

Thermal Decomposition of Ethylene Oxide on Pd(111): Comparison of the Pathways for the Selective Oxidation of Ethylene and Olefin Metathesis

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The product distribution detected in the multimass temperature-programmed desorption of a saturated overlayer of ethylene oxide adsorbed on Pd(111) at ~ 180 K indicates that it decomposes to yield ethylene and acetaldehyde. These observations are interpreted by postulating that ethylene oxide reacts to form an oxymetallocycle. This is proposed to thermally decompose in a manner analogous to carbometalocycles that form during olefin metathesis catalysis by the reaction between an alkene and a surface carbene. Thus, the metallocycle can decompose to yield ethylene and deposit adsorbed atomic oxygen or undergo a β -hydrogen transfer to form acetaldehyde.

Introduction

Ethylene epoxidation is a catalytic process of great industrial importance where the most selective catalysts are based on silver.^{1,2} It has been unequivocally demonstrated that both partial and total oxidation products arise from the reaction of ethylene with adsorbed atomic oxygen and that the presence of dissolved subsurface oxygen enhances the selectivity to ethylene oxide.^{3,4} It has been proposed that this facilitates electrophilic attack of ethylene by adsorbed atomic oxygen by reducing its negative charge. Chlorine is proposed to enhance the selectivity in a similar manner.

The nature of the surface intermediate formed by reaction between $O_{(ads)}$ and gas-phase ethylene remains elusive. This reaction could occur either by direct reaction between ethylenic π -orbitals and adsorbed oxygen to yield adsorbed ethylene oxide directly or alternatively by interaction with adsorbed oxygen and a vacant adjacent metal site to form an oxymetallocycle intermediate. Such an oxymetallocycle has been proposed to form by the reaction of propylene with atomic oxygen on Rh(111),⁵ and in the heterogeneous phase, they have been proposed as intermediates in both epoxidation⁶ and de-epoxidation⁷ reactions. They have also been invoked to explain the silver-catalyzed isomerization of ethylene oxide to acetaldehyde.⁸ Ethylene oxide formation would then occur via a reductive elimination of this species. This suggests that, under suitable conditions, ethylene oxide should adsorb on transition-metal surfaces by cleavage of the C-O bond, forming an oxymetallocycle. It has, however, been found that ethylene oxide adsorbs molecularly on silver

Scheme 1



and desorbs intact at ~ 175 K.⁹ Ethylene oxide adsorbed on oxygen-precovered silver does thermally decompose by reaction with oxygen, and this has been suggested as a pathway to the formation of total oxidation products.³

Once formed, it is likely that such an oxymetallocycle can decompose via a number of pathways. Insights into possible decomposition routes can be gained by noting the similarity between oxymetalocycles formed by reaction of an alkene with adsorbed atomic oxygen and the metalocyclic intermediate formed by reaction between an alkene and a surface carbene ($CH_{2(ads)}$) in the proposed reaction pathway for olefin metathesis.¹⁰ The postulated correspondence between the two reaction pathways is emphasized in Scheme 1 where X is $CH_{2(ads)}$ for metathesis and $O_{(ads)}$ for epoxidation.

The fate of the carbometalocycle (where X is CH_2) is well documented. It can do the following: (i) Eliminate an alkene by the reverse of the formation reaction (Scheme 1).^{10,11} In this context, ethylene desorption has been observed in temperature-programmed desorption following ethylene oxide adsorption on Mo(110) although it should be noted that this was assigned to the direct desorption of ethylene from ethylene oxide and the effect attributed to the strong O-Mo bond formed at the surface.¹² (ii) Reductively eliminate cyclopropane, particularly on low oxidation state surfaces.¹³ An analogous reaction for the oxymetallocycle would yield ethylene

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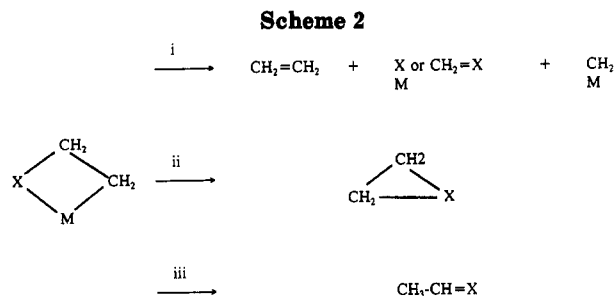
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oxide. (iii) Undergo β -hydrogen transfer,¹⁴ yielding, in the case of the carbometalloycycle, propylene, and oxymetalloycycle decomposition via this route would yield an aldehyde or ketone. Acetone desorption has been detected following propylene adsorption on Rh(111)-(2 \times 1)-O⁵ where a similar hydrogen-transfer mechanism was invoked and the formation of $\eta^2(\text{C},\text{O})$ -acetaldehyde has been detected from ethylene oxide exposure to potassium-promoted Ni(111).¹⁵ In the absence of coadsorbed potassium, ethylene oxide desorbs molecularly from Ni(111).¹⁶

It is hypothesized, on the basis of the analogy with the chemistry of the carbometalloycycle, that an oxymetalloycycle should decompose via route i in Scheme 2 to yield ethylene and deposit adsorbed atomic oxygen or evolve formaldehyde and leave surface carbenes. It would react via route ii to desorb ethylene oxide, and pathway iii would form acetaldehyde. These routes are summarized in Scheme 2.

To test this hypothesis, a transition metal is required that is sufficiently reactive to dissociatively adsorb ethylene oxide, but where the various postulated reaction products ethylene, formaldehyde, and acetaldehyde do not decompose to a substantial extent on the surface or have well-documented decomposition pathways. The surface chemistry of ethylene oxide has not been previously investigated on palladium, although this surface will have a greater tendency to dissociate C—O bonds than silver and is therefore a logical metal on which to investigate the decomposition of ethylene oxide. In addition, the chemistry of the proposed reaction products has been well documented. Ethylene adsorbs intact on Pd(111) at 200 K with its C=C axis parallel to the surface, and the majority of the chemisorbed ethylene desorbs molecularly at \sim 300 K with the small fraction remaining converting to ethylidyne.¹⁷ At low coverages, adsorption is completely reversible. These results also suggest that C—H bond cleavage is relatively slow on Pd(111), indicating that alternative reaction pathways involving rapid C—H bond cleavage should be minor. Approximately 13% of a saturated layer of acetaldehyde desorbs molecularly (at \sim 325 K), the rest decomposing to give CO (35%), hydrogen (20%), and methane (28%).¹⁸ Methane arises from hydrogenation of adsorbed methyl groups and desorbs at \sim 370 K. Carbon is deposited onto the surface after heating to \sim 700 K, and this is ascribed to a competing CH_{3(ads)} dehydrogenation pathway. Surface methylenes formed by oxymetalloycycle decomposition (pathway i,

Scheme 2) can, in principle, also hydrogenate to form methane. However, in this case, the probability of carbon and hydrogen formation from methylene decomposition is likely to be much higher than that for rehydrogenation to methane.

Formaldehyde predominantly decomposes on Pd(111) with only \sim 3% desorbing molecularly.¹⁸ Hydrogen (46%) and CO (51%) are the primary desorption products. In this case, the hydrogen desorbs at 300 K compared with 340 K for hydrogen arising from acetaldehyde decomposition.

Experimental Section

The experiments were carried out in a stainless steel ultrahigh vacuum chamber operating at a base pressure of $<5 \times 10^{-11}$ Torr, which has been described in detail elsewhere.¹⁹ It contained a four-grid retarding field analyzer for LEED/Auger measurements and a computer-multiplexed mass spectrometer which was used to obtain temperature-programmed reaction data. A heating rate of 8 K/s was employed for these measurements. Blank temperature-programmed desorption experiments were also carried out after leaving the sample *in vacuo* for an identical time as required to dose it to estimate the contribution to the spectrum of any background contaminants. Minor amounts of CO and H₂ were detected, but these were negligible ($<5\%$) compared to the signal obtained by saturating the surface with ethylene oxide. The Pd(111) single crystal was prepared by standard methods and cleaned by repeated cycles of argon ion bombardment (800 K, 500 eV, 0.05 A/m²) and annealing to 950 K until no impurities could be detected by Auger spectroscopy. Residual carbon was removed by repeated heating in 1×10^{-8} Torr of O₂ at 850 K, followed by annealing to 1200 K. This procedure was repeated until O₂ adsorption at 300 K resulted in no CO formation in the subsequent desorption sweep. The sample was resistively heated and could also be rapidly cooled by being brought into contact with a movable liquid nitrogen-filled reservoir. The minimum temperature attainable with the sample in contact with the cold finger was \sim 100 K. Ethylene oxide was, however, adsorbed at the maximum temperature (\sim 180 K) consistent with the formation of a chemisorbed overlayer. Gases were introduced into the chamber either by back-filling via a variable leak valve or by means of a calibrated capillary array which was directed at the sample. Research grade ethylene oxide was used. All temperature-programmed desorption spectra were collected for a saturated overlayer. The exposure time required to saturate the surface was measured by monitoring the ethylene oxide pressure due to molecules effusing from the capillary doser after moving the sample to intercept the beam. The time taken for the pressure to reach its original value was taken as that required to saturate the surface.

Results

Figure 1 shows a series of thermal desorption spectra obtained after saturating a palladium(111) surface with ethylene oxide at 180 K collected at 2, 44, 43, and 29 amu. The broad peak centered at 255 K is predominantly attributed to ethylene oxide desorption. This conclusion is confirmed by the data in Table 1 which compares the fragmentation pattern of ethylene oxide with the desorption yield of the 255 K state; the good correspondence between these values indicates that this state is predominantly due to ethylene oxide. Note that the fragmentation pattern of ethylene oxide is very similar to that of acetaldehyde, and the desorption temperature of acetaldehyde from Pd(111) (325 K) is also marked on this figure. Analysis of this peak using the Redhead equation²⁰ and assuming a preexponential factor of 1×10^{13} s⁻¹ with an experimental heating rate of 8 K/s yields a desorption activation energy of \sim 15 kcal/mol for this state. This is

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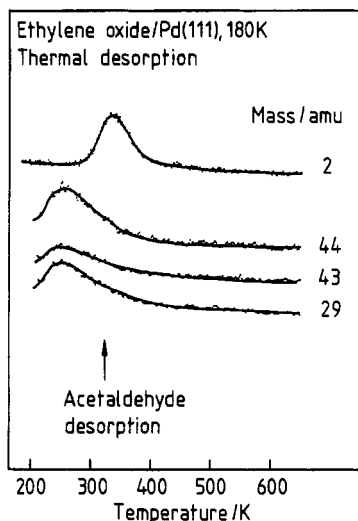


Figure 1. Thermal desorption spectra obtained at 2, 44, 43, and 29 amu following the saturation of a Pd(111) surface with ethylene oxide at 180 K. Marked also is the desorption temperature for acetaldehyde from Pd(111) (325 K).¹⁸

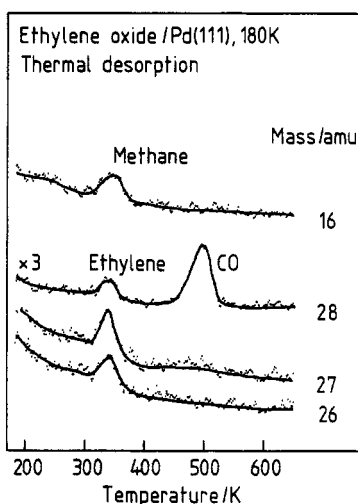


Figure 2. Thermal desorption spectra obtained at 28, 27, and 26 amu corresponding to ethylene (at 320 K) and CO (520 K; 28 amu) and at 16 amu corresponding to methane desorption, following the saturation of a Pd(111) surface with ethylene oxide at 180 K. The 28 amu spectrum has been attenuated by a factor of 3 compared with the other traces.

Table 1. Relative Areas of the ~220 K Desorption State Compared with the Mass Spectrometer Fragmentation Pattern of Ethylene Oxide

mass	thermal desorption yield	fragmentation pattern	mass	thermal desorption yield	fragmentation pattern
44	100	100	42	31	22
29	75	68	26	8	5
43	53	46	14	9	5

somewhat higher than for the ethylene oxide desorption activation energy from other transition-metal surfaces where ~10 kcal/mol is found for Ag(111),⁸ 12 kcal/mol for Cu(110),¹⁶ 13.2 kcal/mol for Fe(110),¹⁶ 14 kcal/mol for Ni(111),¹⁶ and 12 kcal/mol for Pt(111).⁹ In addition, the state shows a marked asymmetry displaying a high-temperature tail extending to ~350 K. This will be discussed in greater detail below.

The 28 amu spectrum (Figure 2) exhibits a major peak at 490 K which is absent in the 27 amu trace (note that the 28 amu spectrum has been attenuated by a factor of 3 compared to the other traces) and can therefore be

attributed to CO desorption, as well as a small peak at 340 K which is assigned to ethylene. This conclusion is confirmed by the desorption spectra obtained by monitoring the major fragments of ethylene (28, 27, and 26 amu; Figure 2). Comparison of the desorption yields (measured from the area under the desorption traces) with the fragmentation pattern of ethylene itself confirms that this peak is indeed due to ethylene. This peak temperature is slightly higher than the corresponding desorption peak for ethylene from Pd(111) which, at low coverages, is centered at ~300 K, suggesting that this state is reaction rather than desorption rate limited. This temperature, using conventional Redhead analysis,²⁰ corresponds to an activation energy of 20.2 kcal/mol.

Figure 2 also shows the desorption trace at 16 amu (corresponding to methane desorption) which exhibits a single peak centered at 345 K. Methane desorption has not been previously detected following ethylene oxide adsorption on transition metals and, given the findings of Davis and Barteau,¹⁸ indicates the deposition of C₁ fragments on the surface which subsequently hydrogenate to yield methane.

Finally, hydrogen evolution is detected in a peak centered at 337 K (Figure 1). This peak temperature is in very good agreement with that observed for hydrogen desorption following adsorption of acetaldehyde on Pd(111).¹⁸

Discussion

It is proposed that ethylene oxide synthesis from the reaction of ethylene with adsorbed atomic oxygen proceeds via the initial formation of an oxymetallocycle. The chemistry of ethylene oxide has been investigated on Pd(111) to test the hypothesis that the oxymetallocycle can react analogously to carbometallic intermediates according to Scheme 2.

While there is no direct evidence that ethylene oxide adsorbs with a concomitant ring opening, the desorption activation energy for ethylene oxide (~15 kcal/mol) is, in this case, somewhat higher than generally observed for other group VIII transition-metal surfaces (between 12 and 14 kcal/mol), in particular, compared with metals that would be expected to be significantly more reactive than palladium. Ethylene oxide adsorbs onto group VIII transition-metal surfaces via oxygen with the molecular plane essentially perpendicular to the surface²¹⁻²³ although angle-resolved X-ray photoelectron spectroscopic studies have recently provided evidence that the molecular plane is tilted with respect to the surface on Ni(110).²⁴ Rapid dehydrogenation of adsorbed ethylene oxide can be excluded since any surface hydrogen formed in this way would desorb from Pd(111) above 337 K.²⁵ Spectroscopic studies are currently underway to establish the precise nature of the surface species formed following ethylene oxide adsorption on Pd(111) at 200 K. Nevertheless, the detection of substantial amounts of CO and hydrogen indicates that a significant amount of the chemisorbed ethylene oxide has decomposed on the surface.

Reaction-limited ethylene formation is detected in a state centered at 340 K (Figure 2). There is no evidence for formaldehyde formation since its decomposition results

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in desorption of H₂ at 300 K and CO at 470 K, temperatures slightly lower than found in this case. Neither is any formaldehyde detected at 30 amu although, in any case, only ~3% of adsorbed formaldehyde desorbs molecularly from palladium.¹⁸

The detection of methane (Figure 2) indicates that CH_x species have formed on the surface and the desorption peak temperature, in this case (345 K), is identical to that for CH_{3(ads)} hydrogenation on Pd(111).¹⁸ There are two possible sources for CH_{x(ads)} in the context of Scheme 2. First, it can be formed by route i in which formaldehyde is evolved and surface carbenes are deposited. Alternatively, methyl groups can be produced by acetaldehyde decomposition (route iii). Note that the methane desorption temperature corresponds to that observed for methyl group rehydrogenation, favoring the latter explanation. Methylene hydrogenation would be expected to yield methane with kinetics different from that observed for methyl group hydrogenation unless the surface reaction step



was extremely fast compared with the methyl group rehydrogenation rate and the equilibrium for this reaction favored methyl group formation. On the contrary, however, adsorbed methyl groups dehydrogenate on Pd(111) to evolve hydrogen at ~410 K.¹⁸ In addition, the complete absence of formaldehyde decomposition products argues strongly that no carbenes are formed via pathway i in Scheme 2. This suggests that the methane arises from methyl group hydrogenation and that this arises from the formation of acetaldehyde via pathway ii of Scheme 2. Unfortunately, because of the mirror symmetry of ethylene oxide, no insights into this pathway can be gleaned by isotopic labeling. However, the hydrogen and CO desorption peak positions are also consistent with the formation of acetaldehyde on the surface.

Acetaldehyde desorbs from an $\eta^2(\text{C},\text{O})$ state on Pd(111) at 325 K,¹⁸ and as noted previously the mass spectrometer ionizer fragmentation pattern for this molecule is very similar to that for ethylene oxide. Note that the ethylene oxide desorption state at 255 K is asymmetric with a high-temperature tail extending to ~350 K. There are several possible explanations for this. It may be due to competitive decomposition and desorption pathways for adsorbed ethylene oxide, resulting in loss of this species and a corresponding decrease in the desorption rate. This would imply that the desorption temperature, in the absence of any thermal decomposition, would be even higher than 255 K, indicating a correspondingly larger desorption

activation energy. It is also possible that ethylene oxide desorption commences at well below the dosing temperature (~180 K) so that only the high-temperature portion of the state is detected. This would imply the onset of ethylene oxide desorption is at ~150 K and yield an anomalously large desorption peak width of ~140 K. An alternative and more likely possibility is that the asymmetric desorption state is composed of two overlapping peaks at 255 K due to ethylene oxide desorption and another state centered at ~325 K corresponding to the temperature at which acetaldehyde desorbs from Pd(111). This final explanation is consistent with the detection of CO, methane, and hydrogen at identical temperatures as observed from acetaldehyde decomposition on Pd(111).¹⁸

The products detected following ethylene oxide adsorption on Pd(111) are consistent with the routes shown in Scheme 2. The detection of CO clearly indicates that ethylene oxide has undergone some decomposition on Pd(111), the detection of methane along with CO indicates acetaldehyde formation (path iii, Scheme 2), and the detection of ethylene is consistent with pathway i.

The data suggest a commonality between alkene partial oxidation and metathesis reaction pathways. These results lead us to propose that the silver-catalyzed selective oxidation of ethylene proceeds via the initial formation of a metallocycle (Scheme 1). This forms ethylene oxide via reductive elimination of the metallocycle (path ii, Scheme 2). The present findings also suggest that ethylene oxide combustion on silver catalysts proceeds through acetaldehyde as a surface intermediate. Although this has been proposed previously, the results of this paper present the first direct indication of this.

Conclusions

The desorption products detected from the thermal decomposition of ethylene oxide adsorbed on Pd(111) at 180 K are consistent with a reaction scheme that assumes the formation of an oxymetallo-cyclic intermediate that decomposes in an analogous manner to that for carbometallicycles. Acetaldehyde has been identified as an intermediate in ethylene oxide decomposition on Pd(111) which supports the suggestion that further oxidation of ethylene oxide on the silver catalysts proceeds via acetaldehyde formation. Desorption products observed following ethylene oxide adsorption on other surfaces⁹ are also consistent with the reaction pathway proposed here.

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