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# Hydroxymethylcyclopropane on Oxygen-Covered Mo(110): A Radical Clock on a Surface

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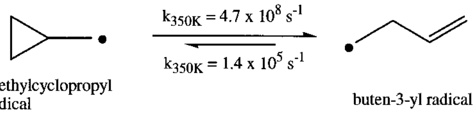
Radicals are proposed as intermediates for a range of heterogeneous reactions, but little is known of their lifetimes because of their transient nature. This study describes the first observation of the methylcyclopropyl−3-butenyl radical clock rearrangement (Scheme 1) on a surface under ultrahigh-vacuum conditions. We use the fact that alkyl radicals are transiently formed from reaction of alcohols on Mo(110) established in previous studies.[1,2] Because both unrearranged *and* rearranged species are trapped on oxygen-covered Mo(110) during the reaction, the lifetime of the radical on the surface is on the order of $10^{-8}$ s. Since their introduction by Giller and Ingold[3] in 1980, free radical clocks[3,4] have become a well-established technique in organic chemistry to determine radical lifetimes.[5,6] The radical rearrangement shown in Scheme 1 is a well-calibrated example of a fast-reacting radical clock.[7]

In practice, a radical clock reacts with a radical of unknown lifetime. The lifetime of the unknown radical is subsequently determined by combining information on product distribution, reactant concentration, and known reaction rates.[8] For example, the viability of a discrete substrate radical species during hydrocarbon oxidation by soluble methane monooxygenase was assessed using substituted cyclopropane probes.[9] Hanzlik et al.[10] used substituent effects on radical clocks to distinguish between single-electron and hydrogen-atom transfer processes. Curtis and Drucker[11] used the rearrangement of the methylcyclopropyl radical formed via cleavage of the thiolate C−S bond to verify the formation of a radical intermediate during hydrodesulfurization of thiols by a Co/Mo/S cluster. Ethyl- and isopropylcyclopropane radical clocks were employed as mechanistic probes in the catalytic oxidation of alkanes and alkenes by titanium silicates in solution.[12] In this study, we probe the relative time scales for competing processes on a metal surface.

There are three requirements for radical clocks on a surface: (i) the molecule must be anchored to the surface, (ii) the radical rearrangement must be controlled via temperature, and (iii) products must be trapped on the surface for detection. Our probe molecule, hydroxymethylcyclopropane, was selected because alcohols are known to react by O−H bond cleavage, yielding an adsorbed alkoxide, on O-covered Mo(110).[13−15]

**Scheme 1**



Hydrocarbon products are formed between 480 and 600 K during temperature-programmed reaction of hydroxymethylcyclopropane on O-covered Mo(110). The products are identified as 1-butene, 1,3-butadiene, and ethene based on analysis of the mass spectrometer fragmentation patterns (Figure 2, Table 1, Supporting Information). The product distribution is estimated to be in a ratio of 22:60:18 for 1-butene:1,3-butadiene:ethene. The only other products formed are H$_2$, water, and CO. Carbon monoxide is formed at ~950 K via reaction of carbon and oxygen, indicating that deposition of carbon competes with elimination of hydrocarbons.

The detection of linear C$_4$-carbon products at elevated temperatures suggests that ring opening has occurred; however, the mass spectra of 1-butene and methylcyclopropane[16] as well as those of 1,3-butadiene and methylenecyclopropane[17] are very similar. Furthermore, the linear C$_4$ carbons could be evolved either via direct desorption of the ring-opened radical or via decomposition of alkyl or alkoxy intermediates bound to the surface.

Infrared reflection absorption spectroscopy is used to probe for ring opening and to distinguish between the two paths. The similarity in the spectrum obtained for hydroxymethylcyclopropane adsorbed on O-covered Mo(110) at 100 K (Figure 1a) to that for gas-phase hydroxymethylcyclopropane[17] (Table 2, Supporting Information) indicates that intact alcohol is present on the surface at low temperature. At high coverage, the broad OH absorption band of hydroxymethylcyclopropane is visible at ~3280 cm$^{-1}$. Heating to 220 K induces sublimation of condensed hydroxymethylcyclopropane and some cleavage of the O−H bond (not shown).

Heating to 350 K leads to completion of OH bond breaking. Two new peaks at 905 and 936 cm$^{-1}$, attributed to the formation of a Mo−O−C bond,[13] develop in the infrared spectrum. There are no shifts in the 800−3010 region when an $^{18}$O-labeled surface is used, indicating that the C−O bond is retained at 350 K. The presence of the $\nu$(C−O) mode at 1029 cm$^{-1}$ further supports this assertion. Hydroxy is identified by the appearance of a sharp $\nu$(OH) band at 3572 cm$^{-1}$ (Figure 1b),[13,18] that shifts to 3561 cm$^{-1}$ when the reaction is carried out on $^{18}$O-covered Mo(110). The labeling experiments demonstrate that hydrogen is transferred to surface oxygen, leaving the C−O bond intact. The remainder of the spectrum is attributed to methylcyclopropyloxide (c-C$_3$H$_5$-CH$_2$O-, Table 2, Supporting Information). There are two sharp features at 1393 and 1434 cm$^{-1}$, in the region expected for the ring-CH$_2$ scissors mode[19] and one dominant peak in the C−H stretch region at 3010 cm$^{-1}$. Notably, there is no peak detected in the region expected for a $\nu$(C=C) mode, 1645 cm$^{-1}$, indicating that ring opening has *not* occurred at 350 K.

Heating to 460 K induces ring opening and disproportionation of adsorbed OH. Two new vibrational peaks appear at 1243 and 1645 cm$^{-1}$, while the ring modes at 1393 and 1434 cm$^{-1}$ and the $\nu$(O−H) at 3572 cm$^{-1}$ disappear (Figure 1c). The appearance of the $\nu$(C=C) peak[20] at 1645 cm$^{-1}$ is strong evidence that ring opening has occurred and that the product is trapped on the

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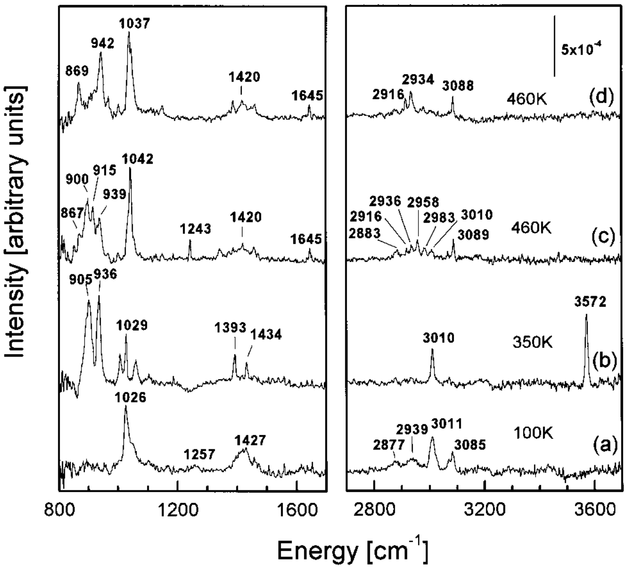


**Figure 1.** FT-IR spectra of adsorbed products of hydroxymethylcyclopropane reaction on oxygen-covered Mo(110) upon heating to: (a) 100 K, (b) 350 K, and (c) 460 K. Trace (d) shows the spectrum obtained for 3-buten-1-ol under the same conditions as (c). The crystal is allowed to cool to 130 K prior to the IR-measurement.

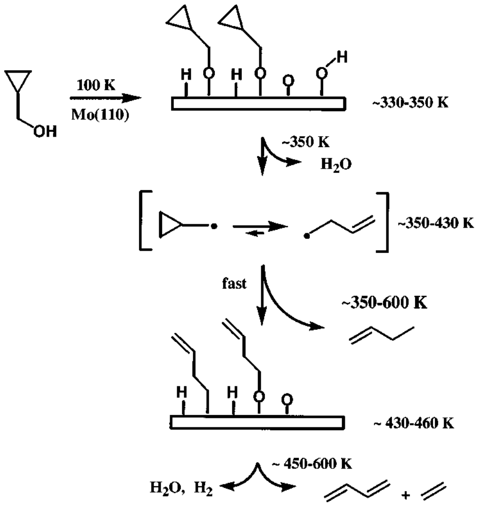
surface. The disappearance of the $\nu$(O−H) peak coincides with the evolution of water.

Changes in the C−O stretch region indicate that one of the ring-opened products is the alkoxide, 3-butenyl-1-oxide. Assignments are facilitated by experiments performed on an $^{18}$O-labeled surface (Table 2). Notably, the two new peaks at 1243 and 1645 cm$^{-1}$ do not shift, whereas shifts are observed in the 850−1100 cm$^{-1}$ region. The shifts are strongest (10 and 8 cm$^{-1}$) for the 900 and 939 cm$^{-1}$ peaks, indicating some component of $\nu$(Mo−O−C).

Further evidence for the formation of the ring-opened alkoxide, 3-butenyl-1-oxide, from reaction of hydroxymethylcyclopropane is obtained via comparison to the temperature-dependent spectrum of 3-buten-1-ol adsorbed on O-covered Mo(110) (Figure 1d). All peaks present in the spectrum obtained after heating 3-buten-1-ol to 460 K are contained in Figure 1c. There are additional peaks at 900, 915, 1243, 1342, and 2958 cm$^{-1}$ in Figure 1c, which are not present in Figure 1d. Modes in the 1200−1250 cm$^{-1}$ region have been attributed to the $\delta$ (CH$_2$) mode of alkyl groups bound to metal atoms,[21,22] thus the 1243 cm$^{-1}$ peak is assigned to a metal-bound butenyl species.[23]

The reaction scheme shown for hydroxymethylcyclopropane on O-covered Mo(110) is formulated based on all of our results (Scheme 2). The ring-closed alkoxide forms at 350 K via O−H bond scission. Some of the hydroxy hydrogens are transferred to oxygen on the surface to form adsorbed OH. Above 350 K,[2,13] the surface hydroxyl decomposes to gaseous water, the C−O bond of the ring alkoxide species breaks, and the methylcyclopropyl radical forms in the vicinity of the surface. It remains there long enough to rearrange and subsequently form either new C−O or C−Mo bonds. The time-scale for ring opening is on the order of $10^{-8}$ s in solution. We suggest that dipole-image dipole[24] and van der Waals interactions[25] between the ring and the surface keep the radical in the vicinity of the surface for a sufficiently long time for ring opening. Once the butenyl radical is formed, it may either form a carbon−metal bond or add to adsorbed oxygen to form the 3-butenyl-1-oxide that is identified by the 1645 cm$^{-1}$ peak. The C−O bond strength of the 3-butenyl-1-oxide is estimated to be 1.2 eV[26,27] greater than the methylcyclopropyloxide providing a thermodynamic driving force for reformation of the C−O bond.

**Scheme 2**



A ring-opening mechanism mediated by the surface[28] that does not involve cleavage of the C−O bond is ruled out by experiments performed recently in our laboratory using 1-cyclopropylethanol.[18] Neither ring opening nor O-containing products are observed for 1-cyclopropylethanol when heated to elevated temperatures; only C$_5$ species desorb—all below 350 K. Further, the formation of a metallacyclobutane species is excluded, because the characteristic band at 2775 cm$^{-1}$ is not detected.[29] The mechanism depicted implies that the radical rearrangement is faster than the trapping of the radical by the surface. The latter, in turn, is faster than hydrogen abstraction from the surface by either the unrearranged or the rearranged radical, which rules out the direct desorption mentioned above.

On the basis of our study, the following relative ordering of rates on O-covered Mo(110) is indicated: $k_{\mathrm{rearrange}} = 4.7 \times 10^8$ s$^{-1}$ > $k_{\mathrm{trap}}$ > $k_{\mathrm{H-abstraction}}$, assuming that the rates of rearrangement are similar on the surface and in solution. Notably, hydrogen abstraction from clean Mo(110) is faster, based on formation of methylcyclopropane from methylcyclopropanethiol.[16] The difference may be due to differing hydrogen reactivity, because the desorption temperature for hydrogen is ~125 K higher on O-covered Mo, indicating that radical trapping rates depend on the nature of the surface. This work provides a general approach to studying radical lifetimes and reactions on surfaces.

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**Supporting Information Available:** Tables and Figure of product distributions for temperature dependent reaction spectroscopy and IR peak assignments (PDF). This material is availabe free of charge via the Internet at http://pubs.acs.org.

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