, (iv) 450 K, and (v) 500 K employing a heating rate of 10 ± 2 K/s.

molecularly on the surface at 100 K, undergoing O–H dissociation at ~ 250 K (Figure 2). The infrared spectrum of condensed multilayers of 2-methylcyclopropylmethanol (Figure 2i) adsorbed on O-covered Mo(110) is similar to the gas-phase infrared spectrum of 2-methylcyclopropylmethanol.²⁸ All peaks in the gas-phase spectrum are present in the spectrum for the multilayer, although intensities of the peaks deviate. At coverages below saturation, the peaks are less pronounced, some disappearing in the noise. The broad $\nu(\text{OH})$ stretch near 3275 cm^{-1} is observed only when the surface is covered with multilayers, a behavior commonly observed for alcohols.^{11,29}

Infrared data provide evidence that O–H bond dissociation occurs upon heating to 250 K, yielding adsorbed 2-methylcyclopropylmethoxide and adsorbed OH. Two new features appear in the infrared spectrum when the 2-methylcyclopropylmethanol-covered surface is heated to 250 K: (i) a broad peak near 900 cm^{-1} and (ii) a sharp $\nu(\text{OH})$ band near 3580 cm^{-1} (Figure 2ii). The 3580 cm^{-1} peak is characteristic of adsorbed OH, indicating that hydrogen has been transferred to surface oxygen.^{11,13,29} Except for the appearance of the 900 cm^{-1} band, the spectrum at 250 K is similar to the intact alcohol. These results provide evidence that 2-methylcyclopropylmethoxide is present and that the 900 cm^{-1} peak is due to some combination of C–O and C–C stretch vibrations.^{11–13} Notably, the 900 cm^{-1} peak shifts to higher energy as a function of coverage. The $\nu(\text{C–O})$ modes in alkoxides are known to shift to higher energy as a function of coverage due to dipole–dipole coupling,^{30–32} reinforcing our assignment. The spectrum characteristic of adsorbed 2-methylcyclopropylmethoxide and OH persists up to 350 K (Figure 2iii).

The infrared spectrum of 2-methylcyclopropylmethanol significantly changes upon heating to 450 K (Figure 2iv). All changes are indicative of the ring-opened 4-penten-1-oxide, as described below. Most notably, a new pronounced band appears at 2937 cm^{-1} in the C–H stretch region, as the 3003 cm^{-1} band disappears (Figure 2 iv). There are several other changes in the spectrum as well: the 900 cm^{-1} band shifts to lower energy and loses intensity; the two peaks at 1024 and 1065 cm^{-1} disappear; a sharp peak at 1060 cm^{-1} appears; and peaks in the $\nu_{\text{ring}}(\text{C–C})$ and CH_2 -scissors region (1330 – 1550 cm^{-1}) shift to lower frequencies. The peak characteristic of adsorbed OH

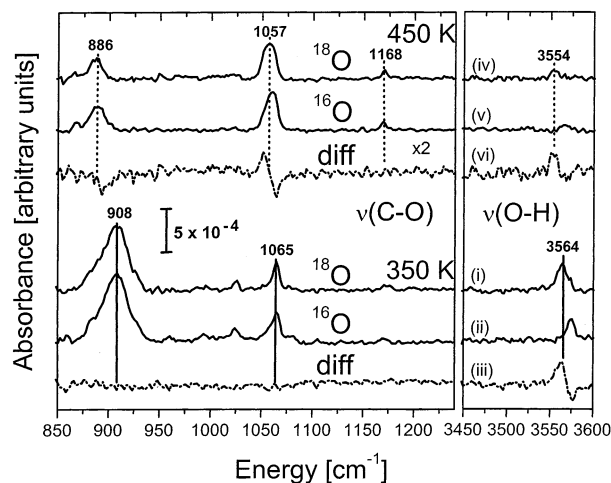


Figure 3. Infrared data for the C–O and O–H stretch region obtained after adsorption of a cis/trans 2-methylcyclopropylmethanol mixture on ^{16}O - and ^{18}O -modified Mo(110) ($\Theta_{\text{O}} = 0.67$ ML) and heating to 350 K (lower panel) and 450 K (upper panel). Traces (iii) and (vi) display the differences obtained by subtracting the spectra for the ^{18}O - from the ^{16}O -labeled surface, i.e., (i)–(ii) and (iv)–(v), respectively.

also loses intensity coincident with formation of $\beta_1\text{-H}_2\text{O}$. Annealing to 500 K (Figure 2v) does not introduce any changes except for an overall decrease in intensity.

Comparison of infrared spectra obtained following reaction of 2-methylcyclopropylmethanol on ^{18}O - and ^{16}O -covered Mo(110) show that there is oxygen exchange into the alkoxide species formed by heating to 450 K (Figure 3). This observation is consistent with our assertion that the C–O bond in the cyclic, surface-bound alkoxide is broken to yield a transient radical that rearranges and subsequently adds to oxygen between 350 and 450 K. There is no difference in the spectral range associated with the alkoxides when the 2-methylcyclopropylmethanol-covered surface is heated to 350 K on ^{18}O - and ^{16}O -covered Mo(110). The only difference between the two at 350 K is in the $\nu(\text{O–H})$ stretch region at 3564 cm^{-1} , due to the presence of ^{18}OH vs ^{16}OH created via H-transfer to surface oxygen.³³ Analogous data obtained after heating to 450 K provide clear evidence for oxygen exchange—there are differential peaks at 886 and 1057 cm^{-1} . These peaks are expected to have significant C–O character, based on previous detailed studies of vibrational coupling in ethoxy on Mo(110).³⁴ There is also a residual differential peak at 3554 cm^{-1} that is attributed to the presence of residual ^{16}OH and ^{18}OH (Figure 3).

The species formed by heating 2-methylcyclopropylmethanol to 450 K is identified as 4-penten-2-oxide by comparison to analogous data obtained for the two ring-opened alcohols, 2-methyl-4-buten-1-ol and 4-penten-2-ol (Figure 4). Specifically, there is a nearly exact correspondence in the infrared spectra obtained after heating 2-methylcyclopropylmethanol (Figure 4ii) and 4-penten-2-ol (Figure 4i) to 450 K on O-covered Mo(110). In contrast, there are several differences in the spectrum obtained after heating 2-methyl-4-buten-1-ol to 450 K (Figure 4iii). Using the 989 and 1076 cm^{-1} peaks characteristic of 2-methyl-4-butenoxide, we derive upper limits of 8 and 12% for the highest possible contribution of 2-methyl-4-butenoxide to the infrared trace shown in Figure 4ii. Detailed analysis of infrared spectra obtained for the two reference compounds, **6** and **7**, as a function of temperature confirm that their respective surface-bound alkoxides are present at 450 K. Tentative vibrational assignments are provided in Tables 4 and 5, based on comparison with literature data. Note that the identification of the specific isomer

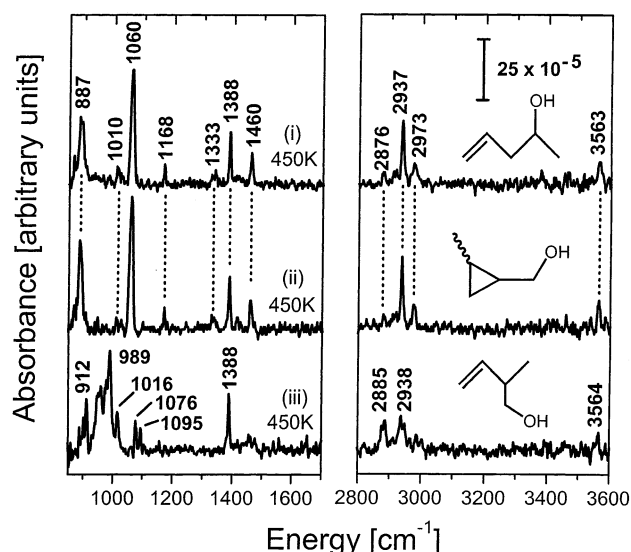


Figure 4. Comparison of infrared data obtained after adsorption of (i) 4-penten-2-ol, (ii) 2-methylcyclopropylmethanol, and (iii) 2-methyl-4-buten-1-ol on O-modified Mo(110) ($\Theta_{\text{O}} = 0.67$ ML) and heating to 450 K.

TABLE 4: Vibrational Assignment of Selected Infrared Modes for a *cis/trans* 2-Methylcyclopropylmethanol Mixture on O-Modified Mo(110)

| Mode | 100 K ^a | 350 K | 450 K | 500 K |
|---------------------------------|------------------------|------------------|---------------------|------------|
| | | | | |
| $\nu(\text{C-O})^b$ | 930 | 908 | 887 | 887 |
| $\nu(\text{C-C})$ | 992, 1037 | 1024 | | |
| $\nu(\text{CC-O})$ | 1067 | 1065 | 1060 | 1052 |
| $\nu(\text{C-C})_{\text{ring}}$ | 1247 | 1258 | | |
| CH_2 scissor | | | 1388, 1460 | 1388, 1460 |
| ring modes | 1409, 1452 | 1409, 1450 | | |
| $\nu(\text{C=C})$ | | | (1643) ^c | |
| $\nu(\text{C-H})$ | 2873, 2954, 3003, 3067 | 2870, 2933, 3003 | 2937, 2973 | 2938, 2975 |
| $\nu(\text{O-H})$ | 3276 | 3575 | 3563 | 3554 |

^a Condensed multilayers. ^b Above 100 K this is the $\nu(\text{C-O-Mo})$ mode. ^c This mode is not observed for 2-methylcyclopropylmethanol and only at very high coverages for 4-penten-2-ol and 2-methyl-4-buten-1-ol.

formed from the 2-methylcyclopropylmethanol reaction does not depend on these assignments.

Discussion

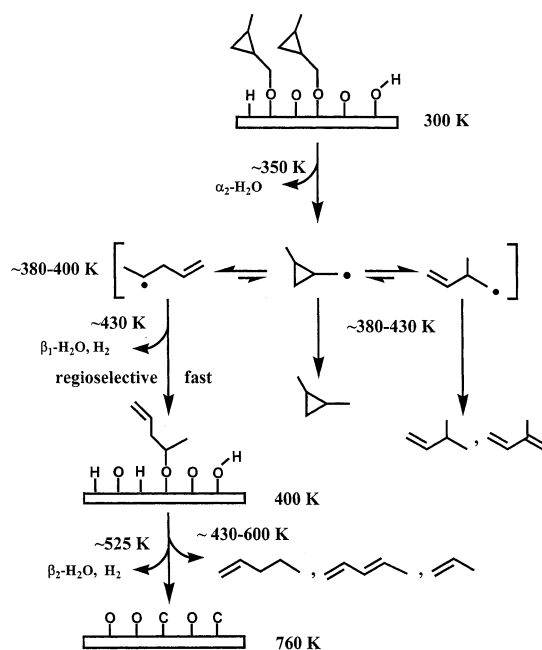
All of our data indicate that a diastereomeric mixture of 2-methylcyclopropylmethanol yields a transient (2-methylcyclopropyl)methyl radical via C–O bond dissociation in the surface-bound alkoxide at a temperature above 350 K on oxygen-covered Mo(110). This transient radical has sufficient time to rearrange prior to leaving the surface, providing us with a means of measuring its lifetime in the vicinity of the surface. Because of the complexity of this system, there are several competing reaction pathways available to the nascent (2-methylcyclopropyl)methyl radical, as summarized in Scheme 3. This

TABLE 5: Vibrational Assignment of Selected Infrared Modes for 4-Penten-2-ol and 2-Methyl-4-buten-1-ol on O-Modified Mo(110)

| | 4-Penten-2-ol | | 2-Methyl-4-buten-1-ol | |
|-----------------------|--------------------|---------------------|------------------------|---------------------|
| Mode | 100 K ^a | 450 K | 100 K ^a | 450 K |
| | | | | |
| $\nu(\text{C-O})^b$ | 918 | 887 | 918 | 912 |
| $\nu(\text{CC-O})$ | 1084 | 1060 | 1037 | 989(?) |
| CH_2 scissor | 1329, 1377, 1450 | 1388, 1460 | 1378, 1417, 1462 | 1388 |
| $\nu(\text{C=C})$ | 1643 | (1643) ^c | 1642 | (1643) ^c |
| $\nu(\text{C-H})$ | 2930, 2976, 3081 | 2876, 2937, 2973 | 2873, 2928, 2974, 3081 | 2885, 2938 |
| $\nu(\text{O-H})$ | 3290 | 3563 | 3278 | 3564 |

^a Condensed multilayers. ^b Above 100 K this is the $\nu(\text{C-O-Mo})$ mode. ^c This mode is not observed for 2-methylcyclopropylmethanol and only at very high coverages for 4-penten-2-ol and 2-methyl-4-buten-1-ol.

SCHEME 3



scheme is constructed on the basis of all of our data. Due to the complexity of this system, we will focus the discussion on a few salient points.

The most important point of our work is that intrinsic kinetics of a system can be used to provide for a high degree of control of selectivity for the reaction of isomeric intermediates in surface processes. The case of 2-methylcyclopropylmethanol provides an intrinsic competition for the formation of different products because of two distinguishable rearrangement reactions that occur with differing rates (Scheme 4, Table 6).

The selectivity for formation of 4-penten-1-oxide is generally consistent with the fact that rearrangement to the 4-penten-2-yl radical is faster than all other rearrangement processes in this system (Scheme 4, Table 6). Although the rearrangement to the 4-penten-2-yl radical, **B**, is most rapid, the relative rearrangement rates alone cannot completely account for the

SCHEME 4

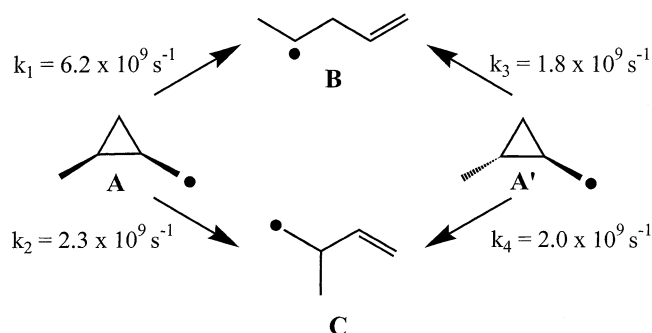


TABLE 6: Rate Constants for Rearrangement of the (2-Methylcyclopropyl)methyl Radical in Solution

| Arrhenius equations ^a | k_x at 380 K [s^{-1}] | k_x at 400 K [s^{-1}] |
|----------------------------------|-----------------------------|-----------------------------|
| $\log k_1 = 12.85 - 5.6/(2.3RT)$ | 4.25×10^9 | 6.16×10^9 |
| $\log k_2 = 12.85 - 6.4/(2.3RT)$ | 1.47×10^9 | 2.25×10^9 |
| $\log k_3 = 12.85 - 6.6/(2.3RT)$ | 1.13×10^9 | 1.75×10^9 |
| $\log k_4 = 12.85 - 6.5/(2.3RT)$ | 1.29×10^9 | 1.99×10^9 |

^a Taken from ref 5.

extremely high degree of regioselectivity. If our sample would only contain *cis*-2-methylcyclopropylmethanol, **4**, the *cis*-radical **A** would be formed upon C–O bond cleavage yielding a 2.7:1 mixture of 4-penten-2-yl, **B**, and 2-methyl-4-butenyl, **C**, radicals. On the other hand, starting from the pure *trans*-alcohol, **5**, only radical **A'** would be produced, yielding **B** and **C** in a ratio of 0.9:1. The B:C ratios are calculated using the rate constants measured for solution-phase rearrangement of (2-methylcyclopropyl)methyl radical (Table 6). Since it is more likely that we have a 1:1 mixture of **4** and **5** in our sample due to the similar stability of the two diastereomers, the absence of 2-methyl-4-butenoxide cannot be due solely to the detection limits in infrared and temperature-programmed reaction data (8:1 and 5:1, respectively).³⁵ The high degree of selectivity for formation of 4-penten-2-oxide must therefore be due to factors other than the rearrangement rates, assuming that the trapping probability on surface oxygen is comparable for radicals **B** and **C**.

We attribute the high degree of selectivity for formation of 4-penten-2-oxide to faster rates of hydrogenation and dehydrogenation of the 2-methyl-4-butenyl radical. The proposed propensity for hydrogenation and dehydrogenation of 2-methyl-4-butenyl radical can be explained on the basis of the intrinsic characteristics of this radical. In particular, dehydrogenation of 2-methyl-4-butenyl radical, **C**, to afford 2-methyl-1,3-butadiene involves cleavage of a tertiary C–H bond, whereas dehydrogenation of the 4-penten-2-yl species involves breaking a secondary C–H bond. It is widely known that dissociation of tertiary is faster than secondary C–H bonds.³⁶ Similarly, hydrogenation to the corresponding alkanes is predicted to be faster for the 2-methyl-4-butenyl species because it is a primary radical, whereas the 4-penten-2-yl is a secondary radical. Hence, hydrogenation of the 2-methyl-4-butenyl radical is expected to be more rapid. While the relative rates for hydrogenation and dehydrogenation may not be the only factor leading to the high degree of selectivity for 4-penten-1-oxide formation, it is probably one of the factors. Other possible factors that we cannot address are steric effects present during rearrangement as a result of the methyl group orientation.

The foundation of our conclusions in this study is provided by earlier extensive studies of alkoxide species on O-covered Mo(110).^{11–13,19,29,37–40} Our previous studies clearly demonstrated that (1) homolytic C–O bond dissociation in alkoxides

bound to O-covered Mo(110) yields transient hydrocarbon radicals;^{19,37} (2) gas-phase hydrocarbon radicals readily add to oxygen on Mo(110) at low temperature in the microscopic reverse of radical elimination from alkoxides;³⁸ (3) the temperature at which radical elimination from the alkoxides occurs correlates with the homolytic C–O bond strengths in the alkoxides;^{11,29,39,40} (4) surface-mediated hydrogenation and dehydrogenation compete with radical elimination, leading to formation of gaseous olefins and alkanes, respectively;^{29,39,40} (5) rearrangement of cyclopropylmethyl radical formed in the vicinity of the surface occurs at ~ 400 K, indicating that the lifetime of this radical is on the order of ~ 1 ns;^{11–13} and (6) rearrangement of cyclopropyl rings is *not* induced by the surface.^{11,41}

An important aspect of our studies of radical-rearrangement processes is that once the radical rearranges, it can react with oxygen and remain stable on the surface to higher temperatures. The C–O bond strengths for the linear, ring-opened alkoxides are estimated to be ~ 1.2 eV higher than the cyclic analogues.^{14,15} The enhanced stability of the linear species relative to the ring-closed isomer is verified based on their relative temperatures for C–O dissociation. For example, the C–O bond of 2-methylcyclopropylmethoxide cleaves at ~ 320 K,²⁵ whereas 4-penten-2-oxide is stable up to ~ 500 K (Figure 1b). In other words, the process of rearrangement lands the species on another potential-energy surface. In the absence of rearrangement, a radical will have a rather short lifetime on the surface because the thermal energy is greater than the depth of the C–O bond potential at the temperature of C–O bond cleavage.

Even in the absence of rearrangement, hydrocarbon radicals formed via elimination from alkoxides must have a finite lifetime on the surface based on the fact that surface-mediated hydrogenation and dehydrogenation occur, yielding alkanes and olefins, respectively. Earlier studies using isotopic labeling clearly demonstrated that radical elimination precedes dehydrogenation and that both hydrogenation and dehydrogenation are surface mediated.⁴⁰ Indeed, our previous studies of radical rearrangement using hydroxymethylcyclopropane indicated that the lifetime of the radical in the vicinity of the surface is on the order of 1 ns at 400 K.¹¹ Briggman et al. have determined Arrhenius parameters for the residence time of methyl radicals created by photocatalytic treatment of a CH_3I film condensed on Mg(100).⁴² Using their Arrhenius parameter we calculate that CH_3 radicals have surface lifetimes on the order of 2 ns at 400 K. A series of papers from Carlsson et al.^{43–45} have investigated the influence of surface corrugation on the residence times of small hydrocarbons on the Pt(111) and the Pt(111)-p(2 \times 1)-O surfaces. They developed a model that relates the number of “hops” a molecule undergoes before being ejected to the gas phase and the desorption-energy barrier, i.e., desorption barriers of 5.0 and 8.8 kJ/mol correspond to 7 and 34 hops, respectively. Dynamics simulation^{46,47} based on a formalism developed by J. C. Tully^{48,49} also predicts trapping of small hydrocarbons on the Pt(111) surface, which is mediated by energy transfer between surface phonons and cartwheel rotational states of the molecule. These studies are all consistent with our findings that nascent radicals have lifetimes on the order of nanoseconds at 400 K and that they sample the surface multiple times during this process. The multiple hops on the surface can lead either to trapping on the surface, C–C bond dissociation, loss of hydrogen, or hydrogenation.

In conclusion, differences in radical stability and H-acidity lead to competition of dehydrogenation and hydrogenation processes with trapping of the primary 2-methyl-4-buten-1-yl radical. As a result, only the more stable, secondary 4-penten-

2-yl radical survives long enough in the vicinity of the surface to find a surface oxygen atom and undergo C–O bond formation. By assuming that the rate constant for rearrangement on the surface is similar to that in solution, we are able to estimate the limits for the rates of hydrogenation, dehydrogenation, and trapping at 380 K: (i) for 2-methyl-4-butenyl radical $k_{\text{rearrange}} = 1.5 \times 10^9 > k_{-\text{H}}(\text{C}), k_{+\text{H}}(\text{C}) > k_{\text{trap}}(\text{C})$ and (ii) for 4-penten-2-yl $k_{\text{rearrange}} = 4.2 \times 10^9 > k_{\text{trap}}(\text{B}) > k_{-\text{H}}(\text{B}), k_{+\text{H}}(\text{B})$.

Conclusion

Adsorption of 2-methylcyclopropylmethanol onto oxygen-modified Mo(110) leads to formation of the 2-methylcyclopropylmethoxide surface species. Between 350 and 400 K the C–O bond of the alkoxide cleaves and the (2-methylcyclopropyl)methyl radical forms. The radical stays long enough in the vicinity of the surface to undergo ring opening. The methyl substitution allows differentiation of two ring-opening pathways leading to formation of the 4-penten-2-yl and 2-methyl-4-butenyl radical species. The 2-methyl-4-butenyl radical is hydrogenated or dehydrogenated, whereas the 4-penten-2-yl species binds to surface oxygen yielding 4-penten-2-oxide. Above 480 K the C–O bond of the 4-penten-2-oxide species cleaves and a 20:70:10 mixture of 1-pentene, 1,3-pentadiene, and propene is formed. At saturation the branching ratio for the dehydrogenation/hydrogenation to trapping processes is determined as 55:45.

Trapping of the linear, ring-opened 4-penten-2-yl radical is in good agreement with earlier studies of the hydroxymethylcyclopropane parent system and solution-phase rearrangement rates. Differences in stability of the linear radical species and strength of the C–H bonds involved in hydrogenation and dehydrogenation processes are identified as additional factors, which lead to the highly selective trapping of the 4-penten-2-yl radical isomer.

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