

Cyclopropylmethyl/Cyclobutyl Rearrangements on Surfaces: Evidence for Transient Cation Formation near O-Covered Mo(110)

Sean H. Wiedemann,^{†,§} Dae-Hyuk Kang,[‡] Robert G. Bergman,[§] and Cynthia M. Friend^{*,‡}

Contribution from the Department of Chemistry and Division of Engineering and Applied Sciences, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, and Department of Chemistry, University of California, and Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received November 17, 2006; E-mail: cfriend@deas.harvard.edu

Abstract: Rearrangement reactions of C_4 -alkoxides on O-covered Mo(110) have been studied using temperature-programmed reaction spectroscopy and reflection-absorption infrared spectroscopy. Cyclobutoxide on Mo(110), prepared from the corresponding alcohol or bromide, is described for the first time in detail. Several reaction mechanisms are considered for the ring-opening rearrangement of cyclopropylmethoxide during high-temperature annealing. In light of compelling new data, previous results are reinterpreted to support the formation of transient cations near O-covered Mo(110). For the first time, we present strong evidence for clean, heterolytic bond cleavage reactions over a metal surface. Our revised reactivity model is based on spectroscopic and reactivity data that show the rearrangement of cyclopropylmethyl groups to cyclobutyl groups and vice versa. Selectively deuterated 1,1- D_2 -cyclopropylmethanol was studied as a test of mechanism and as a probe for the lifetime of reactive intermediates. Isotopic scrambling observed for this substrate is consistent with the formation of a relatively long-lived carbocation during rearrangement. The intermediacy of transient cations is further invoked to explain the rearrangements that are now recognized to occur as alkyl bromides are transformed into alkoxides on Mo(110)-(1 × 6)-O. The observed ring expansion/contraction reactions are characteristic of a cationic process; carbon-centered radicals are not known to rearrange in this manner. However, in none of the cases discussed could contributions from radical pathways be completely ruled out. Our results are compared to analogous reactions in the vapor and solution phases. General trends governing rearrangement mechanisms on Mo(110) are presented with respect to metal-surface coverage, heteroatom incorporation, and temperature. Trends are discussed in the context of heterogeneous hydrocarbon oxidation.

Introduction

Compounds with cyclopropylmethyl groups have been used to probe for both radical and ionic intermediates in a variety of reaction systems.¹ The cyclopropylmethyl radical undergoes ring opening to yield 3-buten-1-yl radical on a nanosecond time scale,² whereas the cyclopropylmethyl-derived cation has been observed to undergo partial rearrangement to a mixture of the cyclobutyl, 3-butenyl, and unrearranged cyclopropylmethyl products in the presence of a nucleophilic trap (Scheme 1).^{3,4} These rearrangements have been used in conjunction with

isotopic labeling to gain insight into the mechanisms of many organic reactions.⁵

One of our groups has studied organic rearrangement reactions that occur in the vicinity of metallic surfaces in an effort to extend this approach to heterogeneous systems.⁶ Organic radicals and cations are often proposed as intermediates in important heterogeneous reactions, especially in catalysis, but direct evidence for these short-lived intermediates is seldom available.⁷ Recently, the rearrangement reactions of cyclopro-

[†] Present address: Department of Chemistry, Princeton University, Princeton, NJ 08544.

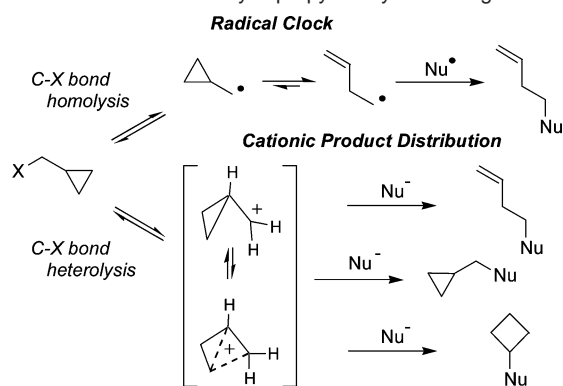
[‡] Harvard University.

[§] University of California, Berkeley.

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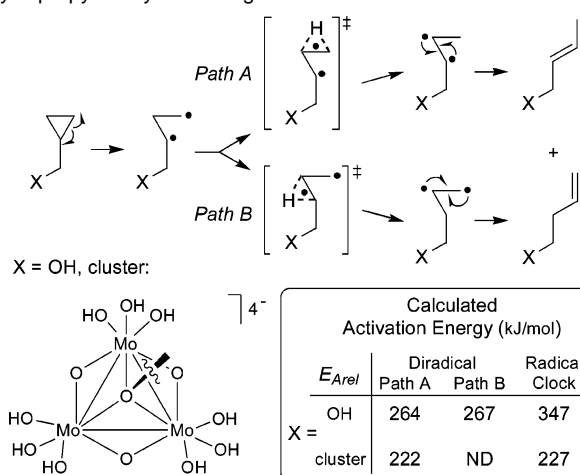
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Scheme 1. Characteristic Cyclopropylmethyl Rearrangements

pylmetoxide on Mo(110) ($\text{Mo}-\text{O}-\text{CH}_2-\text{c}-\text{C}_3\text{H}_7$) were investigated.⁸ Alkoxides on Mo(110) are of special interest because they undergo heteroatom removal—the reverse of hydrocarbon oxidation—to provide free hydrocarbons upon strong heating.⁹ Generally, alkoxides are generated on Mo(110)—(1×6)-O via the corresponding alcohols or bromides. Evidence of cyclopropylmethyl rearrangements can be detected immediately following alkoxide formation (in the case of bromides)¹⁰ and upon moderate heating (~ 400 K).⁸ Eventually, at more elevated temperatures, the C–O bonds of surface alkoxides are broken. Alkenes are the predominant products of this reaction whenever a β -hydride elimination pathway is accessible.¹¹ Otherwise, pathways including the reductive formation of alkanes become significant.

Kretzschmar et al. previously reported that cyclopropylmethoxide ($\text{Mo}-\text{O}-\text{CH}_2-\text{c}-\text{C}_3\text{H}_7$) on Mo(110) rearranges to 3-buten-1-oxide ($\text{Mo}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$) upon heating to 460 K.^{8a} Originally, this isomerization was understood to occur via homolytic C–O cleavage (Scheme 1). We proposed that cyclopropylmethyl radical was formed in the vicinity of the surface, rearranged to 3-butenyl radical, and then was captured by radical recombination to re-form a C–O bond. Because the ring-opening reaction of cyclopropylmethyl radical is known to proceed with a well-defined rate constant under a variety of reaction conditions, it is one of the best known “radical clocks.”¹² If a radical clock could be coupled to other well-defined surface processes, one could begin to calibrate the rates of surface reactions relevant to heterogeneous catalysis.

In an effort to provide support for our proposed mechanism of cyclopropylmethoxide rearrangement on Mo(110), a theoretical study using density functional theory (DFT) was carried out.¹³ Reactions were modeled for gas-phase species and for species bound to a small MoO cluster meant to approximate an

Scheme 2. Calculated Diradical Mechanisms of Cyclopropylmethyl Rearrangement

extended surface. Two nearly isoenergetic, possible mechanisms emerged for the observed reaction, (1) the so-called radical clock mechanism shown in Scheme 1 and (2) a more unusual bifurcated mechanism arising from homolytic C–C bond cleavage (Scheme 2).¹⁴ Herein, we present data demonstrating that 2-buten-1-oxide ($\text{Mo}-\text{O}-\text{CH}_2\text{CH}=\text{CHCH}_3$)—an expected product of one fork of the latter mechanism (Scheme 2, Path A)—cannot be involved in the surface rearrangements of cyclopropylmethoxide. Therefore, diradical mechanisms are ruled out in the present case.

In order to further test the radical clock model of radical formation and rapid rearrangement in the vicinity of O-covered Mo(110), we investigated the surface behavior of selectively deuterated cyclopropylmethanol ($\text{c}-\text{C}_3\text{H}_5-\text{CD}_2-\text{OH}$). For this substrate and all others mentioned in this paper, temperature-programmed reaction (TPR) spectroscopy and reflection-absorption infrared (RAIR) spectroscopy were employed for reaction monitoring and characterization. The results of the isotope-labeling experiment cast serious doubt on the validity of the radical clock mechanism. In the process of considering necessary revisions to our mechanistic model, we were prompted to study the surface behavior of cyclobutoxide ($\text{Mo}-\text{O}-\text{c}-\text{C}_4\text{H}_7$). These, at first tangential, experiments now form the centerpiece of our understanding of cyclopropylmethyl rearrangements near Mo(110). To our surprise, the spectroscopic features characteristic of cyclobutoxide were found to be present in numerous past rearrangement experiments, though at the time, they were not assigned as such.^{8a,10} We now wish to reinterpret those experiments in conjunction with the description of our present findings. Together, data from the reactions of cyclopropylmethyl, cyclobutyl, and 3-buten-1-yl bromides and alcohols reveal that near O-covered Mo(110), cyclopropylmethyl groups can rearrange to cyclobutyl groups and vice versa. Because this behavior is uniquely attributable to cationic intermediates, radical processes alone cannot account for our results.

Experimental Section

Apparatus. All surface experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 1 \times$

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- (14) Importantly, due to limitations of the modeling software, mechanisms involving heterolytic bond cleavage could not be evaluated in comparison to radical mechanisms.

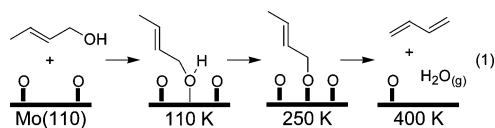
10^{-10} mmHg, described in detail previously.¹⁵ The UHV chamber is equipped with a UTI quadrupole mass spectrometer for temperature-programmed reaction (TPR) experiments, low-energy electron diffraction (LEED) optics, and an Auger electron spectrometer with a cylindrical mirror analyzer (Perkin–Elmer model 15-555). The mass spectrometer is interfaced to a computer that allows the collection of up to 16 separate ion intensity profiles during temperature-programmed experiments. The heating rate was held nearly constant at $\Delta T/\Delta t = (10 \pm 2)$ K/s between 110 and 760 K. The crystal was biased at a voltage of -100 eV during adsorption of all molecules and during collection of temperature-programmed reaction data in order to retard electrons emitted from the mass spectrometer and, thus, preclude electron-induced processes. This practice is commonly used and does not affect the outcome of our experiments because they are carried out in vacuum. Infrared (RAIR) spectra were collected using a commercial spectrometer (Nicolet, series 800) at a surface temperature of 110 K using a MCT (HgCdTe) detector with a resolution of 4 cm^{-1} . In cases where the crystal was heated to a temperature above 110 K, the crystal was then cooled back to 110 K before spectra were acquired. Specific procedures for data collection are described elsewhere.¹⁵

Sample Preparation. Sample cleaning and preparation procedures are described elsewhere.¹⁶ Briefly, the Mo(110) surface was cleaned by oxidation at 1200 K under 1×10^{-9} mmHg of O_2 for 1 min and subsequently flashed to 2300 K to remove residual oxygen. Substrate cleanliness was verified by Auger electron spectroscopy. A saturated oxygen overlayer ($\theta_{\text{O}} = 0.66$ ML) was prepared by exposing the Mo(110) surface to 1×10^{-9} mmHg of O_2 for 1 min at 110 K, with subsequent heating to 500 K.¹⁷

Reagents. Cyclopropylmethanol ($\text{c-C}_3\text{H}_5\text{-CH}_2\text{-OH}$, 98%), cyclobutanol ($\text{c-C}_4\text{H}_7\text{-OH}$, 95%), and cyclobutyl bromide ($\text{c-C}_4\text{H}_7\text{-Br}$, 96%) were obtained from commercial suppliers, stored in glass bottles, and purified by several freeze–pump–thaw cycles before use. Mass spectrometry was used to confirm reagent purity. Oxygen (O_2 , 99.998%, Matheson) was used as received. For a detailed description of synthesis and purification of 1,1- D_2 -cyclopropylmethanol, see Supporting Information.

Results

2-Buten-1-ol. The “diradical” rearrangement mechanism was tested using 2-buten-1-ol. Following the usual reaction protocol (*vide infra*), 2-buten-1-ol was introduced to O-covered Mo(110) and annealed to yield the corresponding alkoxide (eq 1).



Upon further heating, hydrocarbon elimination took place to form butadiene. This assignment is based on the single, sharp, symmetric peak observed near 400 K in the TPR trace (m/e 54, Figure 1a). The peak shape indicates a single mechanism for C_4 -hydrocarbon formation. The peak temperature differs considerably from the temperature at which C_4 -hydrocarbon evolution is observed from cyclopropylmethanol-treated O-covered Mo(110) (550 K).^{8a}

The RAIR spectrum of 2-buten-1-ol-treated O-covered Mo(110) (not shown) is unambiguously attributable to 2-buten-1-oxide. The RAIR peak assigned to $\nu(\text{C}=\text{C})$ of 2-buten-1-oxide (1674

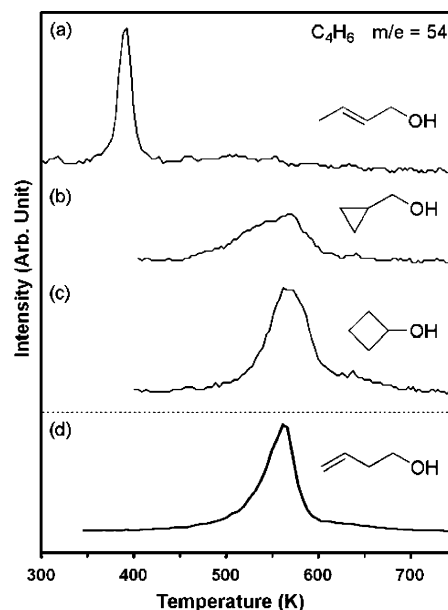


Figure 1. Temperature-programmed reaction (TPR) data comparing the $m/e = 54$ trace for O-covered Mo(110) treated with (a) 2-buten-1-ol, (b) cyclopropylmethanol, (c) cyclobutanol, and (d) 3-buten-1-ol (reproduced from ref 10). The $m/e = 54$ signal corresponds to the parent ion and most intense signal of 1,3-butadiene.

cm^{-1}) is observed at a significantly higher frequency than that assigned to $\nu(\text{C}=\text{C})$ of 3-buten-1-oxide (1644 cm^{-1}). No experimental evidence we have collected suggests that 2-buten-1-oxide is involved in the rearrangement reactions that are the focus of this paper.

Cyclobutanol. The remaining data enable the radical clock versus cationic mechanisms of rearrangement to be differentiated. Experiments involving three well-defined surface species are relevant in this regard: 3-buten-1-oxide, cyclopropylmethoxide, and cyclobutoxide. Cyclobutoxide—the only one of these that has not been previously reported—was prepared according to the usual protocol. First, multilayers of cyclobutanol were condensed onto O-covered Mo(110) at 110 K. Subsequent heating to 350 K led to transfer of H and alkoxide to Mo(110)—(1×6)-O via O–H bond cleavage. This is a general reaction for alcohols on this surface. The newly formed bonds are indicated by the appearance of a sharp $\nu(\text{O–H})$ peak at 3575 cm^{-1} in the RAIR spectrum. This resonance is characteristic of OH adsorbed directly on the metal surface; therefore, it evidences transfer of alcoholic protons to adsorbed oxygen (Figure 2a). All other RAIR peaks can be assigned in terms of the vibrational modes of cyclobutoxide. Of particular importance to the following discussion are the strong resonances at 900, 917, 1048, 1243 (ring- CH_2 scissor), and 2957 cm^{-1} ($\nu(\text{C–H})$). The resonances at 900 and 1048 cm^{-1} are assigned to have a significant component of $\nu(\text{C–O})$. Note that, in this energy range, intramolecular coupling commonly occurs between modes of similar symmetry.¹⁸

The infrared stretching frequencies of gas-phase cyclobutanol, surface-adsorbed cyclobutanol, and surface-bound cyclobutoxide are highly similar in frequency and magnitude (see Supporting Information). Significantly, the RAIR spectrum of cyclobutoxide remains constant following heating to 460 K (Figure 3b).

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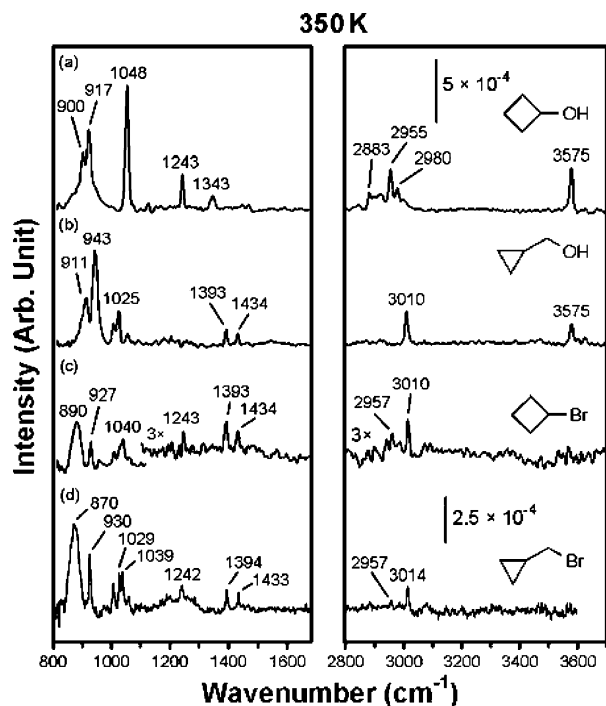


Figure 2. Infrared (RAIR) spectra obtained after condensing multilayers of (a) cyclobutanol, (b) cyclopropylmethanol, (c) cyclobutyl bromide, and (d) cyclopropylmethyl bromide (reproduced from ref 10) onto O-covered Mo(110) and subsequently heating to 350 K. For all compounds, both spectral regions were acquired in a single experiment.

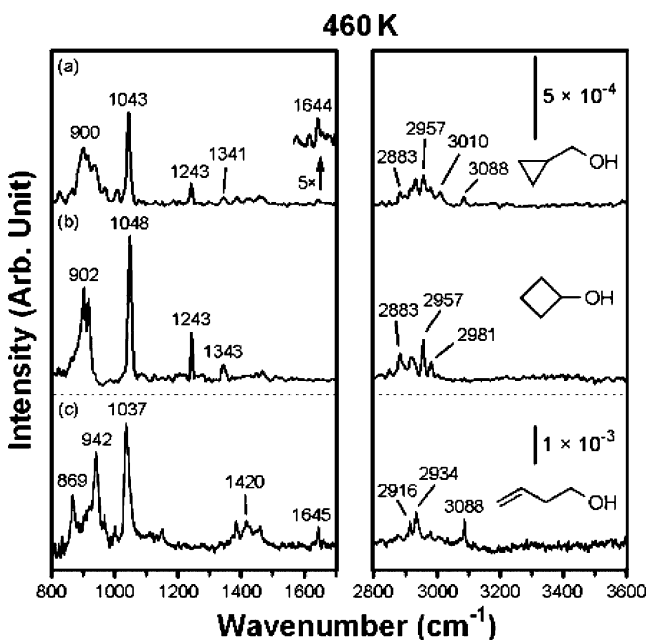


Figure 3. Infrared (RAIR) spectra obtained after condensing multilayers of (a) cyclopropylmethanol, (b) cyclobutanol, and (c) 3-buten-1-ol (reproduced from ref 10) onto O-covered Mo(110) and subsequently heating to 460 K. For all compounds, both spectral regions were acquired in a single experiment.

Together, these data support the conclusion that, from the temperature of alkoxide deposition to the temperature of hydrocarbon elimination, cyclobutanol exists solely as cyclobutoxide on O-covered Mo(110).

TPR data further support a simple interpretation of the surface behavior of cyclobutoxide. The single, sharp, symmetric peak in the m/e 54 TPR trace, which corresponds to butadiene,

provides evidence that cyclobutoxide undergoes heteroatom removal by a single mechanism (Figure 1c).¹⁹ On the basis of MS data alone, is not possible to know whether the primary hydrocarbon product is butadiene or the direct product of β -hydride elimination: cyclobutene.²⁰ At the peak temperature of hydrocarbon extrusion (560 K), cyclobutene readily undergoes exergonic retro-electrocyclization to form butadiene.²¹

Reconsideration of Cyclopropylmethanol. To deconvolute the behavior of surface-bound cyclopropylmethoxide, we will rely on a basis set of characteristic data for cyclobutoxide and 3-buten-1-oxide. Previously published investigations of 3-buten-1-oxide indicate simple surface behavior.^{8a} To briefly summarize, 3-buten-1-ol can be converted to 3-buten-1-oxide on O-covered Mo(110) in the usual way. RAIR absorbances observed after initial annealing (350 K) correlate well with gas-phase FTIR data for 3-buten-1-ol (see Supporting Information). Characteristic resonances of 3-buten-1-oxide relevant to the present discussion are those assigned to $\nu(\text{C}=\text{C})$ at 1645 cm^{-1} and $\nu(\text{=CH}_2)$ at 3089 cm^{-1} (data not shown). The RAIR spectrum of 3-buten-1-oxide remains unchanged upon further heating to 460 K (Figure 3c). The only significant TPR event for 3-buten-1-oxide observed at m/e 54 is a sharp, symmetric peak corresponding to the extrusion of butadiene at a peak temperature near $575\text{ }^\circ\text{C}$ (Figure 1d). Like the case of cyclobutoxide, RAIR and TPR data together show that bond breakage in 3-buten-1-oxide on O-covered Mo(110) is essentially limited to a single process: high-temperature β -hydride elimination.

With a satisfactory basis set in hand, the consideration of cyclopropylmethoxide begins with its synthesis. Our most reliable preparative method calls for adsorption and annealing of cyclopropylmethanol onto O-covered Mo(110). Up to a temperature of 350 K, the only C-containing surface-bound species resulting from alkoxide deposition in this manner is firmly believed to be cyclopropylmethoxide. The RAIR spectrum of cyclopropylmethoxide, which closely resembles the gas-phase FTIR spectrum of cyclopropylmethanol (see Supporting Information), does not significantly overlap with the RAIR spectrum of any other C_4 -alkoxide in our basis set (Figure 2b). Absorbances significant for the sake of this discussion are observed at 1393 and 1434 cm^{-1} (assigned to ring- CH_2 scissor) and at 3010 cm^{-1} (assigned to $\nu(\text{C}-\text{H})$). Below 350 K, no hydrocarbon evolution occurs on cyclopropylmethanol-treated Mo(110) except for molecular layer desorption of $\text{c-C}_3\text{H}_5\text{-CH}_2\text{-OH}$ around 200 K (partial data shown in Figure 1b).

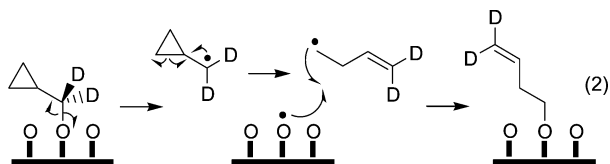
When cyclopropylmethoxide is heated to 460 K, complete skeletal rearrangement takes place. The characteristic RAIR absorbances of cyclopropylmethoxide disappear, and a new set of peaks appears in their place (Figure 3a). We previously

- (19) Like other C_4 -alkoxides, cyclobutoxide can undergo heteroatom removal via minor pathways to form trace amounts of cyclobutane or ethylene. The $\text{C}_4\text{H}_6/\text{C}_4\text{H}_8/\text{C}_2\text{H}_4$ product ratio for cyclopropylmethoxide was estimated to be 60:22:18.^{8a} Compared to this ratio, the products derived from cyclobutoxide seem to be slightly enriched in C_2H_4 (see Supporting Information), whereas the products derived from 3-buten-1-ol are known to be depleted in C_2H_4 .¹⁰ This relationship is consistent with our conclusion that cyclopropylmethoxide is rearranged to a mixture of cyclobutoxide and 3-buten-1-oxide prior to heteroatom removal. Due to limitations of the mass spectral data, a more detailed analysis of hydrocarbon product ratios is not possible. The present discussion will be limited to the major β -hydride elimination pathway of heteroatom removal.
- (20) Butadiene, cyclobutene, and methylenecyclopropane, all of which can produce a m/e 54 signal, have similar m/e 54:53 ratios of 1.3 ± 0.1 , making them indistinguishable in our mass spectrometer.
- (21) (a) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. (b) Carr, R. W., Jr.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.

reported that these new peaks are attributable, in part, to surface-bound 3-buten-1-oxide.^{8a} This claim is borne out by comparison of the appropriate RAIR spectra. Previously, the peaks resulting from cyclopropylmethoxide rearrangement that could not be attributed to 3-buten-1-oxide were assigned to 3-butenylmolybdenum. This assignment was loosely based on literature reports and was not verified by independent synthesis. We now assign the absorbances in question at 900, 1243, and 2957 cm^{-1} to cyclobutoxide. It is readily apparent from side-by-side comparison that the RAIR spectrum of rearranged cyclopropylmethoxide can be described as a linear combination of the individual RAIR spectra of 3-buten-1-oxide and cyclobutoxide (Figure 3).

The TPR data for cyclopropylmethanol-treated O-covered Mo(110) support the same conclusion as that of the RAIR data. A single broad peak in the m/e 54 trace was observed at $T_{\text{max}} = \sim 575$ K (Figure 1b). In general, broad, asymmetric peak shape indicates that more than one pathway is responsible for product formation. Just such a trace would arise from a linear combination of the TPR peaks for 3-buten-1-oxide and cyclobutoxide elimination centered at 550 and 575 K, respectively. Combining newly acquired data with reassigned, previously published data, we conclude that between 350 and 460 K cyclopropylmethoxide on O-covered Mo(110) undergoes quantitative skeletal rearrangement to afford a mixture of cyclobutoxide and 3-buten-1-oxide.

1,1- D_2 -Cyclopropylmethanol. The preparation of D_2 -cyclopropylmethoxide on O-covered Mo(110) was carried out in analogy to the unlabeled case (see Supporting Information). The RAIR spectrum obtained following the thermally induced ring opening of D_2 -cyclopropylmethoxide at 460 K provides little information about the repositioning of labeled hydrogen atoms (Figure 4a). Rearrangement exclusively via radical intermediates would yield 3-buten-1-oxide bearing a $=\text{CD}_2$ group (eq 2).



No such $\nu_a(=\text{CD}_2)$ peak, predicted to appear at ~ 2300 cm^{-1} , was detected.²² In fact, all of the peaks observed in the $\nu(\text{C}-\text{H})$ region for rearranged D_2 -cyclopropylmethoxide were present at approximately the same intensity in the analogous spectrum of unlabeled material (Figure 3a), indicating that no single C-H site was completely substituted by deuterium. In the $\nu(\text{C}-\text{D})$ region, a weak absorbance at 2149 cm^{-1} was intermittently detected above noise; it cannot be reliably assigned to any one labeled C-H position. A signal corresponding to $\nu(\text{C}=\text{CH}_2)$ appears at 1644 cm^{-1} , as in the unlabeled case. This peak is relatively weak, suggesting that at least partial alkene deuteration occurred. Nevertheless, no deuterium-shifted $\nu(\text{C}=\text{C})$ peaks were detectable.²³ Deuterium atoms seem to be nonspecifically redistributed during cyclopropylmethoxide rearrangement.

The only specific piece of structural information that can be derived from RAIR data is the possible presence of deuterium

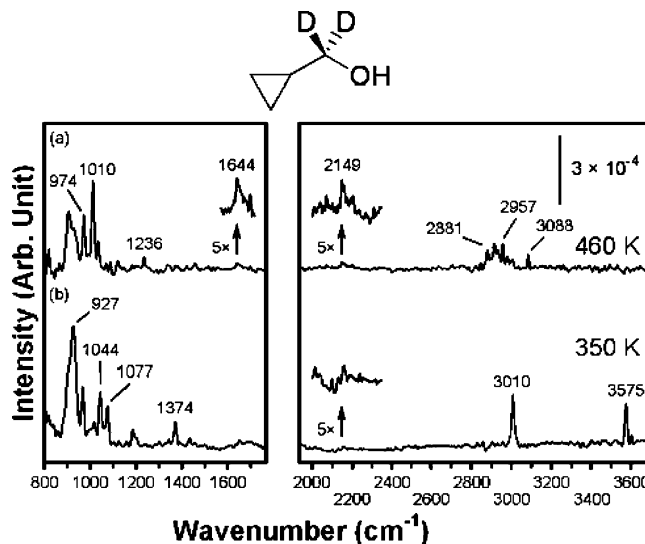


Figure 4. Infrared (RAIR) spectra obtained after exposing O-covered Mo(110) to 1,1- D_2 -cyclopropylmethanol at 110 K with subsequent heating to (a) 460 K and (b) 350 K. The data were collected in a single experiment.

substitution at the alkoxide-carbon position of rearranged products. A strong absorbance band with considerable C-O stretching character is observed at ~ 1040 cm^{-1} for both unlabeled cyclobutoxide and 3-buten-1-oxide (Figure 3). In the spectrum of rearranged D_2 -cyclopropylmethoxide, there are isotope-shifted absorbances apparent at 1010 and 974 cm^{-1} , in addition to a weak unshifted peak at 1040 cm^{-1} . The lower frequency signals presumably indicate the presence of deuterium substitution at the α position ($\text{Mo}-\text{O}-\text{CH}_n$) of cyclobutoxide or 3-buten-1-oxide, though small isotope shifts resulting from β deuteration are known.²⁴ The fact that there are *two* intense isotope-shifted absorbances does not, however, imply that the α positions of both alkoxides are isotopically enriched. The splitting of the $\nu(\text{C}-\text{O})$ signal could be indicative of a reduction in symmetry due to partial deuteration. An analogous splitting has been observed for methoxide on Cu(100).²⁵ In that case, $\nu(\text{C}-\text{O})$ for $\text{Cu}-\text{O}-\text{CH}_3$ appears at 1012 cm^{-1} , while for $\text{Cu}-\text{O}-\text{CHD}_2$, two peaks are observed at 950 and 1017 cm^{-1} . The isotope-shifted peaks were assigned to mixtures of C-O stretching with D-C-O bending and H-C-D bending, respectively. Symmetry reduction can likewise affect the C-O stretch region for more complex alkoxides, such as 2-propoxide on oxidized Mo(110), where there is substantial coupling of $\nu(\text{C}-\text{O})$ with $\nu(\text{C}-\text{C})$ modes.²⁶ Therefore, in the present case, if we choose to make a site-specific interpretation of the RAIR data collected after cyclopropylmethyl rearrangement, then it is as follows: there is either some deuteration at the Mo-O-CH position of cyclobutoxide and at the Mo-O-CH₂ position of 3-buten-1-oxide or just monodeuteration at the latter position. Unfortunately, vibrational data for authentic samples of the suspected α -deuterated alkoxides are unavailable to confirm such an assignment.

(24) For a study on the IR spectra of various isotopomers of cyclobutanol, see: Durig, J. R.; Green, W. H. *Spectrochim. Acta, Part A* **1969**, *25*, 849.

(25) Mudalige, K.; Warren, S.; Trenary, M. *J. Phys. Chem. B* **2000**, *104*, 2448.

(26) The degree of coupling between $\nu(\text{C}-\text{O})$ and $\nu(\text{C}-\text{C})$ modes is affected by the symmetry and the energy (reduced mass) associated with molecular motion. For example, there are two modes with a significant component of $\nu(\text{C}-\text{O})$ for D_0 -2-propoxide at 800 and 910 cm^{-1} and only one at 880 cm^{-1} for the lower symmetry 1,1,1- D_3 -2-propoxide. Computational methods have been used to probe the details of this phenomenon.¹⁸

(22) (a) Silvi, B.; Lambarbe, P.; Perchard, P. *Spectrochim. Acta, Part A* **1973**, *29*, 263. (b) Radziszewski, J. G.; Downing, J. W.; Gudipati, M. S.; Balaji, V.; Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10275.

(23) The signal attributable to $\nu(\text{C}=\text{CD}_2)$, predicted to appear at 1610 cm^{-1} , may be below our detection limit.²²

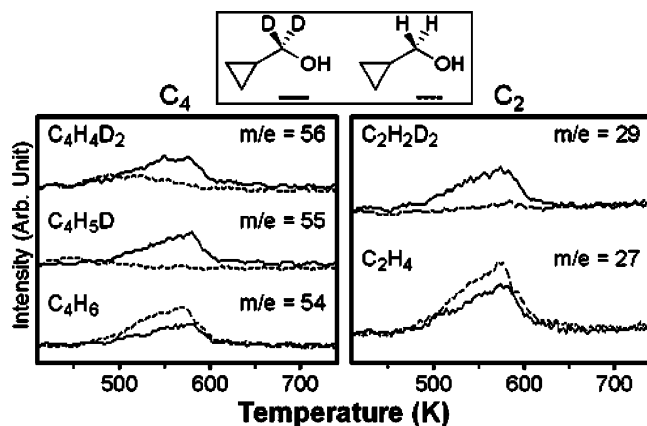


Figure 5. TPR data for various C_4 - and C_2 -hydrocarbons produced after exposing O-covered Mo(110) to cyclopropylmethanol (dashed lines) or 1,1- D_2 -cyclopropylmethanol (solid lines).

The TPR data traces of C_4 -hydrocarbons are essentially the same for labeled and unlabeled cyclopropylmethoxide. They both exhibit broad asymmetric peaks spanning from 500 to 600 K (Figure 5).²⁷ The isotopic composition of D_2 -cyclopropylmethoxide's oxygen-atom-removal products reveals the formation of both D_2 - and D_1 -hydrocarbons. The intense parent ion mass of D_2 -butadiene was detected at m/e 56. Evidence for a significant amount of D_1 -butadiene evolution comes from the measured 1:1 ratio of 56 and m/e 55 signals. Although some of the m/e 55 signal is due to the fragmentation of D_2 -butadiene (by H loss), fragmentation alone cannot account for all of the m/e 55 signal arising from reactions of D_2 -cyclopropylmethoxide.²⁸ A significant TPR peak between 500 and 600 K at m/e 29 is attributable to D_2 -ethylene, mostly derived from fragmentation of D_2 -butadiene (Figure 5). Temperature-programmed reaction data suggest, as the RAIR data do, that nonspecific scrambling of labeled hydrogen takes place during cyclopropylmethoxide rearrangement.

Cyclobutyl, Cyclopropylmethyl, and 3-Butenyl Bromides.

In addition to alcohols, alkyl bromides can provide convenient access to surface-bound alkoxides on O-covered Mo(110).¹⁰ Like alcohols, alkyl bromides are introduced to the surface by multilayer adsorption at 110 K. Following annealing to ~ 250 K, C–Br bond cleavage occurs concomitantly with some molecular layer desorption. Surface molybdenum alkoxides and MoBr are formed via reaction with free Mo–O and Mo sites, respectively. Further heating of the resulting alkoxide-covered surface leads to rearrangement and oxygen-atom-removal reactions identical to those observed for alcohol-treated O-covered Mo(110). Thus, the reactions of alkyl bromides, because they can provide access to the same intermediates as those of reactions of alcohols, provide a check for our surface reactivity models.

On the basis of new results and a reevaluation of previously published work, we now wish to report an additional, heretofore unrecognized, level of complexity inherent to the study of alkyl bromides on O-covered Mo(110). There is evidence for carbon

skeletal rearrangements during C–Br bond cleavage/C–O bond formation, which occurs at a relatively low temperature. Among the three relevant C_4 -bromides, cyclobutyl bromide is the only one whose reactivity has not been previously described. Following the usual adsorption protocol, O-covered Mo(110) was treated with cyclobutyl bromide and annealed to 350 K. The RAIR spectrum of the resulting surface revealed our previous model of alkoxide formation via S_N2 -like displacement to be unsatisfactory (Figure 2c). Whereas we expected to observe an absorbance pattern uniquely indicative of Mo–O– c - C_4H_7 , in fact, the RAIR spectrum collected under these conditions is consistent with a mixture of Mo–O– CH_2 - c - C_3H_5 and Mo–O– c - C_4H_7 . There are peaks corresponding to the cyclopropylmethoxide ring- CH_2 scissor at 1434 and 1393 cm^{-1} and $\nu(C-H)$ at 3010 cm^{-1} . Peaks corresponding to cyclobutoxide $\nu(C-C-O)$ at 1040 cm^{-1} , ring- CH_2 scissor at 1243 cm^{-1} , and $\nu(C-H)$ at 2957 cm^{-1} comprise the remainder of the assignable spectrum. No characteristic absorbances of Mo–O– CH_2 - c - C_3H_5 or Mo–O– c - C_4H_7 are absent, and no additional peaks rise above noise outside of the $\nu(C-O)$ region.²⁹ These data indicate that, during annealing to 350 K, cyclobutyl bromide reacts with Mo(110)-(1 \times 6)-O to form a mixture of cyclobutoxide and cyclopropylmethoxide. Reevaluating the RAIR spectrum obtained from the reaction of cyclopropylmethyl bromide under the same conditions (Figure 2d) leads to the same assignment; the spectra are identical. Cyclobutoxide is formed during the reaction of cyclopropylmethyl bromide with Mo(110)-(1 \times 6)-O. This information supports our new proposal that both bromides pass through a common cationic intermediate during alkoxide deposition.

At higher annealing temperatures, our previous assertion, namely, that alkoxides on Mo(110) rearrange in a manner that does not depend on whether they were originally derived from alcohols or alkyl bromides, holds true. The mixture of Mo-alkoxides resulting from cyclobutyl bromide condensation, when heated to 460 K, affords the expected mixture of metal-bound 3-buten-1-oxide and cyclobutoxide (Figure 6a). The relevant RAIR spectrum can be deconvoluted in the same manner as described earlier for the cyclopropylmethanol case. Figure 6 shows the convergent nature of cationic surface rearrangements. Following heating to 460 K, surfaces treated with cyclopropylmethanol, cyclobutyl bromide, cyclopropylmethyl bromide, and 3-butenyl bromide all produce highly similar RAIR spectra.³⁰ It is especially significant that the 3-butenyl bromide-derived spectrum includes peaks assignable to cyclobutoxide. Because Mo–O– $CH_2CH_2CH=CH_2$ does not undergo rearrangement prior to heteroatom removal, this observation indicates that, like the other bromides, 3-butenyl bromide undergoes cationic skeletal rearrangement to give cyclic alkoxides during C–Br cleavage/C–O bond formation.

TPR data support the conclusions drawn from RAIR data. If surfaces treated with cyclopropylmethanol, cyclobutyl bromide, cyclopropylmethyl bromide, and 3-buten-1-yl bromide all give mixtures of Mo–O– $CH_2CH_2CH=CH_2$ and Mo–O– c - C_4H_7 after rearrangement of Mo–O– CH_2 - c - C_3H_5 at 460 K, then TPR data above 460 K should be similar in all of those cases.

(27) Given precise TPR data, it should be technically possible to measure a kinetic isotope effect for heteroatom removal based on relative peak temperatures for butadiene evolution. Any isotope effect manifest in the present data falls within the experimental error of the technique.

(28) The m/e 56:55 ratio for the pure D_2 -hydrocarbons is predicted to be $\sim 2:1$. This estimate is based on the m/e 54:53 ratio of 1.3:1 measured from the reaction of unlabeled cyclopropylmethanol and a statistical correction for the hydrogen masses in $C_4H_4D_2$.

(29) For a comparison of the $\nu(C-O)$ regions of RAIR spectra of C_4 -alkoxides generated from cyclobutyl bromide (and various other precursors), see Supporting Information.

(30) For a discussion of the low significance ascribed to spectral differences in the $\nu(C-O)$ region between 800 and 1000 cm^{-1} , see the Supporting Information discussion of cyclobutyl bromide.

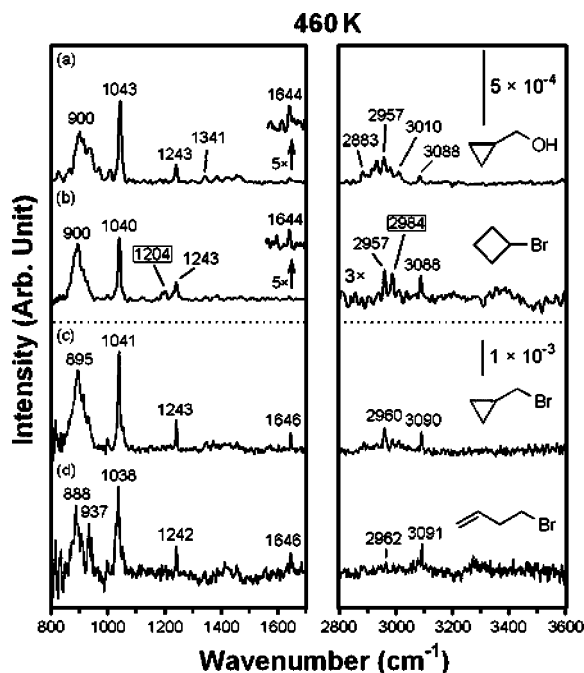


Figure 6. Infrared (RAIR) spectra obtained after condensing multilayers of (a) cyclopropylmethanol, (b) cyclobutyl bromide, (c) cyclopropylmethyl bromide (reproduced from ref 10), and (d) 3-butenyl bromide (reproduced from ref 10) onto O-covered Mo(110) and subsequently heating to 460 K. For all compounds, both spectral regions were acquired in a single experiment. For a discussion of the boxed resonances in spectrum (b), see the Supporting Information discussion of surface metal alkyls.

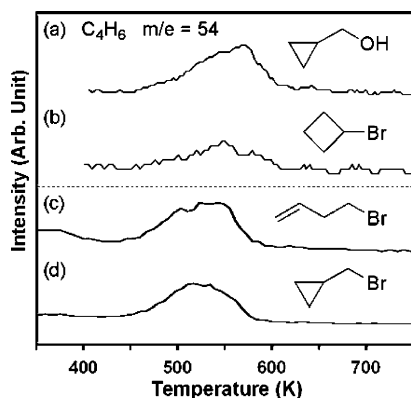


Figure 7. TPR data comparing the $m/e = 54$ trace for O-covered Mo(110) treated with (a) cyclopropylmethanol, (b) cyclobutyl bromide, (c) 3-butenyl bromide (reproduced from ref 10), and (d) cyclopropylmethyl bromide (reproduced from ref 10). The $m/e = 54$ signal corresponds to the parent ion and most intense signal of 1,3-butadiene.

Indeed, all four compounds exhibit one broad asymmetric peak near 550 K in the $m/e = 54$ trace (Figure 7). This peak shape is believed to result from overlap of the two peaks corresponding to butadiene elimination from the two different alkoxides. The slight low-temperature shift of the butadiene peak in the TPR traces produced by 3-butenyl bromide and cyclopropylmethyl bromide is ascribed to systematic instrumental error. The two pairs of compounds were studied during different experimental intervals.

Surface-Bound Metal Alkyls. In the past, we were prevented from recognizing the prevalence of near-surface cationic rearrangements largely by a single misassignment. Infrared absorbances that are now known to be indicative of cyclobutoxide were incorrectly assigned, based on limited evidence,

to vibrational modes of metal alkyls (e.g., $\text{Mo}-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$). Metal alkyls are known to be formed from the reaction of alkyl halides with clean metal surfaces, presumably via radical intermediates.⁷ While we indeed once observed the formation of Mo-alkyls from the reaction of cyclopropylmethyl bromide with clean Mo(110), metal alkyls have never been fully characterized on O-covered Mo(110).³¹

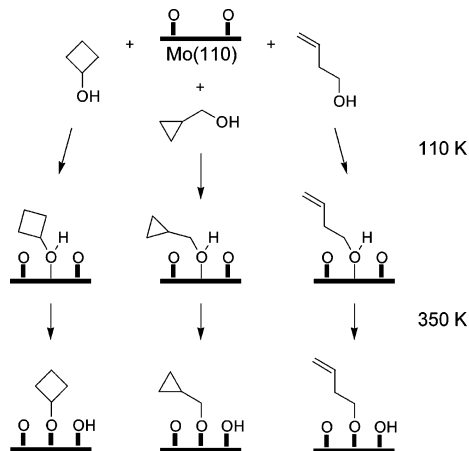
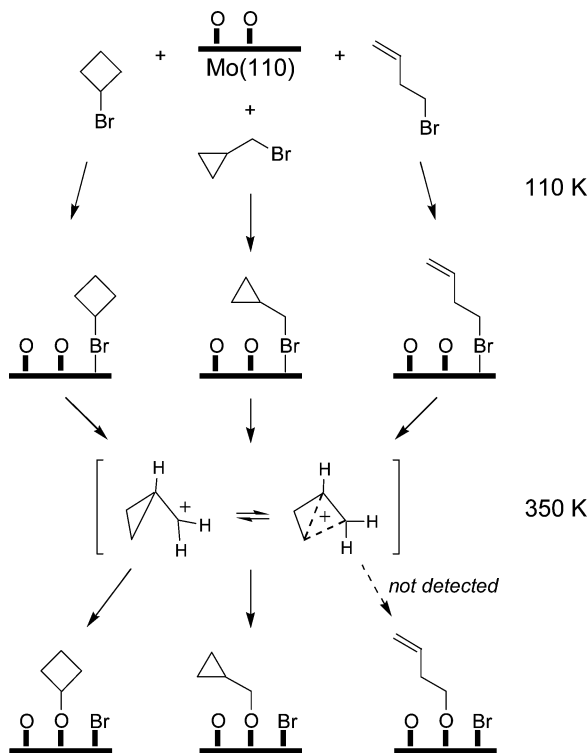
Unfortunately, TPR data cannot be used to verify the possible existence of metal alkyls because on Mo(110) such moieties do not undergo Mo–C or C–C bond cleavage to release hydrocarbons; they decompose nonselectively at high temperatures to give H_2 , CO, and C.⁶ This is in contrast to soluble metal complexes, whose $\text{M}-\text{CH}_2-\text{c}-\text{C}_3\text{H}_5$ groups are often subject to M–C bond homolysis and alkyl rearrangement.³² There is some circumstantial evidence, particularly from infrared data, that small amounts of metal alkyls are generated by the reaction of alkyl bromides with O-covered Mo(110). For a detailed account of this evidence, see Supporting Information. Owing to their minute abundance and inertness, metal alkyls and their chemistry make such small contributions to the present experiments as to be omitted from the following discussion.

Discussion

Diradical Rearrangements. We investigated 2-buten-1-ol as a test for the diradical mechanism of cyclopropylmethoxide rearrangement (Scheme 2). At the outset of this work, there was existing strong evidence against the diradical mechanism because it predicts the formation of 2-buten-1-oxide. Extensive similarities between the RAIR spectrum of rearranged cyclopropylmethoxide and that of independently prepared 3-buten-1-oxide prompted us to conclude with confidence that the major product of rearrangement was buten-1-oxide bearing a terminal double bond. Nevertheless, well-supported computational studies compelled us to reinforce our body of evidence in this regard. Surface-bound 2-buten-1-oxide exhibits a relatively low-temperature TPR peak for butadiene formation (~ 400 K), consistent with facile cleavage of its allylic $\beta\text{-C}-\text{H}$ bonds (Figure 1a). If 2-buten-1-oxide were produced at all during the ring-opening rearrangement of cyclopropylmethoxide, which takes place between 350 and 460 K, then a TPR peak corresponding to rapid elimination of butadiene would be expected in that temperature range. The diradical mechanism is ruled out based on the fact that cyclopropylmethoxide undergoes complete rearrangement without hydrocarbon extrusion until the interval of 500–650 K (Figure 1b). Mismatch between the RAIR spectrum of 2-buten-1-oxide (not shown) and that of rearranged cyclopropylmethoxide further confirms our assertion.

Cationic Rearrangements During Alkoxide Deposition. The alkoxides that are the subject of this study were prepared on O-covered Mo(110) by two methods. The first method, starting from alcohols, reliably gives Mo-alkoxides directly by O–H bond scission. Cyclopropylmethoxide, cyclobutoxide, and 3-buten-1-oxide were prepared cleanly in this manner (Scheme 3).

- (31) Following the reaction of cyclopropylmethyl bromide with clean Mo(110), the appearance of a RAIR signal at 1640 cm^{-1} , assigned to $\nu(\text{C}=\text{CH}_2)$, was taken as evidence of 3-butenyl-molybdenum. This species is believed to be formed by surface-capture of a rearranged 3-butenyl radical.⁶
- (32) Some representative examples: (a) Ti(III): Lehmkuhl, H.; Fustero, S. *Liebigs Ann. Chem.* **1980**, 1361. (b) Co(III): Atkins, M. P.; Golding, B. T.; Sellars, P. J. *J. Chem. Soc., Chem. Comm.* **1978**, 954. (c) Fe(II): Pannell, K. H.; Kapoor, R. N.; Wells, M.; Giasolli, T.; Parkanyi, L. *Organometallics* **1987**, 6, 663.

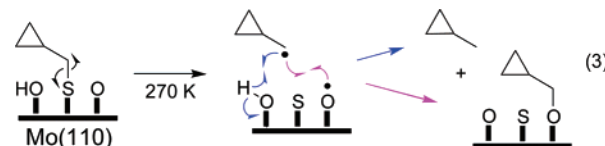
Scheme 3. Alkoxide Deposition on O-Covered Mo(110) from Alcohols via O–H Bond Scission**Scheme 4.** Alkoxide Deposition on O-Covered Mo(110) from Alkyl Bromides via Cation Transfer

The second method, starting from alkyl bromides, has proven to be more complicated. Previously, we suggested that alkoxides are formed from surface-adsorbed alkyl bromides via radical transfer to Mo(110)–(1 × 6)–O. We also considered a concerted substitution mechanism mediated by surface Mo–O.³³ On the basis of present evidence, though, we now believe that surface substitution of alkyl bromides takes place primarily via heterolytic C–Br bond cleavage and then subsequent capture of near-surface carbocations by Mo(110)–(1 × 6)–O (Scheme 4). Evidence for cationic intermediates is provided by our observation that both cyclopropylmethyl and cyclobutyl bromides undergo alkyl transfer with partial rearrangement to give mixtures of cyclopropylmethoxide and cyclobutoxide after

(33) A surface-mediated mechanism for high-temperature cyclopropylmethoxide rearrangement on O-covered Mo(110) was previously ruled out using cyclopropylethanol.^{8a}

annealing to 220 K. Because, in pure form, both alkoxides are stable below 350 K, rearrangement must occur during substitution. Cationic intermediates are uniquely implicated by the cyclopropylmethyl/cyclobutyl interconversion reaction; radical intermediates are not known to rearrange in this manner.

Conceivably, radical intermediates could participate in the oxide substitution of alkyl bromides if they were recaptured without rearrangement. There is precedent for such a rapid radical release and recapture in a related system. Slightly above the temperature at which bromide substitution takes place (270 vs 220 K), cyclopropylmethane thiolate on O-covered Mo(110) undergoes alkyl transfer from Mo–S to Mo–O without isomerization (eq 3).^{34,35}



This reaction is believed to proceed via radical intermediates based on comparison to the behavior of cyclopropylmethane and other thiolates on clean Mo(110).^{6,36} Thus, we cannot rule out the possibility that transient radicals play a role in the oxide substitution of alkyl bromides on Mo(110). It is noteworthy that in neither the bromide nor the thiolate case are products of radical ring opening observed (i.e., Mo–O–CH₂CH₂CH=CH₂). Radical substitution must occur very rapidly indeed to exceed the speed of cyclopropylmethyl rearrangement ($k_{\text{gas phase}}(200 \text{ K}) = 2.5 \times 10^6 \text{ s}^{-1}$).^{2b}

The lack of detectable Mo–O–CH₂CH₂CH=CH₂ following the reaction of cyclopropylmethyl and cyclobutyl bromides with Mo(110)–(1 × 6)–O merits comment in the context of the proposed cationic rearrangement mechanism. In solution phase and gas phase, when cyclopropylmethyl cations are generated transiently in the presence of some trapping agent, product mixtures typically include 3-butenyl-type products in addition to cyclopropylmethyl and cyclobutyl products.⁴ In all cases, 3-butenyl products are the least abundant, but they are usually detectable. It may be that, in our system, the minor pathway to 3-buten-1-oxide is completely blocked by unique surface effects. Alternatively, butenyl products may simply be formed in quantities below our detection threshold.

We can observe the reverse of the 3-buten-1-oxide-forming reaction, namely, the ring closure of a 3-butenyl cation.³⁷ When adsorbed multilayers of 3-butenyl bromide are annealed to ~250 K on O-covered Mo(110), substitution occurs to give a product mixture including cyclic C₄-alkoxides.³⁸ The ring closure

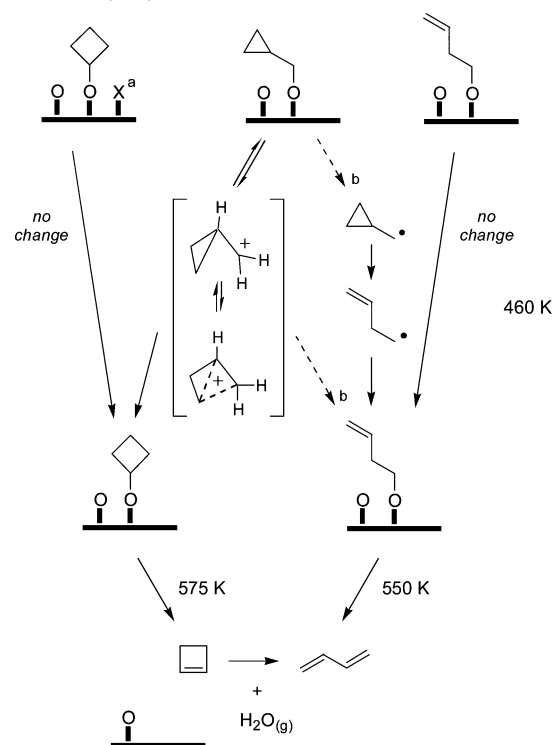
(34) Kretzschmar, I.; Friend, C. M.; Sigman, M. E. *J. Phys. Chem. B* **2002**, *106*, 663.

(35) Unlike the bromide substitution reaction, the thiolate reaction occurs with partial loss of methylcyclopropane because Mo–OH groups left behind during the thiolate deposition process function as a source of H•. The formation of methylcyclopropane in the alkyl bromide substitution reaction does not occur because there are no reducing moieties present on O-covered Mo(110) during the reaction.

(36) On clean Mo(110), there is a strong correlation between Mo–S bond strength and reactivity among thiolates, indicating that homolytic bond cleavage and radical intermediates are involved in the observed surface chemistry.

(37) Attempts to observe this reaction in solution under stable ion conditions failed, apparently due to complexation of the ethylenic bond by SbF₅, thereby making ionizations difficult and allowing side reactions. Lin, C. H. Ph.D. Dissertation, Case Western Reserve University, Cleveland, Ohio, 1969.

(38) Data are not available to further define the composition of this mixture.

Scheme 5. Rearrangements of Cyclopropylmethoxide on O-Covered Mo(110)

^a Reactions of surface X = OH/Br introduced during alkoxide deposition are omitted for simplicity. ^b Neither cationic nor radical mechanisms can be ruled out for the formation of 3-buten-1-oxide from cyclopropylmethoxide.

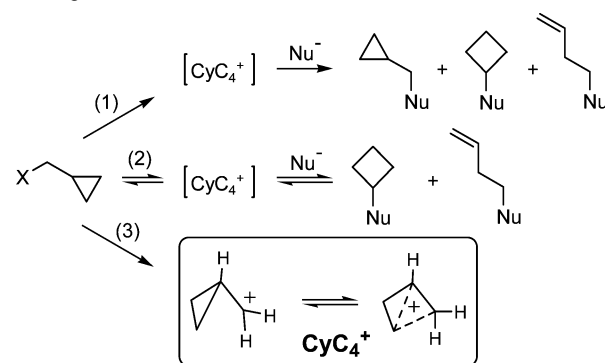
reaction strongly implicates a cationic-type rearrangement during alkoxide deposition.³⁹ Given alkyl bromide's apparent propensity for cationic rearrangements during annealing, we now proceed with caution when introducing hydrocarbyl groups to O-covered surfaces using this substrate class.

Cationic Rearrangements of Cyclopropylmethoxide. The high-temperature (~400 K) carbon skeletal rearrangement of cyclopropylmethoxide on O-covered Mo(110) prompted our original publication on the possibility of near-surface radical clocks. This reaction is amenable to detailed study because it occurs cleanly and completely; cyclopropylmethoxide is converted to a mixture of alkoxide products without significant unselective decomposition or detectable hydrocarbon loss (Scheme 5). In contrast to the behavior of most soluble metal alkoxides, C–O bond cleavage occurs preferentially over M–O bond cleavage.⁴⁰

Reasoning similar to that presented above for the bromide's case can be used to argue that cationic intermediates are involved in the high-temperature rearrangement of cyclopropylmethoxide. Confident analysis of product mixtures is now possible because we have unambiguously prepared authentic samples of 3-buten-1-oxide and cyclobutoxide on O-covered Mo(110). Unlike cyclopropylmethoxide, these two alkoxides do not undergo any

(39) Formation of a cyclic C₄-alkoxide, specifically cyclopropylmethoxide, via homolytic C–Br cleavage of 3-butenylbromide, followed by radical ring closure and surface capture is highly unlikely because of the strong thermodynamic preference for the ring-opened radical. Furthermore, as in the gas phase, radical recombination reactions with surfaces are presumed to be nearly barrierless; therefore, a kinetic preference for cyclopropylmethyl radical recapture over 3-butenyl radical recapture is considered to be quite unlikely, in addition to being completely unprecedented.

(40) The chemistry of the C–O bond in alkoxide ligands of transition-metal complexes has been reviewed. Mayer, J. M. *Polyhedron* **1995**, *14*, 3273.

Scheme 6. Solution-Phase Cationic Cyclopropylmethyl Rearrangements

carbon skeletal rearrangement prior to heteroatom removal at >500 K. Their spectroscopic properties are strong and distinctive. The products of cyclopropylmethoxide rearrangement are, thus in every way, describable as a mixture of 3-buten-1-oxide and cyclobutoxide. As in the alkyl bromide case discussed earlier in this paper, the presence of cyclobutyl products indicates that cationic rearrangements make a significant contribution to the observed reaction.

The Cyclic C₄H₇ Cation. Having established, for the first time, that cations with the empirical formula C₄H₇⁺ are formed in certain heterogeneous organic rearrangements, it is appropriate to consider what is known about the cyclic C₄H₇ cation (CyC₄⁺). Thereby, we can gauge the extent to which CyC₄⁺ is perturbed by proximity to a conducting Mo surface. The study of CyC₄⁺ over the last 50+ years has been reviewed thoroughly.⁴ In solution-phase experiments, CyC₄⁺ is typically generated from a labile cyclopropylmethyl precursor (a chloride, sulfonate, etc.) under one of three sets of conditions (Scheme 6): (1) in the presence of a kinetic nucleophilic trap, (2) in the presence of a reversible nucleophilic trap, or (3) under long-lived stable ion conditions. Under condition (1), CyC₄⁺ is rapidly trapped to form a mixture of cyclopropylmethyl, cyclobutyl, and 3-buten-1-yl products.^{3,41} The product distribution depends on experimental conditions, but 3-buten-1-yl products are always the least abundant. Under condition (2), best exemplified by the acid-promoted rearrangement of aqueous cyclopropylmethanol, the distribution of products is determined by relative thermodynamic stability.⁴² In fact, treatment of cyclopropylmethanol with dilute HCl is the preferred method for preparing nearly pure cyclobutanol.^{43,44} Under condition (3), popularized by Olah and co-workers, superacid media allow carbocations to persist long enough for complete structural characterization.⁴⁵

At low temperatures, CyC₄⁺ exists as an equilibrium between nonclassical bicyclobutonium and πσ-delocalized bisecting cyclopropylcarbinyl cations, regardless of the C₄H₇X precursor used (Scheme 6).⁴⁶ Computational and experimental studies have established that these two nearly isoenergetic cations interconvert rapidly.^{47,48} Due to solvation effects, when CyC₄⁺ is generated transiently in the presence of a kinetic nucleophilic trap

(41) Moss, R. A.; Shulman, F. C.; Emery, E. *J. Am. Chem. Soc.* **1968**, *90*, 2731.

(42) Caserio, M. C.; Graham, W. H.; Roberts, J. D. *Tetrahedron* **1960**, *11*, 171.

(43) The major contaminant is <5% 3-buten-1-ol.

(44) (a) Krumpolc, M.; Rocek, J. *Org. Synth.* **1981**, *60*, 20. (b) Salatin, J.; Fadel, A. *Org. Synth.* **1985**, *64*, 50.

(45) (a) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69.

(b) Prakash, G. K. S. *J. Org. Chem.* **2006**, *71*, 3661.

(46) Olah, G. A.; Jeuell, C. L.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 146.

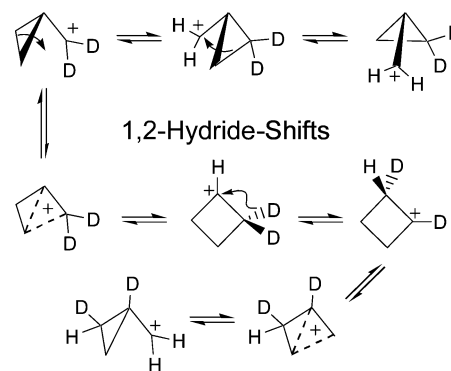
(condition (1)), averaged symmetry cannot be completely attained. Nevertheless, the formulation of CyC_4^+ produced under long-lived stable ion conditions is generally useful.⁴⁹

In contrast to the breadth of solution-phase work summarized in this paper, relatively few experiments have been done to characterize CyC_4^+ in the gas phase. Workers at Argonne National Laboratories first proved its existence by monitoring the nuclear decay of $c\text{-C}_4\text{H}_7\text{T}$.⁵⁰ More recently, Crestoni and co-workers were able to generate CyC_4^+ from the gas-phase reaction of strong Brønsted acids with cyclopropylmethyl and cyclobutyl alcohols.⁵¹ Using nucleophilic trapping techniques that apparently operate on the order of $\leq 10^{-10}$ s, these reactions led to identical product distributions ($\sim 50:42:8$ cyclopropylmethyl/cyclobutyl/3-buten-1-yl). The authors interpreted this result as support for the rapid equilibration of cations derived from different $\text{C}_4\text{H}_7\text{X}$ precursors to a single CyC_4^+ form, perhaps one consistent with Olah and co-workers' structural formulation.

Results of a more recent study contrast with those of Crestoni and co-workers. Gross and co-workers studied cations generated in the gas phase by ionization of $\text{C}_4\text{H}_7\text{Cl}$ in a high-pressure chemical ionization source.⁵² This technique, in which carbocations are produced by $\text{X}\cdot$ loss from an initially formed radical cation, provided early evidence for the existence of gas-phase CyC_4^+ .⁵³ In Gross and co-workers' contribution, nucleophilic trapping of cations produced from cyclobutyl, cyclopropylmethyl, and 3-buten-1-yl chlorides led to different product distributions. The authors thus conclude that the time frame for attainment of an equilibrium CyC_4^+ structure in the gas phase is actually much longer than previously suggested. This apparent reactivity difference may indicate that the two sets of gas-phase experiments are interrogating different internal energy regimes. At the time of this writing, no definitive reconciliation of the claims made by Gross and Crestoni has appeared.

Carbocation Lifetimes near O-Covered Mo(110). We would like to compare our present work to appropriate existing literature; however, being the first study of cations under high vacuum near a metal surface, we have, so far, been unable to locate anything directly comparable to it. A priori, cations produced in the vicinity of a conducting metal surface should experience strongly perturbed dynamics and lifetimes compared to those of the free gas-phase cations as a result of Coulombic attraction to negative "image charge" on the surface. In our hands, the substitutions of various C_4 -alkyl bromides with Mo(110)-(1 \times 6)-O led to qualitatively identical alkoxide product mixtures. This observation suggests that the cations generated during substitution are sufficiently long-lived to reach an equilibrium CyC_4^+ structure prior to nucleophilic trapping. Using the most conservative interpretation of gas-phase studies

Scheme 7. Examples of Rearrangement Reactions of CyC_4^+ Methylene Carbon Scrambling



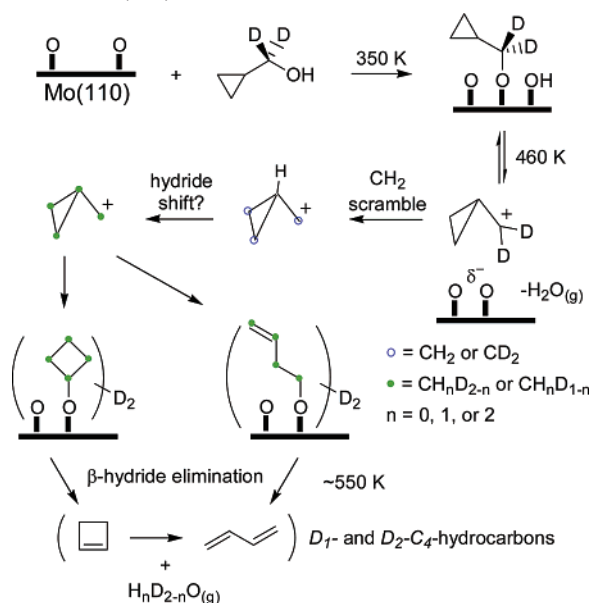
cited above, we, therefore, place a lower bound of 10^{-10} s on the lifetime of free carbocations during bromide substitution, though the true lifetime is likely to be longer than that.

The cationic rearrangement of cyclopropylmethoxide that occurs at higher temperatures (~ 400 K), on the other hand, is distinct from previous gas-phase experiments because nucleophilic trapping can occur reversibly (Scheme 5). The observed reaction compares most favorably with the analogous solution-phase condition (2), shown in Scheme 6. In both cases, heterolytic cleavage of the labile cyclopropylmethyl-X bond can continue repeatedly until starting materials are completely converted into a mixture of cyclobutyl and 3-buten-1-yl products.

Isotope Tracer Experiment. A deuterium-labeling experiment was carried out to further probe the lifetime of CyC_4^+ during cyclopropylmethoxide rearrangement on O-covered Mo(110). In the past, leaps have been made in the understanding of CyC_4^+ rearrangement through isotopic-labeling studies. Two types of isomerization processes with differing relative rates have been detected (Scheme 7), methylene carbon scrambling (faster) and 1,2-hydride shifts (slower). Under solution-phase condition (1), Sunko and co-workers observed nucleophilic trapping to be so rapid that product distributions (cyclopropylmethyl/cyclobutyl/3-buten-1-yl products) exhibited a "memory effect" of the precursor used to generate CyC_4^+ .⁵⁴ As expected, only partial scrambling of isotopically labeled methylene carbons was observed, and there was no scrambling whatsoever at the methine position. Solution reaction condition (2), which resembles the present system, would seem to facilitate longer cation lifetimes. Indeed, the methylene positions of deuterium-labeled cyclobutanol are completely scrambled under aqueous acidic conditions by repeated degenerate ionization/recapture events.⁵⁵ There is no apparent increase in the lifetime of CyC_4^+ during each ionization event, however, because methine scrambling is still not observed. Only "stable ion" solution condition (3) allows CyC_4^+ to persist long enough to undergo isotopic scrambling between methylene and methine positions via hydride shifts.⁵⁶

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- (56) Using NMR line-width analysis, an upper bound for the rate constant corresponding to methine scrambling (hydride migration) was determined in superacid media at -61 °C ($k < 65$ s $^{-1}$). Staral, J. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8018.

Scheme 8. Cationic Rearrangements of 1,1- D_2 -Cyclopropoxide on O-Covered Mo(110)

Interestingly, the rearrangement of 1,1- D_2 -cyclopropylmethoxide on O-covered Mo(110) produces a mixture of cyclobutyl and 3-buten-1-yl products with apparently random isotopic distribution (Scheme 8). Methylene carbon scrambling accounts for the migration of CD_2 away from the alkoxide α position. The C–C bond interconversions alone, however, cannot account for isotopic exchange into CH groups or for the formation of CHD groups. RAIR data provide some evidence for the formation of cyclobutoxide and/or 3-buten-1-oxide groups with exactly one deuterium atom bonded to the alkoxide α position. Hydride shifts would account for these products.

Computational studies suggest that 1,2-H shifts in CyC_4^+ occur via transient planar cyclobutyl cations (Scheme 7).^{47c} As in solution- and gas-phase experiments, we found no evidence for longer-range hydride migrations.⁵⁷ From our isotopic-labeling studies, it is tempting to conclude that CyC_4^+ generated near O-covered Mo(110) is a relatively long-lived species that behaves much as it does in other media. Unfortunately, given the present ambiguous characterization of CyC_4^+ in the gas phase, it is not possible to interpret our findings more rigorously.

Radical Mechanism. Despite a preponderance of evidence for cationic intermediates in the rearrangement of cyclopropylmethoxide at elevated temperatures, we cannot completely rule out some rearrangement via the radical clock mechanism. Hypothetically, if a significant amount of rearrangement did occur via homolytic bond cleavage, preferential formation of 3-buten-1-oxide (and $\text{Mo}-\text{CH}_2\text{CH}_2\text{CH}=\text{CD}_2$, in the selectively deuterated case) would be observed, relative to an exclusively cationic rearrangement reaction. Unfortunately, unlike solution-phase IR data, RAIR data cannot be readily calibrated for quantification (i.e., via a Beer's Law plot); therefore, 3-buten-1-oxide/cyclobutoxide ratios cannot be measured.

(57) Allylic alkoxides on O-covered Mo(110) undergo hydrocarbon elimination near 350 K. Because no free hydrocarbons were detected during cyclopropylmethoxide rearrangement, we conclude that long-range hydride shifts to give allylic products are not energetically accessible to CyC_4^+ near O-covered Mo(110). For our study of 2-buten-1-ol, *vide supra*; for work on 2-propen-1-ol, see: Deiner, L. J.; Serafin, J. G.; Friend, C. M.; Weller, S. G.; Levinson, J. A.; Palmer, R. E. *J. Am. Chem. Soc.* **2003**, *125*, 13252.

A priori, a cationic mechanism is more consistent with the observation that no hydrocarbon release takes place during carbon skeletal rearrangement. A cation formed in the vicinity of a metallic surface will experience a strong attraction to its image charge. Opposite charges would, thus, remain nearby one another, enabling facile bond re-formation following rearrangement. On the other hand, near-surface radicals are much more weakly stabilized by Coulombic and dispersion forces. It is difficult to understand, especially at the high temperatures involved (~ 400 K), how radicals could be retained in the vicinity of O-covered Mo(110) effectively enough to be completely rearranged and recaptured by surface oxygen. On clean Mo(110), at such temperatures, cyclopropylmethoxide is reduced to methylcyclopropane.³⁴ Nevertheless, absent of more detailed quantitative data concerning the composition of rearrangement product mixtures on O-covered Mo(110), we have no compelling reason to rule out contributions from a radical clock mechanism.

Our original report of cyclopropylmethoxide rearrangement on O-covered Mo(110) was an attempt to use well-established information about radical clock reactions to bracket the absolute rates of surface reactions. Because none of the observed rearrangements can be assigned to a single mechanism on the basis of the present data, comparisons to absolute rate constants cannot be made.

Conclusion

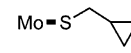
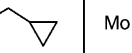

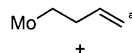

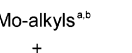

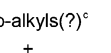

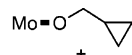
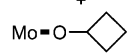
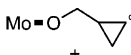

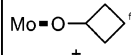
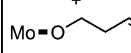
In this report, we have described two examples of unexpected near-surface cationic rearrangements, whereas no previous work in the Friend laboratory was ever interpreted to support cationic reaction mechanisms. In light of this remarkable set of circumstances, we performed a thorough reanalysis of past results obtained on Mo(110). All previously published analyses, apart from those specifically mentioned in the Discussion, withstood this scrutiny. We now have in hand a sufficient body of work on cyclopropylmethyl surface reactions from which to draw conclusions about the factors governing mechanistic selectivity.

We have tested three main substrates—cyclopropylmethyl mercaptan, alcohol, and bromide—on two principle surfaces, clean and O-covered Mo(110). The reaction temperatures, products, and proposed mechanisms are presented in Table 1. The formation of methylcyclopropane is characteristic of reactions believed to proceed via radical intermediates, whereas the formation of cyclobutoxide is characteristic of reactions believed to proceed via cationic intermediates. Compared to those of transient radicals, which in several cases react rapidly without rearrangement, transient cations seem to have relatively long lifetimes. They are sufficiently long-lived to undergo extensive rearrangement prior to being recaptured by Mo(110)—(1 \times 6)-O, even at high temperatures. This observed tolerance for prolonged ionization in heterolytic reactions is consistent with the expected retentive force between cations in the vicinity of a conducting surface and their image charge.

From the composite data, it is apparent that clean Mo(110) promotes radical reactions, while O-covered Mo(110) most often supports cationic processes.⁵⁸ This surface-type effect is pres-

(58) A reaction mechanism involving the formation of near-surface carbocations has been proposed for the hydrogenolysis of methylcyclopropane on O-covered Mo(111). Touvelle, M. S.; Stair, P. C. *J. Catal.* **1991**, *130*, 556.

Table 1. Summary of Cyclopropylmethyl Rearrangements on Mo(110)

Surface	Mo=Br 	Mo=S 	Mo=O 
products on clean Mo(110)	 ^a  Temp: 130 K Mechanism: radical based on ring-opening rearrangement	 ^{ab}  Temp: 200 - 350 K Mechanism: radical based on bond-strength correlation	 ^c  Temp: ca. 400 K Mechanism: unknown
	 ^d  Temp: 220 K Mechanism: cationic ^e based on ring-opening rearrangements	 ^c  Temp: 200 - 350 K Mechanism: radical based on TPRS data from clean Mo(110)	 ^f  Temp: ca. 400 K Mechanism: cationic ^e based on ring-opening rearrangements

^a See ref 6. ^b Approximately 25% of nonselective decomposition accompanies desulfurization. ^c See ref 34. ^d See ref 10. ^e Minor contributions from a radical pathway cannot be ruled out. ^f Present work.

ently difficult to explain. Clean Mo(110) is generally more reactive; nonselective processes complicate the mechanistic study of reactions on this surface. Future experiments on less reactive surfaces (e.g., Au(111)) would be informative.

Mechanistic selectivity trends are apparent for the different organic substrate classes studied. Thiolates prefer to enter into radical reactions, while alkoxides often experience cationic fragmentation, and bromides can access both mechanistic pathways. Our results are consistent with analogous heteroatom-dependent reactivity trends observed in solution and may depend on electronegativity. Unfortunately, similar sets of substrates have not been investigated on other solid surfaces for comparison.

The present work does not provide any direct insight into the mechanism of the final hydrocarbon extrusion event that produces (primarily) butadiene from C₄-alkoxides on O-covered Mo(110), but it does suggest that cationic intermediates may be important in hydrocarbon oxidation processes, which are the reverse of the reactions investigated here. The anticipated longer lifetime of near-surface cations relative to that of the radicals could significantly affect reaction rates and product distributions on surfaces that favor heterolytic bond cleavage by increasing the probability of reactions between released ions and other species present on the surface. Of course, radical processes are likely to be of continued importance in our understanding of heteroatom removal reactions. There is sound support for the operation of bond homolysis mechanisms in a number of cases, and methyl radicals have even been observed to arise from the thermolysis of surface methoxide (Mo–O–CH₃).⁵⁹ Still, further experiments are needed to clarify this issue.

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Supporting Information Available: A detailed experimental procedure for 1,1-*D*₂-cyclopropylmethanol, tables of RAIR peak assignments, expanded discussions of spectroscopic data analyses (as mentioned in the text), and comparisons of surface- and gas-phase IR data for important substrates mentioned in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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