

# Controlling Factors in Deoxygenation Kinetics and Selectivity: Reactions of Ethylene Oxide on Mo(110)

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**Abstract:** Ethylene oxide intramolecularly eliminates ethylene directly into the gas phase at 200 K ( $E_a \sim 12$  kcal/mol) during reaction on Mo(110) with 70% efficiency as shown by temperature-programmed reaction and X-ray photoelectron spectroscopy. Atomic oxygen, a product of this reaction, increases the rate of ethylene formation by slowing the kinetics for the competing nonselective decomposition pathway which accounts for the other 30% of reaction of chemisorbed ethylene oxide. The nonselective decomposition products of reaction are gaseous dihydrogen, surface carbon, and oxygen. At high ethylene oxide exposures, a small amount of molecular desorption is also observed at 150 K. Deposition of an atomic oxygen overlayer ( $\theta_O \sim 0.27$ ) on Mo(110) prior to reaction enhances the selectivity of the ethylene formation reaction to 90%. Reaction saturation is controlled by the buildup of hydrocarbon fragments on clean Mo(110) and by oxygen site blocking on the oxygen precovered surface as shown by isothermal reaction spectroscopy. Carbon-heteroatom bond strength correlates with the temperature of ethylene formation in comparing reaction of ethylene oxide to that of the sulfur-containing analogue, ethylene sulfide, on Mo(110).

## 1. Introduction

The study of the reactions of ethylene oxide on single-crystal metals is relevant to the catalytic epoxidation of ethylene and to adhesion where epoxide groups in polymers are used for binding to surfaces. Our motivation in studying the reactions of ethylene oxide on Mo(110) is to determine the effect of C-X (X = O, S) bond strength on the kinetics and selectivity for the catalytic removal of heteroatoms from cyclic molecules. Previously, the reaction of ethylene sulfide, the sulfur-containing analogue of ethylene oxide, was studied on Mo(110) and found to evolve gaseous ethylene upon adsorption at 100 K with  $\sim 85\%$  selectivity.<sup>1</sup> Competing nonselective decomposition and production of additional ethylene at around 200 K were also observed for high exposures of ethylene sulfide. Since carbon-oxygen bonds are on the average 20 kcal/mol stronger than carbon-sulfur bonds,<sup>2</sup> a difference in the reactivities of ethylene oxide and ethylene sulfide might be expected. A previous study comparing the reaction of phenol on Mo(110) to that of benzenethiol showed that C-X bond strength correlates with the observed reactivity differences of the two molecules on Mo(110).<sup>3</sup>

The reaction of ethylene oxide on Ag(110) has been studied extensively.<sup>4-7</sup> On Ag(110), ethylene oxide adsorbs molecularly via the oxygen atom with the plane of the molecule nearly perpendicular to the surface. Only molecular desorption is observed; no decomposition or reaction to ethylene occurs. Adsorption on Cu(110), Ni(111), and Fe(100) leads to low-temperature molecular desorption; dissociation at temperatures less than 300 K is not observed.<sup>7</sup> Reaction on Pt(111) yields a small amount of molecular desorption and predominantly decomposition to gaseous dihydrogen and carbon monoxide, and surface carbon.<sup>6</sup>

Temperature-programmed reaction, isothermal reaction, and X-ray photoelectron spectroscopies have been used to study the reaction of ethylene oxide on Mo(110), the closest packed face of molybdenum. A small amount of molecular desorption is observed, however, the two predominant reactions are found to be intramolecular gaseous ethylene formation at 200 K and nonselective decomposition to dihydrogen, surface carbon, and oxygen. No evolution of gaseous ethylene is observed upon adsorption at 100 K, as it is in the reaction of ethylene sulfide on

Mo(110). This difference in reactivity can be traced to relative C-X (X = O, S) bond strength in ethylene oxide and ethylene sulfide. The presence of atomic oxygen on the surface was found to inhibit the nonselective decomposition reaction; oxygen stabilizes molecular ethylene oxide with respect to nonselective decomposition. This result is in agreement with studies of the reaction of phenol on oxygen precovered Mo(110) where atomic oxygen was found to have a similar effect.<sup>8</sup>

## 2. Experimental Section

All experiments were performed in one of two ultra-high-vacuum chambers with base pressures of less than  $1.5 \times 10^{-10}$  Torr. The X-ray photoelectron data were collected in a chamber described previously.<sup>9</sup> This chamber is equipped with a Physical Electronics 5300 X-ray photoelectron spectroscopy system, a UTI-100C quadrupole mass spectrometer surrounded by a liquid-nitrogen-cooled shield, electron optics for Auger electron spectroscopy and low-energy electron diffraction, and directed dosing of the sample via a leak valve. X-ray photoelectron data were analyzed using the computer and software provided with the Physical Electronics system. The C(1s), O(1s), and Mo(3d) regions were monitored for collection times of 7, 7, and 2 min, respectively. Temperature-annealed X-ray photoelectron data were collected after exposing the Mo(110) crystal to ethylene oxide at a crystal temperature of 100 K, annealing twice at a heating rate of  $\sim 15$  K/s, and recoiling to 100 K before data collection. A new ethylene oxide exposure was used for each X-ray photoelectron experiment to minimize beam damage. There were no changes in the X-ray photoelectron spectra over time for the collection times used, indicating minimal beam damage to surface species. Experiments were also performed at lower X-ray source power and identical results obtained. The Mo(3d<sub>5/2</sub>) peak at 227.7 eV was used to calibrate binding energies of the C(1s) and O(1s) regions, which were found to be accurate to within  $\pm 0.2$  eV. In order to increase the signal-to-noise ratio of the X-ray photoelectron data, three identical experiments were performed for each spectrum shown and the data added together. Clean Mo(110) spectra were then subtracted from the C(1s) region, where background photoemission structure from molybdenum is present.

The second chamber, also described previously,<sup>10</sup> was used to collect temperature-programmed reaction data. Temperature-programmed reaction experiments were performed with a quadrupole mass spectrometer identical with that in the first chamber which is interfaced with an IBM computer allowing simultaneous data collection for up to 10 masses in a single experiment. Directed dosing of the adsorbate on the crystal was used in all experiments. Auger electron spectroscopy was used to monitor crystal cleanliness and low-energy electron diffraction to check surface order. Oxygen atom overlayers were formed by exposing the crystal to oxygen gas at a crystal temperature of 1200 K. The coverage of the oxygen overlayer formed in this manner was estimated by comparing the integrated atomic O(1s) intensity in X-ray photoelectron spectra to that

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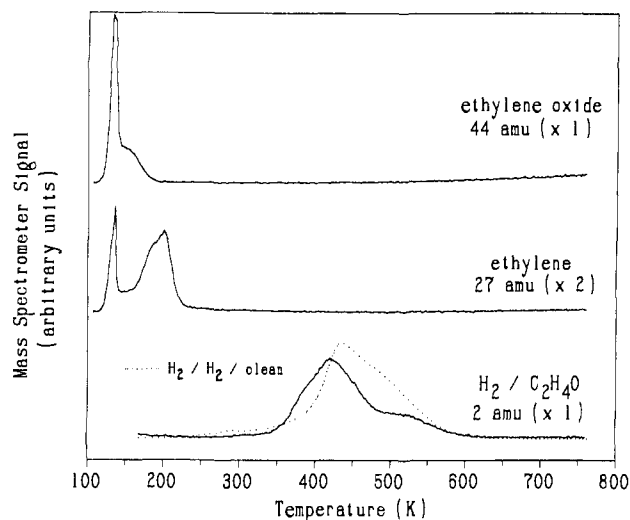
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**Figure 1.** Temperature-programmed reaction spectrum obtained after exposing Mo(110) to multilayers of ethylene oxide at a crystal temperature of 100 K. The temperature-programmed reaction spectrum of dihydrogen formed from hydrogen atom recombination after dosing clean Mo(110) with a saturation exposure of dihydrogen (---) is shown superimposed on the dihydrogen spectrum obtained from reaction of ethylene oxide for purposes of comparison. The clean surface dihydrogen spectrum has been normalized to the ethylene oxide dihydrogen spectrum for clarity. The heating rate used in all temperature-programmed reaction experiments was  $\sim 15$  K/s. The 27-amu spectrum is uncorrected for contributions from cracking of ethylene oxide in the mass spectrometer.

of an oxygen overlayer known to have a coverage of 0.33 monolayer. Isothermal reaction data were collected by holding the clean or oxygen precovered Mo(110) crystal at a constant temperature (100 or 300 K) in a position  $\sim 0.25$  in. from the leak valve doser and then monitoring the rise in the partial pressures of the masses of interest measured by the mass spectrometer as a function of time after opening the doser filled with ethylene oxide. Exposures of ethylene oxide are given in units of Torr-s, which are the product of the backing pressure of the adsorbate in the doser reservoir, and the time in seconds that the doser is open to the ultra-high-vacuum chamber. A "blank" experiment, where isothermal reaction was performed on Mo(110) covered with oxygen to saturation thus rendering it unreactive, demonstrated that reaction products observed during isothermal reaction on clean or oxygen precovered Mo(110) were evolved from reaction on the crystal rather than other surfaces in the chamber.

Preparation of the Mo(110) single crystal was performed in the manner described previously.<sup>10</sup> Ethylene oxide was obtained from Matheson (99.7%), transferred to a glass sample bottle, and degassed at liquid nitrogen temperature repeatedly. Oxygen (Matheson, Extra Dry, 99.6%) was used to clean the crystal after temperature-programmed reaction and to form the oxygen overlayers. Deuterium (99.5%) and ethylene (Research Purity, 99.9%) were also obtained from Matheson. Perdeuterioethylene ( $D_4$  99%) was obtained from Cambridge Isotope Laboratories, Inc.

### 3. Results

**Reaction of Ethylene Oxide on Clean Mo(110).** Ethylene oxide undergoes reaction via three pathways on clean Mo(110): molecular desorption, formation of gaseous ethylene, and nonselective decomposition. The temperature-programmed reaction spectrum obtained after dosing Mo(110) with a multilayer exposure of ethylene oxide at 100 K shows the gaseous products generated by each of these three processes (Figure 1). Ethylene oxide (44 amu), ethylene, and dihydrogen (2 amu) are the only gaseous products evolved. All masses between 2 and 100 amu were monitored during temperature-programmed reaction and no other products were detected. In particular, the fragmentation pattern for masses between 25 and 32 amu were examined carefully to confirm that the only hydrocarbon produced during reaction is ethylene. The ethylene spectrum shown was detected at 27 amu<sup>11</sup> because of the relatively better signal-to-noise ratio compared to

that obtained monitoring 28 amu (parent ion) which has a higher background intensity due to CO in the chamber. Ethylene oxide (44 amu) also contributes to the signal detected at 27 amu, since 27 amu is a fragment of ethylene oxide in the mass spectrometer. The ethylene spectrum in Figure 1 is uncorrected for ethylene oxide fragmentation.

After adsorption of saturation exposures of ethylene oxide on Mo(110) at 100 K, temperature-programmed reaction produces molecular desorption of ethylene oxide in two peaks (Figure 1). The sharp desorption at 140 K detected at 44 amu is attributed to sublimation of ethylene oxide multilayers since this peak increases indefinitely in intensity with increasing ethylene oxide exposure. A small molecular ethylene oxide desorption is also detected at 150 K under the tail of the multilayer desorption peak, which is more apparent at low coverage. The reaction product, ethylene, is detected in a single peak centered at 200 K for multilayer exposures of ethylene oxide. All other features in the ethylene spectrum are due to detection of 27 amu generated from cracking of ethylene oxide in the mass spectrometer and not from ethylene evolution, as is evident in comparison of the 44-amu and 27-amu spectra. The third gaseous product detected, dihydrogen, arises from nonselective decomposition of ethylene oxide to dihydrogen, surface carbon, and oxygen. Dihydrogen arising from recombination of hydrogen atoms adsorbed to saturation on clean Mo(110) desorbs in a peak centered at 450 K.<sup>12</sup> The temperature-programmed reaction spectrum of dihydrogen evolved from reaction of a saturation dose of dihydrogen obtained in a separate experiment (dotted line in Figure 1) has been superimposed onto that of dihydrogen formed from ethylene oxide for comparison.

Atomic oxygen and carbon detected by both Auger and X-ray photoelectron spectroscopy (results discussed below) remain on the surface after temperature-programmed reaction of ethylene oxide to temperatures above 700 K. The areas of the C(1s) and O(1s) X-ray photoelectron atomic peaks detected after reaction of a saturation dose of ethylene oxide to 700 K were used to calculate the relative amounts of ethylene formation and nonselective decomposition.<sup>13</sup> Of the atomic oxygen present after reaction to 850 K,  $\sim 70\%$  arises from deoxygenation to gaseous ethylene and atomic oxygen and 30% from nonselective decomposition of ethylene oxide.

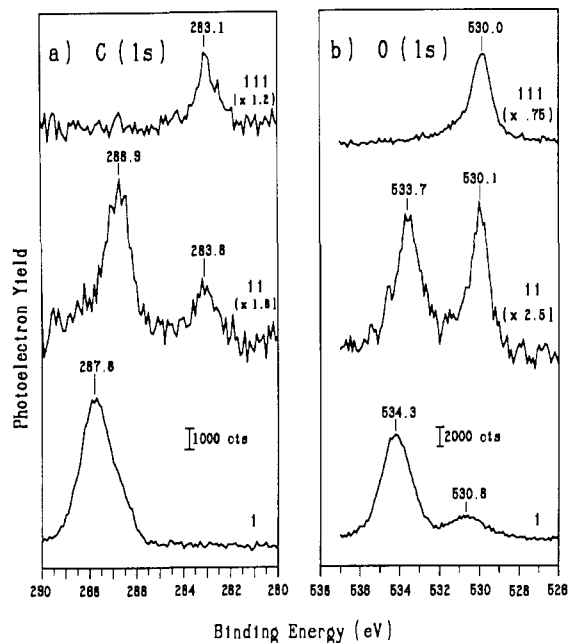
Deuterium preadsorption experiments show that the surface species which evolves gaseous ethylene oxide and ethylene during temperature-programmed reaction of ethylene oxide does not undergo reversible C-H bond breaking. No incorporation of deuterium into the ethylene oxide molecular desorption or ethylene desorption at 200 K is observed during temperature-programmed reaction of ethylene- $d_4$  oxide ( $<1.0$  of saturation exposure) on a Mo(110) surface which has been precovered with a less than saturation dose of deuterium atoms. Similarly, deuterium atoms adsorbed after ethylene oxide exposure at a crystal temperature of 100 K were not incorporated into the ethylene or ethylene oxide produced from temperature-programmed reaction of ethylene- $h_4$  oxide.

X-ray photoelectron data were obtained after adsorption of ethylene oxide on Mo(110) in order to determine the temperature of the onset of nonselective decomposition and to determine what surface species are present prior to ethylene formation. C(1s) X-ray photoelectron data obtained after exposing Mo(110) to multilayers of ethylene oxide, and after annealing a saturation exposure to 150 K and 300 K, are shown in Figure 2a, i-iii, respectively. Corresponding O(1s) data collected in the same experiments are shown in Figure 2b, i-iii. Multilayers of ethylene oxide adsorbed at 100 K have a C(1s) binding energy of 287.8

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(13) Since ethylene formation produces only atomic oxygen on the surface and nonselective decomposition produces both atomic carbon and oxygen in the ratio of 2:1, the area of the C(1s) peak should be twice that of the contribution to the O(1s) peak by nonselective decomposition, after correction for X-ray photoelectron atomic sensitivity factors. Thus the ratio of oxygen from nonselective decomposition to that from ethylene production may be calculated, assuming that the escape of photoelectrons from carbon and oxygen atoms on the surface is equally likely.

(11) In the mass spectrum of pure ethylene, 27 amu is  $\sim 55\%$  as intense as 28 amu.



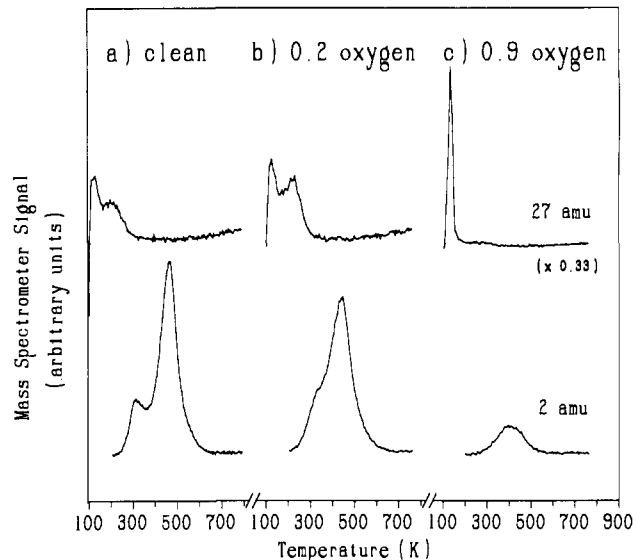
**Figure 2.** C(1s) X-ray photoelectron spectra obtained for (a-i) multilayers of ethylene oxide on Mo(110) after dosing at 100 K, (a-ii) a saturation exposure of ethylene oxide after annealing to 150 K, and (a-iii) a saturation exposure after annealing to 300 K. O(1s) data collected in the same experiments are shown in (b-i) for multilayers, (b-ii) after annealing to 150 K, and (b-iii) after annealing to 300 K.

eV and an O(1s) binding energy of 534.3 eV (Figure 2, a-i and b-i). A second low-intensity peak appears in the O(1s) multilayer spectrum at 530.8 eV. This peak was found to appear only in spectra obtained after dosing many ethylene oxide multilayers and was found to have no effect on either the intensities or binding energies observed in spectra obtained by annealing multilayers of ethylene oxide to higher temperatures.

C(1s) and O(1s) X-ray photoelectron data collected after annealing to 150 K show that some adsorbed ethylene oxide has undergone C–O bond cleavage by this temperature. After annealing a saturation exposure of ethylene oxide to 150 K (Figure 2-ii), peaks attributed to adsorbed intact ethylene oxide are detected at 286.9 and 533.7 eV in the C(1s) and O(1s) spectra. These binding energy values are in good agreement with those observed previously for ethylene oxide adsorbed on Ag(110): 286.8 and 533.2 eV.<sup>6</sup> The other peaks present in the C(1s) and O(1s) spectrum after annealing to 150 K at 283.6 and 530.1 eV are assigned respectively to a hydrocarbon fragment on the surface and atomic oxygen. Hydrocarbons with some intact C–C and C–H bonds generally have C(1s) binding energies near 284 eV.<sup>14</sup> Clearly, some adsorbed ethylene oxide has undergone C–O bond cleavage by 150 K.

The annealing temperature of 150 K used to collect the spectra shown in Figure 2-ii is also the temperature where desorption of molecular ethylene oxide is at a maximum for saturation exposure (Figure 1). In order to show that not all of the molecularly adsorbed ethylene oxide desorbs at temperatures below that of ethylene formation (200 K), X-ray photoelectron spectra were also collected after annealing to 180 K (data not shown), a temperature past molecular ethylene oxide desorption. Both molecular ethylene oxide peaks and those due to surface fragments are still present in the C(1s) and O(1s) data after annealing to 180 K.

After annealing a saturation coverage of ethylene oxide to 300 K, a temperature past all ethylene and ethylene oxide desorption, only hydrocarbon fragments and atomic oxygen are present on the surface (Figure 2-iii). The intensity of the low binding energy C(1s) peak does not decrease on annealing from 150 to 300 K (Figure 2a, ii and iii), but the high binding energy carbon vanishes in this temperature range. Therefore, gaseous ethylene evolved

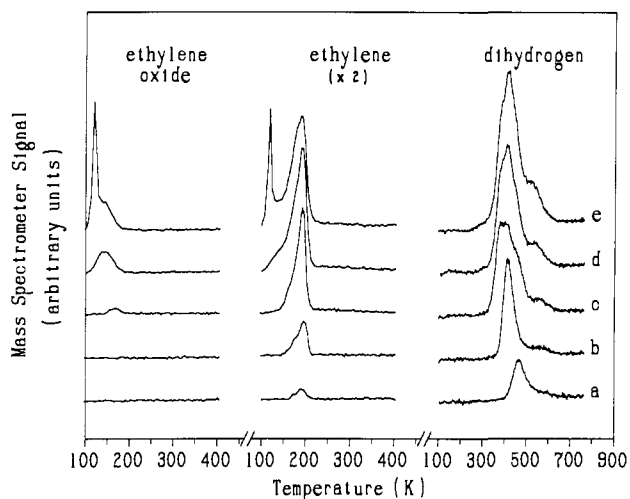


**Figure 3.** Temperature-programmed reaction spectrum obtained from reaction of ethylene after saturation exposure at 100 K on (a) clean Mo(110), (b) Mo(110) covered with  $\sim 0.2$  monolayer of atomic oxygen, and (c) Mo(110) covered with  $\sim 0.9$  monolayer of atomic oxygen.

at 200 K must arise from the high binding energy species, adsorbed ethylene oxide. No further changes are observed in the O(1s) spectrum after annealing to temperatures higher than 300 K. Approximately 0.17 monolayer of atomic oxygen is deposited from decomposition of ethylene oxide after saturation exposure based on comparison of the 300 K spectrum O(1s) intensity to that of an oxygen overlayer known to have a coverage of 0.33 monolayer. Since it is hard to distinguish atomic carbon from –CH groups on the basis of binding energy, after annealing to 300 K either atomic carbon and hydrogen, or carbon in hydrocarbon fragments is present on the surface along with atomic oxygen. X-ray photoelectron data are not shown for lower than saturation exposures of ethylene oxide since the signal-to-noise ratio is too high to allow reasonable interpretation of the data.

A comparison of the reactions of ethylene on clean and oxygen precovered Mo(110) shows that ethylene evolved during reaction of ethylene oxide is unlike ethylene desorption arising from reaction of ethylene. Adsorption of ethylene at 100 K on clean Mo(110) and Mo(110) precovered with low and high coverages of oxygen atoms yields gaseous ethylene and the nonselective decomposition product, gaseous dihydrogen, during temperature-programmed reaction (Figure 3). Although molecular ethylene is evolved in the range of 100 to 300 K on the clean and  $\sim 0.2$  monolayer oxygen precovered surfaces (Figure 3, a and b), ethylene desorption does not occur in a sharp peak centered at 200 K or in nearly as large amounts as from reaction of ethylene oxide (Figure 1). Integration of the area of the temperature-programmed reaction peaks of ethylene evolved from saturation doses of ethylene and ethylene oxide in separate experiments shows that the amount of ethylene desorbed after adsorption of ethylene itself is only 30% that evolved during ethylene oxide reaction on clean Mo(110). At high oxygen atom precoverages, ethylene desorption occurs in a low-temperature peak well below 200 K and decomposes only in very small amounts (Figure 3c). Thus desorption kinetics and selectivity for the reaction of ethylene on clean and oxygen precovered Mo(110) are not the same as those of ethylene evolution arising from reaction of ethylene oxide.

Further experiments where ethylene oxide and ethylene-*d*<sub>4</sub> were co-adsorbed on Mo(110) at a crystal temperature of 100 K were performed to show that ethylene formed from reaction of ethylene oxide is different from ethylene desorbing from the surface. The experiment was performed in two ways: by making a mixture of ethylene oxide and ethylene-*d*<sub>4</sub> and dosing the molecules simultaneously onto the clean crystal or by first adsorbing ethylene oxide, then ethylene-*d*<sub>4</sub> to saturation. For both cases all deuterium-containing ethylene desorbed only in peaks characteristic

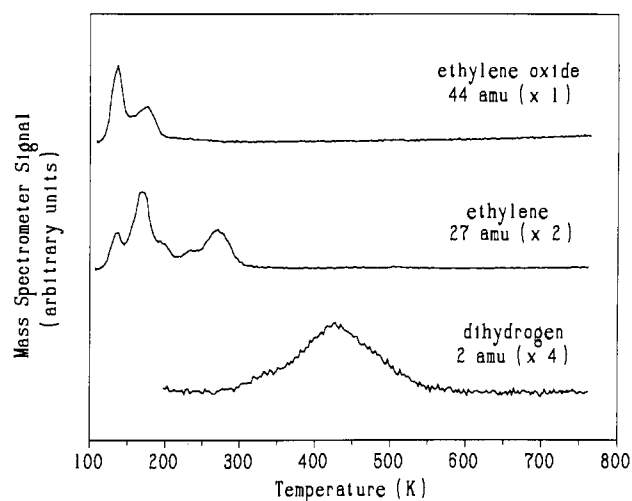


**Figure 4.** Temperature-programmed reaction spectra obtained after dosing ethylene oxide on Mo(110) at 100 K as a function of ethylene oxide exposure. The exposures shown correspond to (a) 0.10, (b) 0.23, (c) 0.67, (d) 1.00, and (e) >1.00 of saturation. The ethylene spectra (27 amu) shown is uncorrected for fragmentation of ethylene oxide (44 amu) at 27 amu. Dihydrogen spectra were taken at 2 amu.

of ethylene- $d_4$  desorption from the clean surface, not in the relatively sharp desorption at 200 K observed from reaction of ethylene oxide. In the mixture experiment, the ratio of ethylene oxide to ethylene- $d_4$  was varied from approximately 1:1 to 1:3. It was found that mixtures rich in ethylene- $d_4$  inhibited the production of ethylene- $h_4$  from ethylene oxide.

**Reaction of Ethylene Oxide on Clean Mo(110) at Low Exposures.** The evolution of the three gaseous reaction products as a function of initial ethylene oxide exposure was also studied by temperature-programmed reaction (Figure 4). Saturation exposure (denoted 1.0) is defined as the exposure where no further changes in the temperature-programmed reaction spectrum are detected with increasing initial ethylene oxide exposure, except for increased multilayer sublimation. This exposure corresponds to the data depicted in Figure 4d. At the lowest exposures studied (0.10 of saturation), ethylene and dihydrogen are the only gaseous products detected during temperature-programmed reaction (Figure 4a). Ethylene (27 amu) appears at 200 K, and the decomposition product, dihydrogen, is formed in an asymmetric peak centered at 475 K. As the exposure is increased, the ethylene peak increases in intensity but exhibits no shift in the temperature of the peak maximum within the resolution of our experiment. The dihydrogen formation spectrum shows a higher temperature tail growing in at  $\sim 575$  K with increasing exposure, which shifts to 550 K by saturation exposure. The dihydrogen spectrum is also broadened on the low-temperature side as the exposure is increased (Figures 4, a through d). At an ethylene oxide exposure of 0.67 of saturation (Figure 4c), molecular ethylene oxide desorption commences in a peak centered at 170 K. As the exposure increases, this molecular feature broadens and shifts to lower temperature, until at saturation exposure it appears at 150 K. Finally, multilayers of ethylene oxide are detected at 140 K (Figure 4e) in the ethylene oxide spectrum (44 amu) and as a cracking fraction in the 27-amu spectrum.

**Reaction of Ethylene Oxide on Oxygen Precovered Mo(110).** Clearly, it is important to determine the effect of atomic oxygen on the reaction kinetics of ethylene oxide since oxygen is produced via nonselective decomposition at temperatures as low as 150 K during reaction on the clean surface. Temperature-programmed reaction of a multilayer dose of ethylene oxide on Mo(110) precovered with 0.27 monolayer of atomic oxygen is shown in Figure 5. No new reaction products are observed. Multilayers of ethylene oxide appear at 140 K as for the clean surface. The exposure necessary to saturate reaction on the oxygen precovered surface is 80% that necessary to saturate reaction on the clean surface. Integration of the area of the dihydrogen formation peaks from saturation doses on the oxygen precovered and clean surfaces



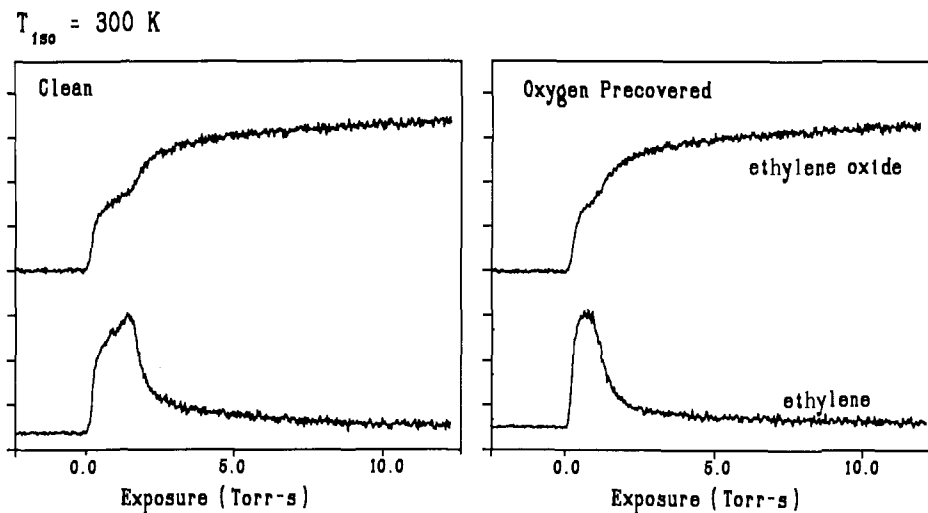
**Figure 5.** Temperature-programmed reaction spectra obtained after exposing a multilayer dose of ethylene oxide to Mo(110) at 100 K which had been precovered with 0.27 monolayer of atomic oxygen. The ethylene spectrum is uncorrected for fragmentation of ethylene oxide at 27 amu.

show that the amount of nonselective decomposition on the clean surface is 4 times as much as on the oxygen precovered surface. Even after accounting for the lower saturation coverage of the oxygen precovered surface, it is evident that there is significantly less nonselective decomposition on the oxygen precovered surface. In addition, integration of the area of the ethylene peaks of the clean and oxygen precovered surfaces shows that a slightly larger amount of gaseous ethylene is produced on the oxygen precovered surface after reaction of a saturation exposure of ethylene oxide adsorbed at a crystal temperature of 100 K. On the oxygen precovered surface  $\sim 90\%$  of the reacting ethylene oxide forms ethylene and 10% nonselectively decomposes, compared to 70% ethylene formation and 30% nonselective decomposition observed for reaction on the clean surface. The relative amounts of molecular ethylene oxide desorption remains approximately the same on the two surfaces. There are also qualitative differences in the ethylene desorption on the oxygen precovered surface: most of the gaseous ethylene produced evolves in the peak centered at 175 K, however, there are also higher temperature ethylene formation peaks up to 275 K.

X-ray photoelectron data (data not shown) demonstrate that the kinetics for nonselective decomposition are slower on the oxygen precovered surface than clean Mo(110). Only molecular ethylene oxide is present on the surface with a binding energy of 286.8 eV for C(1s) and 533.2 eV for O(1s) after annealing a saturation exposure of ethylene oxide to 150 K on the oxygen precovered surface, indicating that no decomposition occurs until above 150 K on the oxygen precovered surface. After annealing to 300 K, a temperature past all ethylene evolution, only atomic oxygen is detected in the X-ray photoelectron spectrum. Although some atomic carbon must be formed on the surface after reaction as shown by the temperature-programmed reaction results, it is not present in amounts measurable by X-ray photoelectron spectroscopy. The low carbon coverage confirms the high selectivity for ethylene formation on the oxygen precovered surface but precludes quantitative determination of the selectivity using X-ray photoelectron spectroscopy.

If a lower precoverage of oxygen (0.17 monolayer), essentially equal to that observed after reaction of a saturation dose of ethylene oxide on clean Mo(110), is used, we find that although more nonselective decomposition is observed than on the 0.27 monolayer oxygen precovered Mo(110), the total amount of nonselective decomposition is still less than on the clean surface. The formation temperature for most of the ethylene is still 200 K, however, higher temperature peaks are also observed.

**Isothermal Reaction of Ethylene Oxide at 300 K.** The results presented above clearly demonstrate that the presence of atomic



**Figure 6.** Isothermal reaction spectra for exposure of clean Mo(110) and Mo(110) precovered with 0.27 monolayer of atomic oxygen to ethylene oxide at a crystal temperature of 300 K. The partial pressures of ethylene oxide (44 amu) and ethylene (27 amu) in the mass spectrometer were monitored as a function of dosing time. The abscissa axis scale was obtained by multiplying the dosing time in seconds by the backing pressure of ethylene oxide in the leak valve. The backing pressures were identical in the two experiments and the leak valve was opened the same amount; thus the same flux of ethylene oxide was used for dosing in each experiment. The 44-amu spectrum of ethylene oxide has been normalized to the 27-amu spectrum and subtracted from it to correct for fragmentation of ethylene oxide at 27 amu. Thus the ethylene spectra shown represents only contributions from the reaction product ethylene.

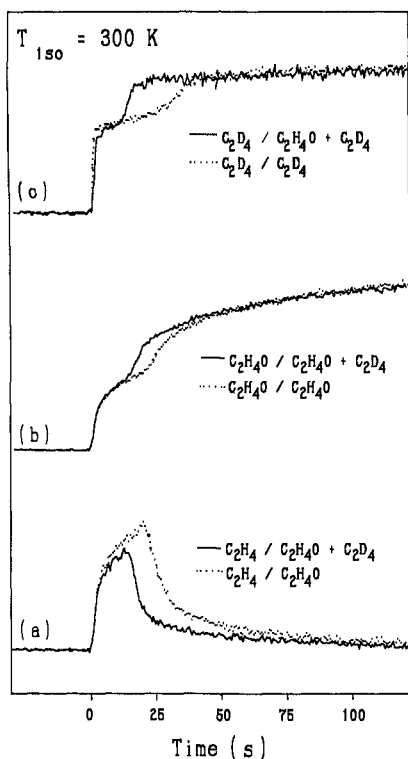
oxygen slows the kinetics for nonselective decomposition of ethylene oxide. To determine which surface species influence the kinetics of ethylene formation on Mo(110), a series of isothermal reaction experiments were performed at a crystal temperature of 300 K, a temperature above that of ethylene production in temperature-programmed reaction on both the initially clean and oxygen precovered surfaces. Isothermal reaction experiments were also performed at 100 K on clean Mo(110) to show conclusively that ethylene oxide does not form gaseous ethylene until 200 K.

The rate of ethylene production at a crystal temperature of 300 K was compared on the clean and 0.27 oxygen precovered surfaces by monitoring the isothermal reaction spectra while dosing ethylene oxide on the two surfaces (Figure 6). The intensity of the ethylene signal shown in Figure 6 is directly proportional to the rate of ethylene production after correction for contributions from ethylene oxide fragmentation in the mass spectrometer. The 44-amu ethylene oxide spectrum has been normalized to the 27-amu spectrum and subtracted from it to eliminate signal due to cracking of ethylene oxide at 27 amu. Thus the isothermal spectrum of ethylene depicted in Figure 6 shows only contributions from gaseous ethylene evolved from reaction of ethylene oxide. The data for the two experiments shown were collected under identical conditions with the same flux of ethylene oxide impinging on the crystal and may thus be compared directly. Several differences are apparent in isothermal reaction on the two surfaces. As expected from the temperature-programmed reaction results described above, the amount of ethylene oxide necessary to saturate the surface and stop the ethylene formation reaction is less on the oxygen precovered surface than on the initially clean surface. A difference of  $\sim 20\%$  is measured at 300 K by determining the area above the ethylene oxide isothermal curve enclosed by a vertical line starting at 0.0 Torr-s exposure and a horizontal line corresponding to maximum ethylene oxide signal for both the initially clean and oxygen precovered surface spectra.

Secondly, the initial rate of ethylene evolution is very different on the two surfaces, demonstrating that the deposition of a reaction product from either ethylene formation (atomic oxygen) or nonselective decomposition (C, H, CH, or  $C_xH_y$  and atomic oxygen) on the initially clean surface modifies the kinetics of the ethylene evolution reaction. After an initial sharp rise, the rate of ethylene production increases in an approximately linear fashion on the initially clean surface (Figure 6). The rate of ethylene production then drops sharply after reaching its maximum value. In contrast, the rate of ethylene production on the 0.27 oxygen precovered surface initially assumes its maximum value and re-

mains essentially constant until saturation. This difference indicates that on the clean surface the kinetics for ethylene production are being altered as ethylene oxide exposure proceeds, while on the oxygen precovered surface the rate of ethylene production is essentially constant until the surface is saturated and reaction can no longer occur. The changing kinetics on the initially clean surface must be associated with the production of one or more species on the surface during reaction.

The area under the ethylene formation curve is greater for the clean surface:  $\sim 30\%$  more ethylene is produced at 300 K from reaction of ethylene oxide on the clean surface than on the 0.27 monolayer oxygen surface. In order to investigate which factors control the saturation of the ethylene formation reaction under these conditions, the following experiments were performed. For each of the two surfaces, isothermal reaction was performed at a crystal temperature of 300 K to reaction saturation. The presence of carbon and oxygen on the initially clean surface after isothermal reaction at 300 K was confirmed by X-ray photoelectron spectroscopy in a separate experiment. A temperature-programmed reaction equipment to 750 K was performed after isothermal reaction to remove hydrogen contained in hydrocarbon fragments or present as surface hydrogen from the nonselective decomposition reaction. After temperature-programmed reaction, the crystal was allowed to cool to 300 K, and then a second isothermal reaction was performed with ethylene oxide. For the initially clean crystal, additional ethylene was produced showing that the presence of a hydrogen containing surface species arising from ethylene oxide inhibits ethylene formation under isothermal conditions. On the oxygen precovered surface, no ethylene production was observed during the second exposure of ethylene oxide. Since very little nonselective decomposition producing surface hydrogen-containing fragments occurs on the oxygen precovered surface, it is expected that the presence of atomic oxygen will limit reaction rather than hydrocarbon fragments. X-ray photoelectron results support site blocking by oxygen limiting reaction saturation on the oxygen precovered surface; on the initially clean surface, the amount of oxygen deposited after the first isothermal reaction to saturation is less than the amount of oxygen in the overlayer on the oxygen precovered crystal. After the second isothermal reaction on the initially clean surface, the amount of oxygen increases to an amount slightly greater than that in the overlayer of the oxygen precovered crystal. For the oxygen precovered crystal, no increase in atomic oxygen coverage is observed between X-ray photoelectron data collected after the first and second isothermal re-



**Figure 7.** Isothermal reaction spectrum of (a) ethylene- $h_4$ , (b) ethylene- $h_4$  oxide, and (c) ethylene- $d_4$  obtained while dosing an  $\sim 1:1$  mixture of ethylene- $h_4$  oxide and ethylene- $d_4$  on initially clean Mo(110) at a crystal temperature of 300 K (—). The ethylene- $h_4$  spectrum has been corrected for fragmentation of ethylene- $h_4$  oxide as in Figure 6. The isothermal reaction spectra of ethylene- $h_4$  oxide and ethylene- $h_4$  obtained from dosing only ethylene- $h_4$  oxide onto initially clean Mo(110) at the same flux as ethylene- $h_4$  oxide in the mixture experiment is shown in (b) and (a) as dotted lines (---). For comparison, the isothermal reaction spectrum of ethylene- $d_4$  (---) obtained by dosing only ethylene- $d_4$  on initially clean Mo(110) at a higher flux has been normalized to and superimposed on the ethylene- $d_4$  spectrum obtained in the mixture experiment (c). No hydrogen-deuterium mixed isotopes of ethylene were detected during isothermal reaction of the mixture.

actions as expected since no ethylene formation is observed in the second reaction.

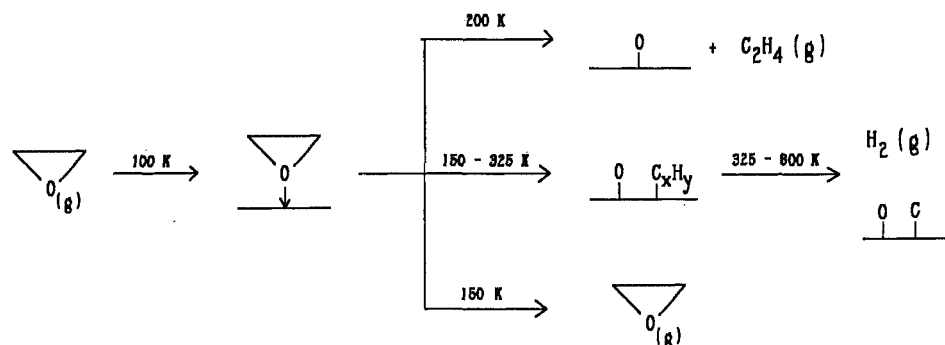
Isothermal reaction of an  $\sim 1:1$  mixture of ethylene- $h_4$  oxide and  $C_2D_4$  on initially clean Mo(110) shows conclusively that atomic oxygen is the surface species accounting for the increase in the rate of ethylene production as reaction proceeds on the initially clean surface. Figure 7a shows the isothermal production of ethylene- $h_4$ , while Figure 7, b and c, shows the adsorption isotherms for ethylene- $h_4$  oxide and ethylene- $d_4$  obtained during dosing of an  $\sim 1:1$  mixture of  $c-C_2H_4O$  and  $C_2D_4$  onto the initially clean crystal at a crystal temperature of 300 K. In the mixture experiment, masses between 29 and 31 amu were monitored in addition to the ones shown in Figure 4, but no mixed isotope

ethylene species were detected. At 300 K,  $C_2D_4$  (32 amu) adsorbs and nonselectively decomposes on the surface until saturation coverage is reached.  $c-C_2H_4O$  adsorbs and reacts to produce ethylene or nonselectively decomposes to yield surface oxygen and hydrocarbon fragments. The isothermal reaction spectra of ethylene- $h_4$  oxide and ethylene- $h_4$  obtained during dosing of *only* ethylene- $h_4$  oxide are compared to those where ethylene oxide is dosed in the mixture at the same flux in Figure 7, a and b (dotted lines). The initial rate and slope of ethylene production from ethylene oxide reaction are the same during exposure of the mixture and pure ethylene oxide (Figure 7a). Also, the adsorption isotherm for pure  $C_2D_4$  on the initially clean surface is very similar to that for the mixture after normalization for differences in dosing flux (Figure 7c). The only significant difference in data obtained during dosing of the mixture is that saturation is reached more quickly for the mixture.  $C_2D_4$  and ethylene oxide adsorption and the production of  $C_2H_4$  from ethylene oxide cease at earlier times for the mixture than for adsorption of the pure samples. This is consistent with the observation that hydrocarbon fragments arising from nonselective decomposition of ethylene oxide during the reaction on the clean surface inhibit reaction since  $C_2D_4$  present in the dosing mixture also nonselectively decomposes to hydrocarbon fragments on the surface.

Notably, the slope of the  $C_2H_4$  production signal and  $C_2D_4$  adsorption are qualitatively different in the mixture experiment. The rate of  $C_2H_4$  production as a function of time increases in an approximately linear fashion, then saturates, whereas the amount of  $C_2D_4$  scattered from the surface is nearly constant. This confirms that ethylene arising from reaction of ethylene oxide is not trapped on the surface after its formation since we would expect  $C_2D_4$  or other mixed isotope ethylene species (not observed) to show a reaction curve very similar to that of  $C_2H_4$  if the reaction product, ethylene, were trapped on the surface prior to release into the gas phase. Importantly, these data also confirm that the increasing rate of ethylene production during reaction on the initially clean surface is due to the presence of oxygen on the surface, not hydrocarbon-derived species, since the  $C_2H_4$  production curve of the mixture would be expected to have a shape different from that obtained from reaction of pure ethylene oxide if hydrocarbon-derived species played a role in altering ethylene production kinetics as dosing of ethylene oxide proceeds. Clearly, the curves are very similar; thus atomic oxygen must be increasing the rate of ethylene production.

#### 4. Discussion

After adsorption at 100 K, ethylene oxide reacts via three competing channels as shown in Figure 8: intramolecular elimination to form gaseous ethylene, nonselective decomposition, and molecular desorption. The relative contribution of each of these channels depends on coverage and the presence of surface species, in particular atomic oxygen and hydrocarbon fragments. On initially clean Mo(110), a significant portion of chemisorbed ethylene oxide has undergone C-O bond cleavage by 150 K, ultimately resulting in nonselective decomposition to gaseous dihydrogen, surface carbon and oxygen. In a parallel reaction channel,  $\sim 70\%$  of the chemisorbed ethylene oxide deoxygenates



**Figure 8.** Scheme for reaction of ethylene oxide on clean Mo(110) at saturation exposure, showing the three observed reaction channels: ethylene evolution, nonselective decomposition, and molecular desorption.

at 200 K to intramolecularly eliminate gaseous ethylene and leave atomic oxygen on the surface. For high coverages of ethylene oxide, a small amount of adsorbed ethylene oxide also molecularly desorbs at 150 K. This is a minor reaction channel which is not observed for ethylene oxide exposures less than 0.60 of saturation.

Temperature-programmed reaction, isothermal reaction, and X-ray photoelectron data support a reaction mechanism in which ethylene is evolved directly into the gas phase at 200 K by intramolecular elimination from adsorbed ethylene oxide. There is no evidence for the two other mechanisms which could be envisioned for production of ethylene: intramolecular elimination with adsorption of ethylene on the surface followed by desorption at higher temperature, and ring opening via breakage of one C–O bond to form an alkoxide-like intermediate which then further reacts to form ethylene. Adsorption of ethylene on the surface followed by desorption at higher temperature is unlikely in light of temperature-programmed reaction data for ethylene adsorbed on clean and oxygen precovered Mo(110). Ethylene desorption kinetics are sufficiently different from that of ethylene formed from ethylene oxide to rule out trapping of ethylene on the surface before desorption at 200 K. Isothermal reaction of the C<sub>2</sub>D<sub>4</sub> and *c*-C<sub>2</sub>H<sub>4</sub>O mixture shows conclusively that ethylene formed from reaction of ethylene oxide is kinetically distinguishable from adsorbed ethylene. The ring-opening mechanism is also not likely to be operative since no deuterium is incorporated into the ethylene product in the coadsorption experiment. Incorporation of deuterium into the alkoxide-like intermediate formed in a ring-opening mechanism is expected since formation of an alkoxide involves C–O bond hydrogenolysis. Also, X-ray photoelectron results show no evidence of a stable alkoxy-like intermediate. Methoxy groups on Pd(111) have been measured to have a C(1s) binding energy of 285.9 eV,<sup>15</sup> a value clearly inconsistent with C(1s) binding energies observed here after annealing ethylene oxide to 150 K. Oxygen (1s) binding energies in the range of 530.7 to 531.0 eV have been measured for alkoxy groups on Cu(110),<sup>16</sup> values also very different from those measured here after annealing ethylene oxide to 150 K. Thus intramolecular elimination of ethylene directly into the gas phase at 200 K is the most reasonable mechanism for ethylene formation with nonselective decomposition being a parallel, rather than sequential, process in ethylene oxide reaction.

The intramolecular elimination of ethylene from ethylene oxide is qualitatively similar to reactions of epoxides with organometallic complexes. WCl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub> undergoes oxidative addition of ethylene oxide to form W(O)Cl<sub>2</sub>(PMePh<sub>2</sub>)<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>).<sup>17</sup> The complex Li<sub>2</sub>WCl<sub>6</sub> reacts with alkyl-substituted ethylene oxide to produce an alkene and a tungsten–oxygen complex. The mechanism by which this reaction is thought to occur is by bonding of the epoxide to tungsten via oxygen followed by epoxide ring opening to form an oxametallacyclobutane which undergoes carbon–oxygen and carbon–tungsten bond cleavage to form the observed products.<sup>18</sup> The reaction of ethylene oxide to ethylene on Mo(110) may occur in a step similar to that observed for the second complex or via a concerted transition state as has been suggested for the reaction of ethylene sulfide on Mo(110).<sup>1</sup> It is important to note that there may be no directly analogous reaction of an organometallic complex with an epoxide to the reaction of epoxides on the molybdenum surface. Extended Hückel calculations for the reaction of ethylene sulfide on Mo(110) have shown that it is much easier to eliminate ethylene via a concerted mechanism on the Mo(110) surface than it is in a model molybdenum complex, suggesting that the relative barriers for competing channels may be quite different in a cluster compared to an extended surface.<sup>19</sup> Also, the oxametallacyclobutane

transition state would not be expected to exhibit the same reactivity on a metal surface as in a mononuclear complex since coordination to more than one metal atom is possible in the surface case and the formation of a metal–carbon bond would be expected to lead to a significant amount of nonselective reaction.

Atomic oxygen, a decomposition product, dramatically alters the kinetics and selectivity of ethylene oxide reaction. The selectivity for ethylene production is increased by slowing the kinetics of the competing nonselective decomposition reaction channel. X-ray photoelectron results clearly show that some ethylene oxide has undergone C–O bond cleavage at temperatures as low as 150 K on the initially clean surface. In contrast, no C–O bond cleavage is evident at 150 K on the oxygen precovered surface. Since nonselective decomposition rather than ethylene production arises from C–O bond cleavage below 200 K, C–H or C–C bonds are being stabilized with respect to nonselective decomposition by the presence of atomic oxygen, in this case. The stabilization of molecular ethylene oxide with respect to nonselective decomposition thus increases the selectivity of reaction for intramolecular elimination of gaseous ethylene.

Comparison of the rates of ethylene production on the clean and oxygen precovered surfaces and of the ethylene oxide/ethylene-*d*<sub>4</sub> dosing mixture at 300 K shows that atomic oxygen deposited during reaction, rather than hydrocarbon species, increases the rate of ethylene formation although hydrocarbon fragments do eventually limit the ethylene formation reaction on the initially clean surface. On the oxygen precovered surface, the ethylene formation reaction is ultimately limited by the buildup of atomic oxygen during reaction. The alteration of ethylene production kinetics by surface modification is clearly evident in the apparently linear rate increase observed in the ethylene spectrum for reaction of ethylene oxide on the initially clean surface at 300 K. This rate increase can be attributed to the presence of atomic oxygen since ethylene production commences at the maximum rate for reaction on the oxygen precovered surface and since the presence of coadsorbed C<sub>2</sub>D<sub>4</sub> in the mixture experiments does not alter the rate increase on the initially clean surface. The increase in the rate of ethylene production by the presence of atomic oxygen is due at least in part to the increased selectivity of ethylene production caused by the inhibition of the nonselective decomposition reaction. The activation barrier for ethylene production may also be changed by the presence of atomic oxygen, however, we cannot deconvolute this effect from that of the former one.

The factors controlling saturation of the ethylene formation reaction differ on the initially clean surface and the oxygen precovered surface. The ethylene production reaction is halted by the presence of surface species arising from the hydrocarbon part of the molecule formed during nonselective decomposition on the initially clean surface as shown by the isothermal reaction experiment performed after annealing previously reacted surfaces to desorb hydrogen and by the mixture experiments where the coadsorption of C<sub>2</sub>D<sub>4</sub> causes the ethylene formation reaction to saturate more quickly than when just ethylene oxide is reacted alone. On the oxygen precovered surface, reaction is saturated by the buildup of atomic oxygen rather than carbon and/or hydrogen-containing species.

A primary goal of this study was to elucidate the role of C–X (X = heteroatom) bond strength on heteroatom removal reaction kinetics. The difference in the kinetics for intramolecular elimination of ethylene from ethylene oxide ( $E_a = 12$  kcal/mol)<sup>20</sup> and ethylene sulfide ( $E_a < 6$  kcal/mol)<sup>1</sup> correlates with the enthalpy of heteroatom removal in the two molecules. Recall that gaseous ethylene is produced from ethylene sulfide at a surface temperature of 100 K, while reaction to ethylene is not observed for ethylene oxide until ~200 K on Mo(110). If we consider only the relative ring strain in the two molecules, the more highly strained ethylene oxide would be expected to form ethylene *more* readily than

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ethylene sulfide, since the contribution of ring strain to the enthalpy of formation for ethylene oxide is 26.9 kcal/mol compared to 17.7 kcal/mol for ethylene sulfide.<sup>21</sup> However, the relative enthalpies of reaction of ethylene sulfide and ethylene oxide are also controlled by the large difference in C-X (X = O, S) bond strengths. The heat of formation of ethylene sulfide is 19.9 kcal/mol<sup>22</sup> while that of ethylene oxide is -12.5 kcal/mol,<sup>23</sup> hence it will take less energy to decompose ethylene sulfide than ethylene oxide. Subtracting out the contribution of ring strain, which works in the opposite direction, this leaves an ~40-kcal/mol energy difference in the enthalpies of the two molecules which is attributable to the difference in strength of the two C-X bonds in each molecule. Thus the relative weakness of the C-S bond in ethylene sulfide favors reaction to ethylene at lower temperature, other factors being equal.

A factor which also should be considered is the enthalpy of the metal-heteroatom bond formed after ethylene elimination, since it may provide a significant thermodynamic driving force for reaction. The Mo-S bond on Mo(110) is known to be 100 kcal/mol.<sup>24</sup> The strength of the Mo-O bond has not been measured explicitly, however, the chemisorption enthalpy of atomic oxygen on Mo(110) is expected to be as large or larger than that of sulfur based on the relative heats of formation of MoS<sub>2</sub> and MoO<sub>3</sub>.<sup>3</sup> Furthermore, structural differences in the reactants cannot account for the observed difference in reactivity of the two molecules at 100 K. We expect the adsorption geometries of ethylene oxide and ethylene sulfide on Mo(110) to be similar, with coordination of the molecule to the surface via the heteroatom. The C-C bond length is 1.47 Å in ethylene oxide and 1.48 Å in ethylene sulfide.<sup>25</sup> The product, ethylene, has a C-C double bond length of 1.34 Å, therefore, we would expect about the same amount of reorganization in the two molecules if the transition states are similar in the reaction to form ethylene.

The stronger C-O bond in ethylene oxide qualitatively correlates with the observed difference in reactivity of ethylene oxide and ethylene sulfide at 100 K. This is consistent with conclusions drawn earlier in comparing the reactions of phenol and benzenethiol on Mo(110)<sup>3</sup> where the greater C-O bond strength is thought to lead to nonselective decomposition of phenol, since C-O bonds in phenol do not cleave until temperatures at which C-H bond activation occurs also. In contrast, benzenethiol readily reacts at temperatures 100 K lower to the hydrogenolysis product, benzene.<sup>26</sup>

Finally, an important difference in the reaction kinetics of ethylene oxide and ethylene sulfide is the role that the respective decomposition products have on the kinetics for intramolecular

elimination. Isothermal reaction of ethylene sulfide at 100 K produces ethylene at a rate which is initially constant and then drops gradually to zero.<sup>1</sup> Atomic sulfur produced during reaction is thought to stabilize molecular ethylene sulfide adsorption with respect to reaction to ethylene. Thus as atomic sulfur builds up on the surface, ethylene production decreases gradually since more ethylene sulfide adsorbs rather than reacts; the kinetics for ethylene production are slowed by the presence of sulfur. Extended Hückel calculations suggest that sulfur blocks the pseudo-three-fold site which is most effective in ethylene sulfide desulfurization;<sup>19</sup> electronic effects do not appear to be important. Although site blocking by oxygen must play a role, the effect of atomic oxygen on ethylene oxide reactivity is qualitatively different. In this case, the selectivity of the ethylene production reaction is increased by the inhibition of the nonselective decomposition reaction channel by atomic oxygen. The inhibition of nonselective decomposition results in the apparent increase in the rate of ethylene production during isothermal reaction performed at 300 K. At 300 K, the ethylene formation reaction is eventually saturated by the buildup of fragments arising from the hydrocarbon portion of the molecule produced during nonselective decomposition rather than a decrease in the rate of the ethylene formation reaction due to buildup of the atomic heteroatom. Since nonselective decomposition is only a minor reaction channel for ethylene sulfide reaction, presumably due to the low barrier for intramolecular elimination, the suppression of nonselective decomposition does not play a role in the kinetics of ethylene production from ethylene sulfide. The specific nature of the oxygen induced change in the kinetics for intramolecular elimination is unknown and awaits further investigation.

## 5. Conclusions

After adsorption at 100 K, ethylene oxide reacts on Mo(110) via three competing channels. The predominant reaction is intramolecular elimination of ethylene from ethylene oxide directly into the gas phase at 200 K, leaving atomic oxygen on the surface. Competing nonselective decomposition commencing at temperatures around 150 K is a parallel channel by which approximately 30% of the chemisorbed ethylene oxide reacts. The final decomposition products evolved at higher temperatures are gaseous dihydrogen, surface carbon, and oxygen. At saturation ethylene oxide exposures, a small amount of ethylene oxide also molecularly desorbs at 150 K. Atomic oxygen is found to slow the kinetics for nonselective decomposition, thus increasing the selectivity for ethylene evolution. Ethylene from ethylene oxide is not evolved upon adsorption at 100 K, as it is from ethylene sulfide on Mo(110). This difference in reactivity is attributed to the higher bond strength of the C-O bond in ethylene oxide than of the C-S bond in ethylene sulfide.

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**Registry No.** Mo, 7439-98-7; O, 17778-80-2; ethylene oxide, 75-21-8.

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