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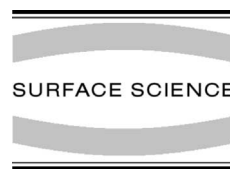**25** PUBLICATIONS **137** CITATIONS

Rearrangement as a probe for radical formation: bromomethylcyclopropane on oxygen-covered Mo(1 1 0)

J.A. Levinson, I. Kretzschmar, M.A. Sheehy, L.J. Deiner, C.M. Friend *

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Abstract

The reactions of bromomethylcyclopropane on oxygen-covered Mo(1 1 0) were studied in order to investigate the lifetimes of radical intermediates, which are important in heterogeneous oxidation catalysis. The methylcyclopropyl radical is known to rearrange on the nanosecond time scale, providing us with a means of probing for radical formation. Surprisingly, no rearrangement occurs subsequent to C–Br bond dissociation, which commences at ~220 K. Instead, displacement of bromine by oxygen occurs to yield adsorbed methylcyclopropoxide, which is identified using infrared spectroscopy. The C–O bond of methylcyclopropoxide is cleaved at ~400 K to yield a transient methylcyclopropyl radical. As shown previously, the methylcyclopropyl radical rearranges and the ring-opened butenyl species is trapped on the surface. Addition to oxygen yields 3-buten-1-oxy and addition to the metal affords the butenyl–Mo moiety. Infrared spectroscopy is used to identify these intermediates. The same linear species are formed from the reaction of 4-bromo-1-butene. The 3-buten-1-oxy species is also formed from reactions of 3-buten-1-ol on O-covered Mo(1 1 0). Upon further heating, the 3-buten-1-oxy reacts to form 1,3-butadiene, 1-butene, water, and dihydrogen between 450 and 600 K. Ethene is also evolved at ~560 K. The primary mechanism for ethene evolution is elimination from metal-bound butenyl. Carbon monoxide is also formed above 900 K, due to reaction of surface carbon and oxygen. The implications of our results for studies where alkyl halides are used as models for radical reactions on surfaces are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Surface chemical reaction; Thermal desorption spectroscopy; Vibrations of adsorbed molecules; Molybdenum; Low index single crystal surfaces; Alcohols

1. Introduction

The study of radical reactions on transition metal surfaces is of great interest because of its importance in hydrocarbon processing; e.g., the synthesis of alternative fuels and the production of chemical building blocks. Accordingly, there have been extensive studies of alkyl sources on metal surfaces as a means of studying radicals. Among the most widely studied precursors for radical reactions on surfaces are alkyl halides.

Alkyl halides have been studied extensively on a variety of transition metal surfaces. The reactivity of both linear and cyclic alkyl halides have been

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studied on Cu [1–6], Ag [7], Ni [8], Rh [9–12], and Pt [13]. In all of these cases, there is the presumption that the carbon–halide bond breaks to yield a transient radical species.

We have likewise investigated the reactions of radical species with oxygen on Mo(1 1 0). In earlier work, we investigated the direct addition of methyl radicals to oxygen on Mo(1 1 0) [14]. In these studies, we demonstrated that methyl radicals readily add to surface oxygen, forming adsorbed methoxy at 100 K. An interesting aspect of this system is that the reaction can be reversed thermally. Methyl radicals are evolved into the gas phase via homolytic C–O bond cleavage in methoxy at ~550 K [14–16]. Indeed, we have shown that alkoxides generally react via homolytic C–O bond cleavage on O-covered Mo(1 1 0) [14,17–20]. In all cases, C–O bond cleavage occurs above 400 K. For alkoxides other than methoxide, the transient radical formed from C–O bond cleavage undergoes rapid β-hydrogen elimination, yielding the corresponding alkene. For example, ethoxide, formed from ethanol, yields ethene at 460 K [17].
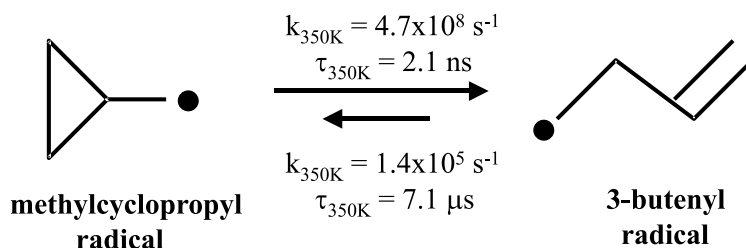
Notably, we have previously shown that the methylcyclopropyl radical, formed from C–O bond dissociation of methylcyclopropoxide, rearranges to a butenyl radical that is trapped on the surface [21]. The use of radical rearrangement as a gauge for determining radical lifetimes and relative reaction time scales (i.e., as a free radical clock) [22,23] is a well-established technique in both gas- and solution-phase chemistry [24,25]. In particular, the radical rearrangement of the methylcyclopropyl to the 3-butenyl radical (Scheme 1) is a well-calibrated example of a fast-reacting radical clock [26]. The ring-opened radical, formed from methylcyclopropoxide, adds to both oxygen

and open Mo centers. The ring-opened 3-buten-1-oxide is identified using infrared spectroscopy. Thus, our earlier studies established that the transient methylcyclopropyl radical has a sufficiently long lifetime to rearrange prior to addition to oxygen. Therefore, this is an excellent system to probe for formation of the transient radical in the case of the corresponding Br-compound.

In this study, we extend our earlier investigations of radical reactions on oxygen-covered Mo(1 1 0) by investigating bromomethylcyclopropane as a potential source of the methylcyclopropyl radical. Surprisingly, no rearrangement is detected upon C–Br bond dissociation. Instead, the methylcyclopropoxide species is formed. These results indicate that oxygen displaces the Br, i.e. that a radical is not formed. These results are discussed in the context of using alkyl halides as sources of radicals in surface reactions.

2. Experimental

All experiments were performed in two ultra-high vacuum chambers described previously with base pressures of $\leqslant 2 \times 10^{-10}$ Torr [27,28]. Both chambers were equipped with a UTI quadrupole mass spectrometer, low energy electron diffraction (LEED) optics, and an Auger spectrometer with a cylindrical mirror analyzer. The infrared spectra were collected using a single beam, clean air purged Fourier transform infrared spectrometer (Nicolet, Series 800) and averaged over 500 scans using an MCT detector at 4 cm^{-1} resolution; the scan time was approximately 3 min. Sample spectra were compared to a background spectrum taken immediately after the sample scans by flash-

$k_{350K} = 4.7 \times 10^8 \text{ s}^{-1}$

$\tau_{350K} = 2.1 \text{ ns}$

$k_{350K} = 1.4 \times 10^5 \text{ s}^{-1}$

$\tau_{350K} = 7.1 \text{ μs}$

methylcyclopropyl radical   **3-butenyl radical**

Scheme 1.

ing the crystal to 760 K. The background scan was initiated after the crystal had returned to a baseline temperature of approximately 130 K.

The Mo(1 1 0) crystal (Metal Crystals) could be cooled to 100 K, heated to 900 K radiatively, or heated to 2300 K via electron impact bombardment. Prior to each experiment, the Mo(1 1 0) surface was cleaned by oxidation at 1200 K in 1×10^{-9} Torr of O_2 for 5 min. The crystal temperature was allowed to return to approximately 100 K and subsequently flashed to 2300 K to remove residual oxygen. No surface carbon or oxygen was detected in the Auger electron spectra of the surface after this treatment. A sharp (1×1) low energy diffraction pattern was also observed. The oxygen-covered surface ($\theta_o = 2/3$ ML) was prepared by saturating the surface at 100 K in 1×10^{-9} Torr of O_2 for 1 min followed by flashing transiently to 500 K.

Bromomethylcyclopropane, 4-bromo-1-butene, and 3-buten-1-ol were purchased from Aldrich. Several freeze–pump–thaw cycles were performed to increase the purity of these samples, and each material was characterized by comparison with its tabulated gas-phase mass spectra [29]. After dosing a particular species onto the oxygen-covered crystal at 100 K, the crystal was positioned approximately 2 mm from the aperture (3 mm in diameter) of the mass spectrometer shield during the collection of temperature programmed reaction data. The crystal was biased at -70 V during temperature programmed reaction to minimize reactions induced by the electrons generated by the mass spectrometer. The mass spectrometer was computer interfaced, and the data were collected with a program capable of collecting up to 16 separate ion intensity profiles during a single experiment. The heating rate was constant at 10 ± 2 K/s between 100 and 750 K.

3. Results

3.1. Temperature programmed reaction spectrometry

Competition between desorption and reaction to produce open-chain hydrocarbons is observed during temperature programmed reaction of bromomethylcyclopropane on oxygen-covered Mo-(1 1 0) ($\theta_o = 2/3$ ML). Three hydrocarbon products – 1,3-butadiene, 1-butene, and ethene – are formed between 400 and 600 K (Fig. 1). 1-Butene is formed in two poorly resolved peaks at 450 and 525 K, denoted as α and β. 1,3-Butadiene forms coincidentally with the β-butene peak at 525 K. Ethene is formed in an asymmetric peak with a maximum at approximately 560 K. The asymmetry of this peak is mainly due to overlap from
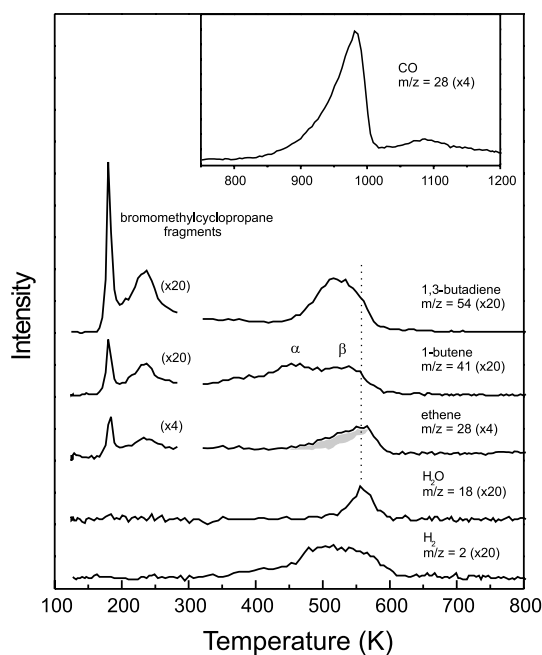

Fig. 1. Temperature programmed reaction data obtained following adsorption of multilayers of bromomethylcyclopropane on oxygen-covered Mo(1 1 0) ($\Theta_O = 0.67$ ML). The ions shown are characteristic of the products indicated: butadiene ($m/z = 54$), 1-butene ($m/z = 41$), ethene ($m/z = 28$), water ($m/z = 18$), and dihydrogen ($m/z = 2$). All data are uncorrected for fragmentation and in some cases contain contributions from other products. Carbon monoxide ($m/z = 28$) is produced at high temperature (inset). The signal at 41 amu is representative of 1-butene, as it is the most abundant fragment ion and has no contributions from 1,3-butadiene formation (Table 1). All spectra are taken with a heating rate of 10 ± 2 K/s. The shaded area displays the contribution of 1-butene (37% of amu 41) and 1,3-butadiene fragmentation (111% of amu 54) to the $m/z = 28$ peak. The low-temperature features are all fragments of desorbing bromomethylcyclopropane.

1-butene and 1,3-butadiene fragmentation, indicated by the shaded area (Fig. 1). The ethene yield peaks as the production of C_4 species diminishes. All products are identified by quantitative comparison of mass spectral data with the fragmentation patterns measured for the most intense masses of authentic samples (Tables 1 and 2).

Water and H_2 formation accompany the hydrocarbon production; note that hydrogen is lost during butadiene formation and that ethene formation must yield surface-bound hydrocarbon fragments that ultimately dehydrogenate. Water is produced in a symmetric peak at ∼560 K. A minor amount of gaseous H_2 is also detected between 400 and 600 K. Some of the H_2 arises from adsorption of hydrogen from the background. In independent experiments, hydrogen adsorbed from the background also desorbs as H_2 between 400 and 550 K with an intensity approximately one-third that measured for bromomethylcyclopropane. Hence, all processes involving C–H bond cleavage have to occur below 600 K.

CO is formed, via coupling of adsorbed carbon and oxygen, starting around 850 K and peaking at 950 K (Fig. 1 inset). The carbon can be deposited via complete decomposition of the bromomethylcyclopropane and/or in conjunction with ethene elimination. The ratio of ethene (560 K) to CO (950 K) formation is 1:12 after correction for contributions from 1-butene and 1,3-butadiene fragmentation, indicating that there is adsorbed carbon arising from non-selective decomposition of adsorbed species in addition to carbon left behind in the evolution of ethene from the C_4 intermediates. Calculation of the ionization efficiencies, ε, based on the number of electrons in the molecule [30] leads to a very similar value, $\varepsilon \sim 1$, for CO and C_2H_4. C_4H_6 has a somewhat higher ionization ef-

ficiency of $\varepsilon \sim 1.7$. Basic sensitivity factors (S_B) calculated using ionization efficiencies and mass spectrometer transmission values for the respective fragment ions lead to $S_B = 1.1$, 1.2, and 1.3×10^{-3} for CO, C_2H_4, and C_4H_6, respectively. The similarity of the values for CO and C_2H_4 should allow for similar detection efficiencies for these ions. Thus, if the C_2 fragment left behind during ethene desorption was the only source for evolution of CO, a CO:C_2H_4 ratio of 2:1 would be expected, instead of the measured ratio of 12:1. The peak area ratio of the 54 amu at 525 K to the 28 amu peak at 950 K is 1:3. The formation of CO coincides with desorption of Br at 860 K peaking at 1000 K (data not shown).

A detailed analysis of the mass spectral data indicates that no other C-containing products evolve. Specifically, there is no detectable production of C_3-hydrocarbons, cyclic species, or oxygenates. The fact that there is no residual intensity in the range of 36–44 amu after accounting for the three primary reaction products rules out the possibility that C_3-species or oxygenates are formed. The absence of intensity at 31 and 32 amu further confirms that no oxygen-containing species are evolved, other than water, because these fragments are characteristic of oxygenates. Further, the fact that the only change in the spectrum for reaction on ^{18}O-labeled Mo(1 1 0) is a shift of 2 amu for the water peak indicates that no surface oxygen is incorporated in any product other than water. The possible formation of cyclic compounds (e.g., cyclopropane, methylcyclopropane, cyclobutane, and cyclobutene) is ruled out based on key differences between their relative mass fragment intensities and those of the desorbed products. Similarly, formation of methane (16 amu) and acetylene (26 amu) is ruled out. Fi-

Table 1
Mass fragmentation patterns of authentic samples

Species	m/z									
	26	27	28	29	39	41	53	54	55	56
Bromomethylcyclopropane	22	57	32	24	45	8	21	22	100	26
1,3-Butadiene	27	58	78	1	100		48	70	19	
1-Butene	14	37	37	14	54	100	7	4	21	37
Ethene	67	62	100	2						

Table 2
Mass fragmentation of products[a]

Species	m/z									
	26	27	28	29	39	41	53	54	55	56
Intensities from multilayer peak for bromomethylcyclopropane	21	55	39	26	45	11	18	20	100	25
All products from reaction peaks for bromomethylcyclopropane, 400–600 K	80	107	132	8	100	42	34	49	28	17
Residual correcting for 1-butene	95	118	150	3	100		41	62	25	
Residual after correcting for 1-butene and 1,3-butadiene leaving ethene	94	84	100							
All products from reaction peak for 4-bromo-1-butene	68	96	115	8	100	27	37	52	24	10
Residual correcting for 1-butene	75	101	123	5	100		41	60	22	
Residual after correcting for 1-butene and 1,3-butadiene leaving ethene	107	95	100							
All products from reaction peak for 3-buten-1-ol	62	92	111	13	100	40	40	62	28	12
Residual correcting for 1-butene	72	99	122	10	100		48	77	24	
Residual after correcting for 1-butene and 1,3-butadiene leaving ethene	101	92	100							

[a] 1-Butene was identified on the basis of peaks at 41 and 56 amu, the most intense ion and parent, respectively. The other hydrocarbons were identified by subtracting the contribution of 1-butene to other masses in the product spectrum. The residual 54 amu signal is attributed to 1,3-butadiene. After accounting for fragmentation of both 1-butene and 1,3-butadiene, significant signals at 26, 27, and 28 amu remain, which are attributed to ethene.

nally, no other species with more than four carbons are formed based on a comprehensive search of masses in the 2–140 amu range; i.e., no masses above 57 amu are detected.

The formation of open-chain hydrocarbon products during temperature-programmed reaction of bromomethylcyclopropane demonstrates that the C_3-ring opens at some point along the reaction path. Hence, the reactions of the linear analogues, 4-bromo-1-butene and 3-buten-1-ol, were also studied as a means of accessing the same intermediate(s) as those formed from bromomethylcyclopropane.

The temperature-programmed reaction spectrum of 4-bromo-1-butene (Fig. 2) is similar to that of bromomethylcyclopropane, which suggests that both react via the same intermediate. Again, 1,3-butadiene, 1-butene, ethene, water, and H_2 are produced in the range of 400–600 K. Interestingly, α-butene production is enhanced relative to the reactions of bromomethylcyclopropane. The relative yield of products is similar for 4-bromo-1-butene and bromomethylcyclopropane; however, the absolute amount of product formation is smaller for 4-bromo-1-butene. For example, the amount of CO formed via atom re-combination is ~70% that formed from bromomethylcyclopropane. The ratio of CO production to ethene formation is 11:1, which is similar to the bromomethylcyclopropane. The butadiene:CO ratio is 1:12, which is smaller than the ratio of 1:3 for bromomethylcyclopropane. Quantitative analysis of the mass spectra was again employed to identify the products using the same approach as described for bromomethylcyclopropane (Table 2).

Reaction of 3-buten-1-ol on oxygen-covered Mo(1 1 0) also leads to similar products (Fig. 3) as in the bromomethylcyclopropane and 4-bromo-1-butene systems. However, there are also some distinct differences. For instance, the α-butene
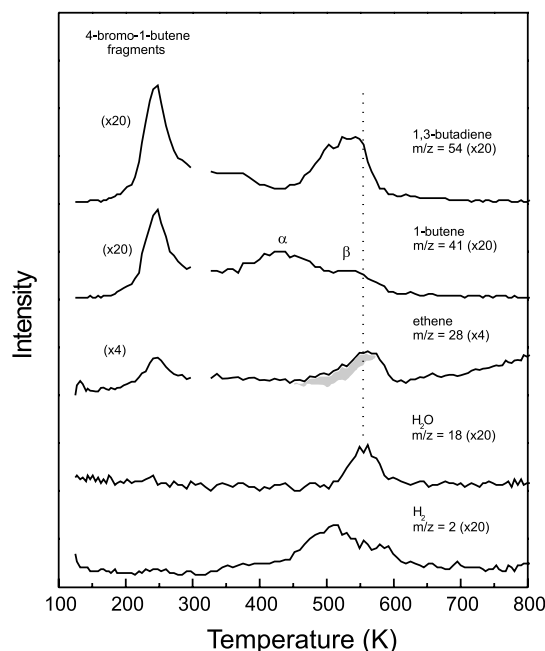
Fig. 2. Temperature programmed reaction data obtained after adsorption of 4-bromo-1-butene on oxygen-covered Mo(1 1 0) showing formation of 1,3-butadiene ($m/z = 54$), 1-butene ($m/z = 41$), ethene ($m/z = 28$), water ($m/z = 18$), and dihydrogen ($m/z = 2$). Data are uncorrected for fragmentation. The features at ∼220 K are due to desorption of molecular 4-bromo-1-butene. The shaded area displays the contribution of 1-butene (37% of amu 41) and 1,3-butadiene fragmentation (111% of amu 54) to the $m/z = 28$ peak. All spectra are taken with a heating rate of 10 ± 2 K/s.
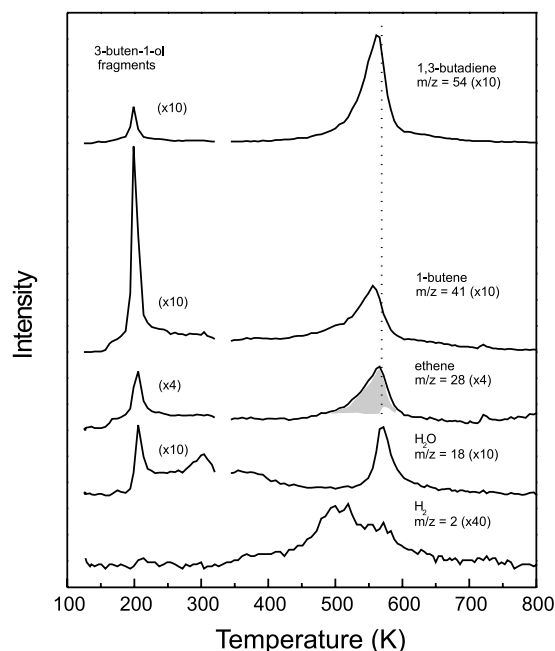
Fig. 3. Temperature programmed reaction data obtained after adsorption of multilayers of 3-buten-1-ol on oxygen-covered Mo(1 1 0) showing formation of 1,3-butadiene ($m/z = 54$), 1-butene ($m/z = 41$), ethene ($m/z = 28$), water ($m/z = 18$), and dihydrogen ($m/z = 2$). All spectra are taken with a heating rate of 10 ± 2 K/s and are uncorrected for fragmentation. The shaded area displays the contribution of 1-butene (37% of amu 41) and 1,3-butadiene fragmentation (111% of amu 54) to the $m/z = 28$ trace.

peak is missing, so that butene is formed in a single, nearly symmetric peak at 550 K. The butadiene peak is also narrower; however, the peak temperature is nearly the same as for the Br-compounds. Table 2 summarizes the results of the quantitative analysis of the mass spectra performed to identify the products. The similar formation temperatures and product mass distributions measured for the alcohol and the Br-compounds suggests that the products formed above 500 K evolve from a common intermediate, most likely a surface-bound butenoxy species.

Water also forms at 560 K in the reactions of 3-buten-1-ol. The oxygen in the water originates mainly from the surface-bound oxygen, since most water formed from reaction on ^{18}O-covered

Mo(1 1 0) is $H_2{}^{18}O$. There is also some production of $H_2{}^{16}O$ at the same temperature which arises from reaction with oxygen deposited when the hydrocarbon products are evolved. Carbon monoxide is again formed at high temperature (data not shown).

The selectivity for hydrocarbon production from 3-buten-1-ol is greater than for the Br-compounds, based on the smaller CO:butadiene ratio of 6:1 and the almost negligible amount of C_2H_4 (CO:C_2H_4 = 53:1) estimated after subtraction of the 1-butene and 1,3-butadiene contributions. Furthermore, the absolute amount of C_4H_6 formed compared to bromomethylcyclopropane is 328%, indicating a much higher selectivity for C_4-hydrocarbon formation for the alcohol.

3.2. Fourier transform infrared vibrational spectroscopy

Infrared absorption studies provide evidence that the ring in bromomethylcyclopropane opens in the range of 400–450 K and that butenoxy is formed from all three reactants studied. Our evidence for ring opening is that the infrared spectra obtained for all three reactants – bromomethylcyclopropane, 4-bromo-1-butene, and 3-buten-1-ol – after heating to 450 K are very similar (Fig. 4). Most notably, there are peaks at 1645 cm^{-1} and near 3090 cm^{-1} that are assigned to the $v(C=C)$ and the alkene $v(=C-H)$ modes [31], respectively, in all three cases. These results demonstrate unequivocally that the ring in bromomethylcyclopropane opens below 450 K (Table 3).

There are also important differences in the infrared spectra obtained after heating the Br-compounds and the alcohol to 450 K (Fig. 4). Most notably, there is a peak at 1242 cm^{-1} in the spectra of the Br-compounds that is absent in the spectrum of the alcohol. We assign this feature to a $\delta(Mo-CH_2)$ bending-mode of an alkyl species bound to the Mo(1 1 0), based on analogy with surface-bound alkyls, such as methylene [4,32,33].

The presence of this peak indicates that there is competition between addition to open metal centers and oxygen following C–Br bond dissociation and ring opening.

The other major difference in the spectra obtained after heating the three reactants to 450 K is in the region below 1000 cm^{-1}. The intermediate formed from the alcohol is presumed to be the butenoxy species, based on analogy with other alcohols studied on oxygen-covered Mo(1 1 0) [14, 17–20]. The most prominent features in the spectrum for the alkoxy are centered at 942 and 1037 cm^{-1} (Fig. 4). The most prominent feature in the spectra obtained after heating the two Br-compounds to 450 K is a peak at ~1040 cm^{-1}, which is similar to the alkoxy. However, there is not a well-defined peak near 940 cm^{-1} for bromomethylcyclopropane, and the peak near 940 cm^{-1} for 4-bromo-1-butene is also not as pronounced as in the infrared spectrum of the alcohol. The latter differences are attributed to additional peaks near 900 cm^{-1} due to the Mo–alkyl.

The contributions of the additional species to the infrared spectra of the Br-compounds at 450 K are highlighted in the differences between spectra for the Br-compounds and 3-buten-1-ol (Fig. 5).
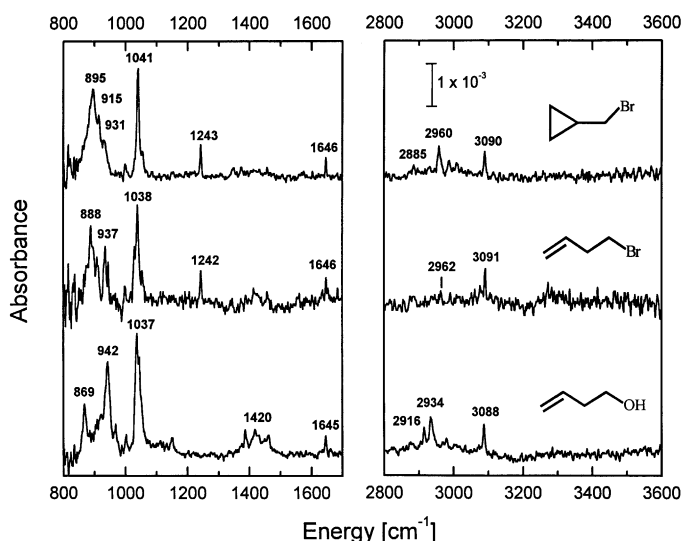

Fig. 4. Infrared reflection absorption spectra obtained after heating bromomethylcyclopropane, 4-bromo-1-butene, and 3-buten-1-ol to 450 K. All reactants were adsorbed onto oxygen-covered Mo(1 1 0) at ~100 K and transiently heated to 450 K. These data are referenced to the corresponding surface heated transiently to 760 K.

Table 3
IR vibrational assignments for bromomethylcyclopropane, 4-bromo-1-butene, and 3-buten-1-ol on oxygen-covered Mo(1 1 0)

| IR vibrational assignments	c-$(C_3H_5)CH_2O$-bromomethylcyclopropane	C_4H_7O-bromomethylcyclopropane	C_4H_7-bromomethylcyclopropane	Intermediates from 4-bromo-1-butene[a,b]	Intermediate from 3-buten-1-ol[b]
v(C–O)	880	895	890–930	888–940	942
v(C–H)	2957, 3014	2960		2962	2916, 2934
v(C–H)[c]		3090		3091	3088
v(C–C–O)	1029	1041[d]	1040	1038	1037
v(C=C)		1646		1646	1645
Ring modes	1394, 1433				
δ(Mo–CH_2)			1243	1242	

[a] Mixture of linear alkyl and alkoxy species; see text.
[b] Infrared data at 450 K.
[c] Alkene.
[d] Mixture of both C–C and C–C–O stretches; see text.
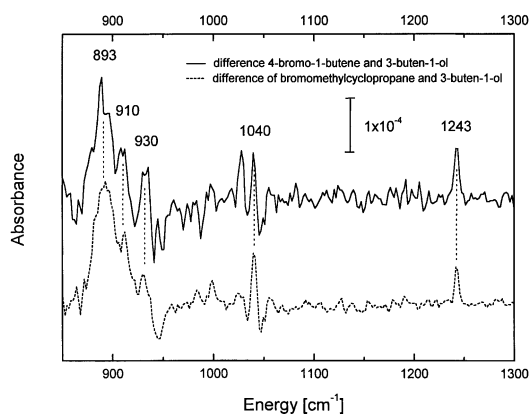
Fig. 5. Difference spectra for infrared reflection absorption data obtained after heating bromomethylcyclopropane and 3-buten-1-ol (—) and 4-bromo-1-butene and 3-buten-1-ol (- - -) on oxygen-covered Mo(1 1 0) to 450 K.

By subtracting the infrared absorption trace of the linear alkoxy species after scaling the spectra so that the peaks in the 930–940 cm^{-1} region are equal in intensity, the remaining features must be attributed to a surface species other than 3-buten-1-oxy. The difference spectra obtained between the alcohol and the two Br-compounds are virtually identical, indicating that the remaining intermediate is similar in the two cases. Infrared peaks in the 1245 cm^{-1} region have been assigned as δ(Mo–CH_2) modes [32,34]. The residual peaks in the vicinity of 891 and 1040 cm^{-1} are attributed to v(C–C) modes. Thus, we assign the residual peaks to a straight-chain alkyl species; however, based

on our results we cannot rule out the formation of other surface species, such as an oxametallacycle [35,36].

The evolution of the infrared spectra as the bromomethylcyclopropane-covered surface is transiently heated provides more information on the temperature required for C–Br bond cleavage and ring opening for bromomethylcyclopropane (Fig. 6). The spectrum at 100 K is representative of multilayers of the intact molecule, which is consistent with temperature programmed reaction. Comparison of the multilayer spectrum with the vapor-phase IR [37] shows good agreement. Thus, we assign the modes in the 1225 cm^{-1} region to C–C ring modes of intact bromomethylcyclopropane and the 1428 cm^{-1} peak to the CH_2 scissors mode [38]. The CH(Br) in-plane bend of bromocyclopropane has been assigned as 1269 cm^{-1}, in analogy to studies on Cu [6]. By 350 K, intact bromomethylcyclopropane is no longer present on the surface as indicated by the disappearance of the associated peaks. Ring modes at 1394 and 1433 cm^{-1} (associated with an adsorbed cyclic species) and a δ(Mo–CH_2) mode at 1242 cm^{-1} (associated with an adsorbed alkyl species) are present in the spectrum at 350 K. These modes start to appear around 220 K (data not shown), which we interpret as the point at which the C–Br bond breaks and both metal- and oxygen-substituted alkyl and alkoxy intermediates are formed, respectively; similar observations are made for 4-bromo-1-butene. Most notably, *no ring opening* occurs at
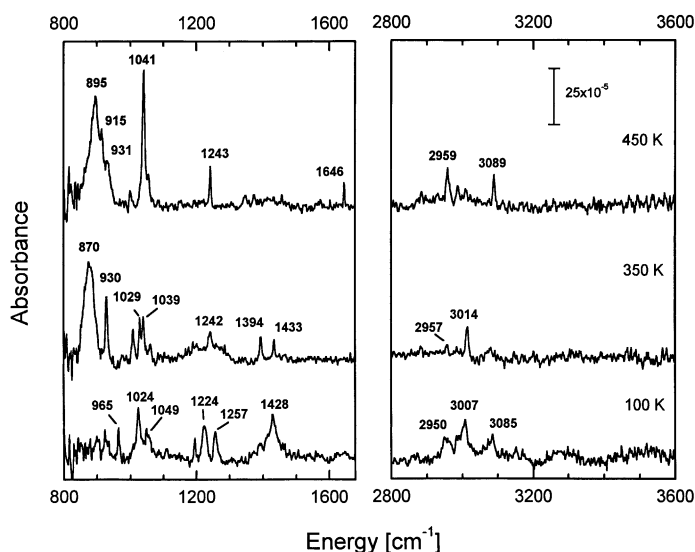
Fig. 6. Infrared reflection absorption spectra obtained after transient heating of bromomethylcyclopropane adsorbed on oxygen-covered Mo(1 1 0) to various temperatures.

350 K, because no $v(C=C)$ mode at 1646 cm^{-1} is detected. Thus, we assert that the bromine in bromomethylcyclopropane is substituted by either oxygen or a Mo atom at around 220 K to form methylcyclopropyl–O and methylcyclopropyl–Mo. Notably, there is a strong correspondence between the infrared spectrum for methylcyclopropyl–O formed from hydroxymethylcyclopropane [21] and the spectrum for bromomethylcyclopropane heated to 350 K on oxygen-covered Mo(1 1 0).

Further heating to 450 K induces ring opening, signified by the disappearance of the modes associated with the cyclopropyl ring at 1394 and 1433 cm^{-1} (Fig. 6) and the appearance of the 1646 cm^{-1} peak. The intensity at 1242 cm^{-1} increases and the mode at 1041 cm^{-1} gains intensity while the 1029 cm^{-1} peak loses intensity after heating bromo-methylcyclopropane to 450 K.

Isotopic shifts due to ^{18}O substitution are expected to be small due to intramolecular coupling of vibrations near 1000 cm^{-1} for alcohols with two or more carbons [39]. Nevertheless, changes below 950 cm^{-1} are observed that are consistent with formation of both alkoxide and alkyl species from reaction of the Br-compounds on the O-covered surface. Differences between the spectra obtained

after heating the Br-compounds to 350 and 450 K on ^{16}O- and ^{18}O-covered surfaces show that there are subtle shifts in the low-frequency region (Fig. 7). There is no difference between ^{16}O- and ^{18}O-labeled spectra for modes above 1050 cm^{-1}. Difference spectra highlight changes upon labeling (Fig. 7(c) and (f)). Peaks that are sensitive to ^{18}O-labeling should appear as differential peaks with positive and negative areas of equal amplitude in the difference spectra. It should be noted that at least part of the difference may be due to intensity variations. Since the positive peak at $\sim$880 cm^{-1} in Fig. 7(c) lacks an equal negative counterpart, this peak is assigned primarily to C–C stretching modes. However, the difference in peak widths in the vicinity of 860 cm^{-1} in Fig. 7(a) and (b) suggests that this peak has some C–O stretch character and that the corresponding peak for the ^{18}O trace may coalesce with the C–C component of the peak. The small positive peak at $\sim$1040 cm^{-1} in Fig. 7(c) may indicate some C–O character as well. Similarly, the difference spectrum in Fig. 7(f) compares the surface intermediates formed at 450 K for the ^{16}O- and ^{18}O-covered surfaces. A differential but asymmetric peak is observed at $\sim$890 cm^{-1}, again suggesting partial C–C and C–O
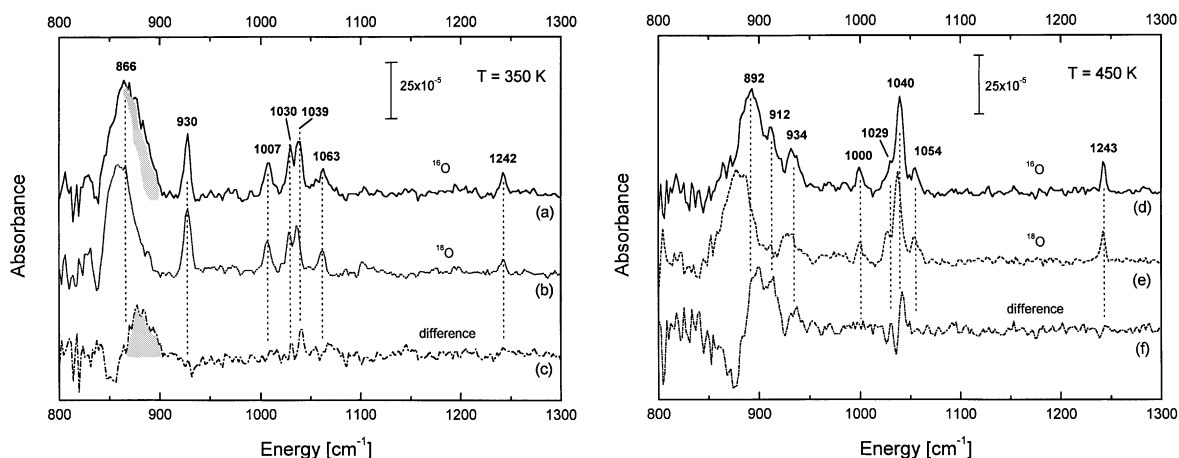
Fig. 7. Infrared spectra for bromomethylcyclopropane on (a) [16]O- and on (b) ^{18}O-labeled surfaces heated transiently to 350 K; (c) the difference between the spectra in (a) and (b); bromomethylcyclopropane on (d) [16]O- and (e) ^{18}O-labeled surfaces heated transiently to 450 K; and (f) the difference between the spectra in (d) and (e). Shaded regions in (a) and (c) represent the peak intensity attributed to C–[16]O stretching (see text).

character in the broad peak centered at 892 cm^{-1} (Fig. 7(d)). A double peak now appears more clearly at 1040 cm^{-1}, indicating C–O character in this region.

4. Discussion

Our studies clearly demonstrate that the C$_3$-ring of bromomethylcyclopropane does not open upon C–Br bond scission. This indicates that bromine is replaced by oxygen to form adsorbed methylcyclopropoxide (Fig. 8), on a time scale that is more rapid than rearrangement. This result suggests the possibility that the reaction proceeds via a concerted mechanism rather than formation of a radical upon C–Br bond scission.

The proposed formation of methylcyclopropoxide from replacement of Br by O is supported by the fact that there is strong evidence for C–Br bond scission, commencing at ~220 K and that the intermediates remaining on the surface have an intact cyclopropyl ring. Our data are consistent with formation of both alkyl and alkoxy intermediates as the C–Br bond breaks. There is no evidence for ring opening up to 400 K (data not shown). Specifically, the ring modes at 1394 and

1433 cm^{-1} persist and there is no visible ν(C=C) mode at 1645 cm^{-1} (Fig. 6).

Infrared spectra provide evidence that methylcyclopropoxide and Mo–methylcyclopropyl species are present on the surface after heating bromomethylcyclopropane to 350 K. There is a strong correspondence between the spectra obtained for methylcyclopropoxide formed from hydroxymethylcyclopropane [21] and the intermediate formed from heating bromomethylcyclopropane to 350 K. Furthermore, a detailed analysis of the infrared spectra obtained on [16]O- and ^{18}O-covered surfaces provides evidence for C–O bond formation.

There is also clear evidence for formation of a metal–alkyl species as C–Br bond cleavage is induced by heating bromomethylcyclopropane to 350 K. The presence of the alkyl species is indicated by the δ(Mo–CH$_2$) mode at 1242 cm^{-1} and the development of peaks involving C–C bonds below 900 cm^{-1}.

The fact that there is no detectable ring opening upon C–Br bond scission suggests that either this reaction step does not proceed via a radical mechanism or that the radical is so short-lived that it does not rearrange. In other words, we propose that the methylcyclopropoxide results from substitution of bromine by oxygen in a concerted
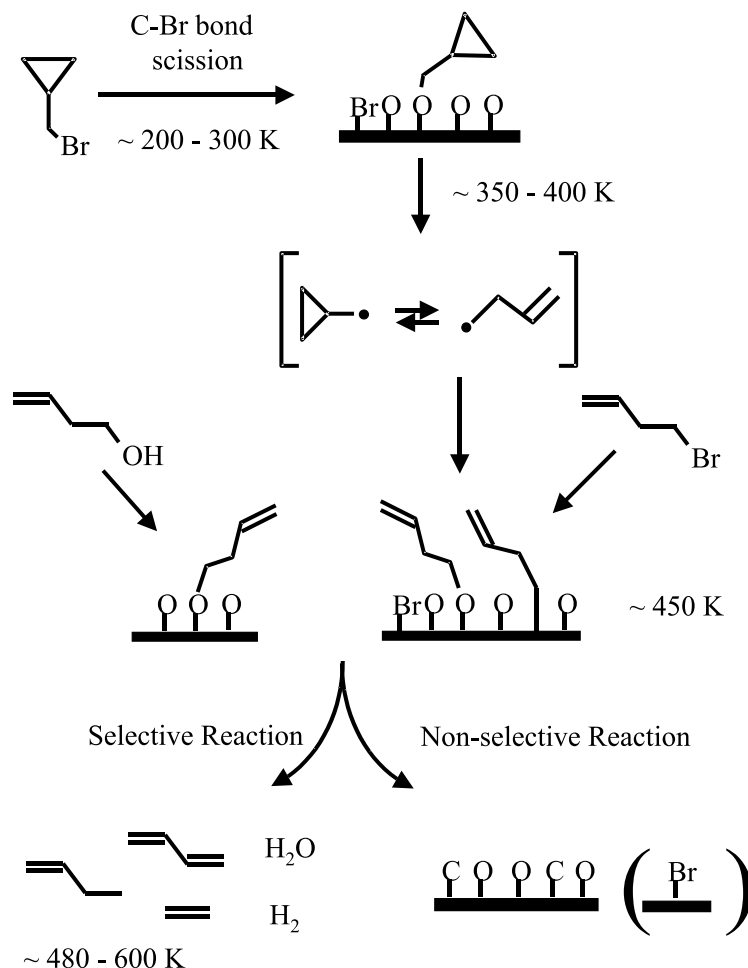
Fig. 8. Proposed reaction scheme for bromomethylcyclopropane on oxygen-covered Mo(1 1 0).

process. If C–Br bond dissociation yielded a methylcyclopropyl radical, rearrangement should have been observed at temperatures as low as 220 K, the temperature where the onset of C–Br bond cleavage occurs (data not shown). The time scale for radical addition to oxygen should be the same independent of the source of the radical. We have already established that the methylcyclopropyl radical formed from C–O bond scission in methyl-cyclopropoxide rearranges prior to addition to surface oxygen to form the butenoxy species [21]. As discussed in earlier work, the observation of rearrangement places a lower bound on the time scale for addition of the radical to oxygen of ~1 ns

[21]. We note that the temperature for C–Br bond dissociation is lower than for C–O bond breaking – 300 vs. 400 K (data not shown). The rate of re-arrangement of the radical will depend on tem-perature. The rate constant at 300 K is estimated to be 8.76×10^7 s^{-1}, i.e. a characteristic reaction time of 11 ns, based on an expression for the T-dependence of the rate derived by Halgren et al. [26]. We propose that rearrangement should still occur at this temperature if a radical is formed, and that the absence of ring opening is strong evidence for displacement of Br by oxygen, as opposed to formation of a transient radical spe-cies. We are currently investigating substituted

hydroxymethylcyclopropanes that have lower rate constants in order to determine the time scale necessary for addition to oxygen as well as the thermal and electron induced ring opening of bromomethylcyclopropane on oxygen-covered Mo(1 1 0).

The fact that C–Br bond scission does not generate a radical has important implications regarding the use of alkyl halides to model the reactions of alkyl radicals. Alkyl halides have been used extensively to model the reactions of radical species on metal surfaces. Our work shows that there are at least some instances where C–X bond cleavage does not generate a radical. Therefore, it is important to establish whether a transient radical is, indeed, formed on other surfaces if such studies are to be used as models for radical reactions. In our case, it is possible that the surface oxygen affects the mechanism for C–Br bond dissociation. The oxygen creates a partial negative charge at the surface that may affect the interaction of the Br-compound with the surface. In addition, oxygen occupies adsorption sites that would otherwise be available for bromine. These points are being addressed in independent studies.

Once the methylcyclopropoxide intermediate is formed from bromomethylcyclopropane, it behaves identically to hydroxymethylcyclopropane. Specifically, heating to ∼400 K induces homolytic C–O bond breaking, which generates a cyclopropylmethyl radical. The radical quickly rearranges to a 3-butenyl radical and is trapped on the surface to yield ring-opened alkyl and alkoxy moieties (Fig. 8). Heating the surface to higher temperatures then leads to selective product formation and to non-selective decomposition on the surface.

The elimination of a radical via homolytic C–O bond cleavage in methylcyclopropoxide is consistent with previous studies of alcohols on oxygen-covered Mo(1 1 0) [14,17–20]. Generally, C–O bond dissociation of alkoxides occurs above 500 K on oxygen-covered Mo(1 1 0). Direct evidence for formation of a radical is observed in the case of methoxy – methyl radicals are evolved into the gas phase at ∼550 K [15,16]. Alkoxides with longer chains react via a radical mechanism to form a combination of alkane and alkene products in conjunction with water in the range of 500–600 K. In these cases, the temperature required for C–O bond dissociation correlates with the homolytic C–O bond strength, providing evidence for a radical intermediate [19,40]. Furthermore, isotopic labeling studies showed that the predominant products, alkenes, are formed via dissociation of the C–O bond followed by dehydrogenation at the 2-carbon [19]. It is well known that dehydrogenation of radical species occurs via elimination of hydrogen at the carbon adjacent to the radical site, the 2-carbon. In contrast, it is well-established that dehydrogenation prior to C–O bond cleavage occurs preferentially at the C–H bonds adjacent to the oxygen because they are the weakest and most subject to attack. Dehydrogenation of primary and secondary alkoxides yields aldehydes and ketones, respectively, on Rh(1 1 1) [41] or Pd(1 1 1) [42], for example.

The observation of ring opening in the reactions of methylcyclopropoxide is in itself strong evidence for a radical mechanism, as discussed in previous work [21]. A surface-mediated ring opening mechanism can be ruled out based on recent experiments performed in our laboratory using 1-cyclopropylethanol [21]. Notably, the ethylcyclopropyl radical cannot rearrange homogeneously like the methylcyclopropyl radical. Hence, the reactions of 1-cyclopropylethanol are a good test for a possible surface-mediated ring opening; however, no ring opening is observed. Only C_5 species are evolved (all below 350 K); none of these species are straight-chain products and none contain oxygen. The absence of a surface-mediated mechanism implies that the transient methylcyclopropyl radical rearranges independently of the surface – i.e., it shows 'gas-phase' behavior in the vicinity of the surface.

Upon elimination and subsequent rearrangement of the methylcyclopropyl radical to the butenyl radical, hydrocarbons are produced. 1,3-Butadiene is formed via β-H elimination from the butenyl radical, whereas 1-butene is formed via hydrogenation. The hydrogen eliminated from the radical reacts with surface oxygen to form water. These reactions are very similar to those previously observed for other alkoxides, e.g. ethoxide [17], on oxygen-covered Mo(1 1 0).

Differences in the temperature programmed reaction spectra for the three reactants when correlated with infrared data also show that the metal-bound alkyl contributes to the reaction products. Specifically, our data indicate that the metal-bound alkyl reacts to form C_4-hydrocarbons at lower temperature than the alkoxide and that they are the primary source of ethene. Specifically, the product peaks are sharp for the alcohol and are broad for the Br-compounds. Notably, the lower temperature α-butene formation peak is absent in the temperature programmed reaction spectrum of the 3-buten-1-ol. In addition, the 1242 cm^{-1} peak attributed to a metal-bound alkyl is absent in the infrared spectrum of the 3-buten-1-ol, but present for both Br-compounds after heating to 350 K. The correlation between the β-butene formation and the $\delta(Mo–CH_2)$ peak is evidence that the β-butene evolved at low temperature arises from the alkyl. The fact that the amount of ethene produced in the reactions of 3-buten-1-ol is negligible also leads to the conclusion that the ethene produced from the reactions of the Br-compounds arises mainly from decomposition of the metal-bound alkyl. This is consistent with other studies of alkoxides on O-covered Mo(1 1 0) since there are no examples of gaseous hydrocarbon elimination via C–C bond dissociation in any alkoxide studied to date.

5. Conclusions

No rearrangement occurs subsequent to C–Br bond scission for bromomethylcyclopropane on oxygen-covered Mo(1 1 0). Instead, the methylcyclopropyl group is transferred to oxygen. The absence of rearrangement indicates that a radical intermediate is not formed, since the methylcyclopropyl radical is known to rearrange prior to addition to oxygen on this surface. As a result, methylcyclopropoxide and metal-bound methylcyclopropyl are formed after heating to 350 K. Subsequently, rearrangement occurs upon dissociation of the C–O bond of methylcyclopropoxide, commencing at ∼400 K. The transient methylcyclopropyl radical rearranges and the ring-opened butenyl species is trapped on the surface. Addition

to oxygen yields 3-buten-1-oxy and addition to the metal affords the butenyl–Mo moiety. Infrared spectroscopy is used to identify these intermediates. The same species are formed from the reaction of 4-bromo-1-butene. The 3-buten-1-oxy species is also formed from the reaction of 3-buten-1-ol on oxygen-covered Mo(1 1 0). Upon further heating, 1,3-butadiene, 1-butene, ethene, water, and dihydrogen evolve between 450 and 600 K. Carbon monoxide is also formed above 900 K, due to reaction of surface carbon and oxygen. The same products are formed from all three reactants – bromomethylcyclopropane, 4-bromo-1-butene, and 3-buten-1-ol. These studies raise the issue as to whether or not the reactions of alkyl halides on metal surfaces can be used to model radical reactions.

Acknowledgements

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