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The Rate-Limiting Step for Olefin Combustion on Silver: Experiment Compared to Theory

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The oxidation of propylene by atomically adsorbed oxygen on Ag(110) has been studied over a wide range of oxygen adatom coverages between 0.05 and 0.5 monolayers. Over the entire range of coverage combustion occurs easily, the only products observed are CO_2 and H_2O, and all absorbed oxygen is found to react readily. The absence of acrolein as a product mitigates against the formation of allyl oxide as a combustion intermediate under these conditions. These results are in contrast to theoretical predictions concerning the mechanism of olefin combustion which invoke both homolytic C–H cleavage and oxygen insertion into a C–H bond to produce allyl oxide as an intermediate. Combustion of propylene and higher molecular weight 1-alkenes is proposed to occur predominantly via an acid–base reaction with chemisorbed oxygen. © 1993 Academic Press, Inc.

INTRODUCTION

Silver has been for some time the catalyst of choice for industrial epoxidation of ethylene. Normally supported on alumina and promoted both with electropositive and electronegative additives, silver catalysts are used to produce several million tons of ethylene oxide yearly (*1*). Although a completely satisfactory mechanism for the reaction of oxygen with ethylene remains to be developed, it is clear at this point that atomically chemisorbed oxygen on the silver surface is active for oxygen addition to the carbon–carbon double bond. The same atomically adsorbed oxygen also appears to be largely responsible for the competing and undesirable oxidative process of ethylene combustion to carbon dioxide and water (*1*, *2*). Similarly effective epoxidation of higher molecular weight linear alkenes is not achieved over silver catalysts, however (*3*, *4*). In this paper we address the mechanism of combustion of propylene and higher alkenes.

Carter and Goddard have used generalized valence bond (GVB) theory to calculate the energetics of the elementary steps for olefin oxidation on silver surfaces (*5*). Based on these calculations they suggested that:

(i) Two types of atomic oxygen exist on an Ag(110) surface. At low coverages a closed shell form predominates, whereas for $\theta_0 > 0.5$ ML an open shell, oxyradical is preferentially formed. The oxyradical is active for epoxidation and for combustion of higher olefins via a direct attack of the double bond followed by γC–H bond activation, whereas the closed shell form is relatively unreactive.

(ii) Molecularly adsorbed oxygen plays no role in the epoxidation reaction.

(iii) Little or no barrier exists for epoxidation of ethylene or propylene via the oxyradical.

(iv) The energetics for olefin combustion over silver are controlled by the *homolytic* bond dissociation energy of the reacting C–H bond(s).

(v) The combustion of higher olefins such as propylene, competes effectively with epoxidation due to formation of alkoxide

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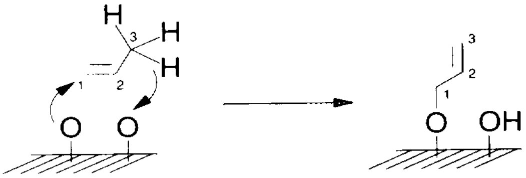

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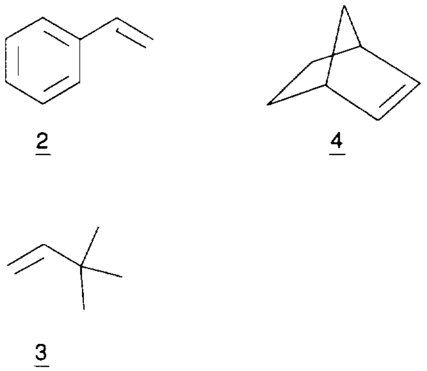
FIG. 1. Pathway proposed by Carter and Goddard for the oxidation of propylene over a silver catalyst (5). The reactions indicated by the arrows occur sequential, not in concerted fashion.

intermediates (1), not allylic intermediates (Fig. 1). For ethylene this route is much less favorable, and epoxidation selectivity is correspondingly higher.

The mechanism proposed by Carter and Goddard successfully rationalizes the extremely low epoxidation selectivities of propylene, 1-butene and 2-butene, and it successfully accounts for the highly selective (>50%) epoxidation of styrene (2) (3, 6), and 3,3-dimethylbutene (3) (7) over silver (see Scheme 1). However, norbornene (4) is epoxidized over Ag(110) with a selectivity of approximately 50% *regardless of the oxygen adatom coverage between 0.05 and 0.50 monolayers* (8). As discussed elsewhere (8), this result contradicts the first conclusion above, namely, that high selectivity for olefin oxidation requires an $O_{(a)}$ coverage greater than 0.5 ML on Ag(110).



SCHEME 1

In this paper, we show that combustion of propylene via an allylic intermediate is facile for oxygen coverages from 0.05 to 0.5 ML. Olefin combustion is not controlled by the homolytic dissociation energy of the reacting C–H bond; the key intermediate on the pathway for propylene combustion is not surface allyloxy (1), produced by the direct attack of the double bond and γC–H bond activation. The rate-limiting step for olefin combustion over silver is an *acid–base reaction* between an acidic C–H bond on the olefin and $O_{(a)}$ (a Brønsted base). For linear olefins, the products of the initial reaction step are an adsorbed hydrocarbon fragment and a surface hydroxyl group. The energetics for initial C–H bond activation are largely controlled by the gas-phase *acidity* of the reacting C–H bond, i.e., the heterolytic C–H bond dissociation enthalpy:

$$R\text{–}H_{(g)} \rightarrow R^-_{(g)} + H^+_{(g)} \quad \Delta H = \Delta H_{\mathrm{acid}}. \quad (1)$$

Combustion products then result from *scavenging* of these fragments by adsorbed oxygen.

EXPERIMENTAL

Temperature-programmed reaction mass spectroscopy experiments were carried out in a stainless-steel ultrahigh vacuum apparatus to be described in detail elsewhere (9). The operating base pressure of the chamber was $\approx 1 \times 10^{-10}$ Torr. The Ag(110) crystal surface was cleaned by repeated cycles of Ar^+ ion bombardment (500 eV, $\approx 5\ \mu A/cm^2$, 300 K) followed by annealing to 700 K until no impurities could be detected by Auger electron spectroscopy. Residual carbon-impurities were removed by oxygen adsorption/desorption cycles until the integrated temperature programmed reaction yield of CO_2 produced from carbon oxidation was less than 5% of the yield of desorbed dioxygen. Oxygen coverages were determined by comparing to $O_{(g)}$ yield for a particular oxygen exposure to that obtained for a saturation exposure, previously determined to deposit 0.50 monolayers (ML) $O_{(a)}$ (10). The crystal was in thermal contact with a liquid nitrogen cooled reservoir and could be cooled to 120 K, the temperature at which propylene adsorption was carried out. The crystal was mounted in a tantalum foil holder which was spot-welded to two tantalum support wires. The support wires were in turn mounted on the sample manipulator. The support wires were heated resistively, and the crystal was heated via thermal conduction from the supports. Heating rates between 120 and 700 K were approximately constant at ≈5 K/s. Temperature programmed reaction data were acquired using a UTI 100 C mass spectrometer interfaced to a microcomputer. Initially, product distributions were determined using a program allowing for the simultaneous collection of 150 consecutive ions in the mass spectrometer in order to absolutely identify all products (*11*), although with reduced temperature resolution. Temperature programmed reaction spectra reported here were acquired using a program allowing for the collection of up to ten ions. The mass spectrometer ionizer was shielded by a glass cap with an entrance aperture of diameter ≈3 mm. The crystal, 15 mm in diameter, was positioned approximately 2 mm from the mass spectrometer entrance aperature during temperature programmed reaction. This configuration allowed for the preferential detection of products from the center of the single-crystal face, minimizing detection from crystal edges and support wires.

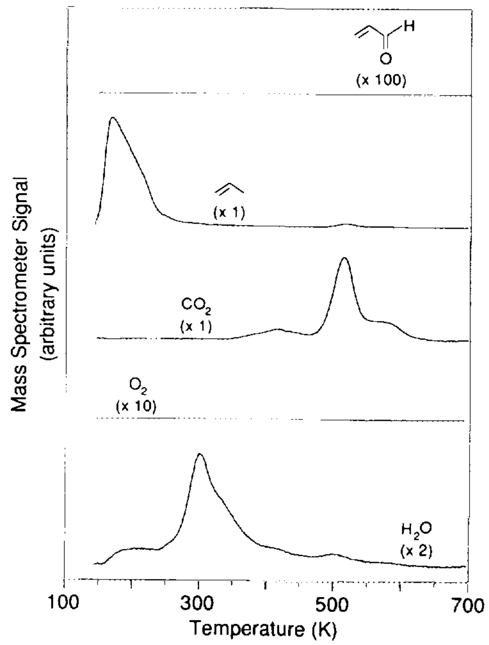


FIG. 2. Temperature-programmed reaction spectra of propylene on Ag(110) precovered with 0.50 monolayers of atomically adsorbed oxygen. Products detected in this case were water (detected as *m/e* 18), dioxygen (*m/e* 32), carbon dioxide (*m/e* 44), propylene (*m/e* 42), and acrolein (*m/e* 56). Adsorption occurred at 140 K, and the heating rate was approximately 5 K/s. Multiplication factors are referenced to the propylene spectrum.

RESULTS

The reaction of propylene on oxygen-atom precovered Ag(110) was studied over a wide range of oxygen coverages, from 0.05 to 0.5 monolayers (the saturation coverage under ultrahigh vacuum), using temperature-programmed reaction spectroscopy. Earlier work for oxygen coverages of less than ≈0.3 monolayers, the only gas-phase reaction products observed during temperature-programmed reaction were carbon dioxide and water, along with unreacted propylene (*12*). At high propylene-to-$O_{(a)}$ ratios and low oxygen coverages, adsorbed carbon-containing fragments can also be formed. In the work reported here, earlier results were entirely reproduced, and greater care was taken to search for higher molecular weight products in low yields by taking TPRS data at higher mass spectrometer sensitivities and observing a wider range of oxygen coverages. Except for different product yields, exactly the same reactions are observed when propylene is reacted on a surface with an oxygen coverage as high as 0.50 monolayers (Fig. 2). Unreacted propylene desorbs in a broad peak with a maximum desorption rate at 170 K. Water evolves principally at 300 K with a shoulder at 340 K, and in a broad feature extending out to 500 K. Carbon dioxide evolves in three peaks, at 415, 510, and 580 K. Importantly, *no* other gas-phase products are detected, even at this extremely high oxygen coverage. Specifically, no oxygenated products such as acrolein (CH_2CHCHO), propionaldehyde (CH_3CH_2CHO), or propylene oxide were observed, even at the highest mass spectrometer sensitivity. The noise limit of the TPRS spectra places an upper limit of approximately 0.0005 ML for the yield of any of these products. Reaction of propylene with 0.50 monolayers of $O_{(a)}$ also results in the deposition of carbon on the surface, which was removed by subsequent oxidation of the surface, as described in the Experimental section.

Interpretation of the temperature-programmed reaction data is straightforward and based on a large body of earlier work. Propylene evolution is due to desorption of reversibly and molecularly bound propylene from the Ag(110) surface. Water evolution at 300 K is attributed to the disproportionation of two surface hydroxyl groups:

$$2\,OH_{(a)} \rightarrow H_2O_{(g)} + O_{(a)}. \qquad (2)$$

The shoulder on the water evolution curve at 340 K is tentatively assigned to $O_{(a)}$-stabilized hydroxyl recombination, by analogy to previous work (*13*). The very broad, higher temperature water feature probably results from the scavenging of some surface-bound hydrocarbon fragments by $O_{(a)}$; carbon dioxide evolution likely results either from a similar process and/or from reaction of atomically chemisorbed carbon with $O_{(a)}$.

The above results conclusively demonstrate that only H_2O and CO_2 are formed from propylene on oxygen precovered Ag(110) independent of oxygen coverage between 0.05 and 0.5 monolayers. We therefore infer that combustion is affected by a *single* chemically distinct form of atomically chemisorbed oxygen on Ag(110) at all oxygen coverages employed here. We note further that there is no residual oxygen which desorbs at 590 K, clearly indicating that *all* of the adsorbed oxygen participates in the combustion. Also, the fact that low-temperature water evolution proceeds via hydroxyl disproportionation, not molecular desorption, strongly suggests that the initial oxidation step is C–H bond activation via an acid–base reaction between $O_{(a)}$ and propylene. EELS measurements show proton transfer to $O_{(a)}$ to occur by 150 K, indicating a very low activation barrier for initiating combustion. Carter and Goddard, however, proposed a combustion pathway involving the reaction of two oxygen atoms, one first attacking the double bond, and the other then activating the γC–H bond in the oxypropanyl radical via homolytic cleavage (Fig. 1).

This two-step mechanism is highly unlikely in our studies because the expected gas-phase products were not detected by temperature-programmed reaction mass spectrometry. The intermediate product of the Carter and Goddard mechanism is the chemisorbed allyl alkoxide species (1) (*5*). Surface alkoxides have been independently prepared on Ag(110) via reaction of the corresponding alcohol with $O_{(a)}$ (*4, 14, 15*). Primary and secondary alkoxides are stable on silver until approximately 300 K, at which temperature they decompose to form, among other products, gas-phase aldehydes or ketones (*4, 14, 15*). Allyl alkoxide (1) decomposes extremely selectively on Ag(110) during temperature-programmed reaction to form H_2, acrolein (CH_2CHCHO), and allyl alcohol (*16*). The fact that *no* oxygenated products except CO_2 are formed during temperature programmed reaction of propylene on Ag(110) precludes the existence of alkoxides as important intermediates for complete oxidation of propylene. It cannot be argued that γC–H bond activation is precluded by the inaccessibility of surface oxygen over this wide range of coverage, though it is possible that this reaction would become important at oxygen coverages above 0.5 ML.

As a final test for the existence of a surface-stable alkoxide, we attempted to chemically displace the intermediate formed from the reaction of propylene and $O_{(a)}$. Alkoxides on Ag(110) are readily displaced as alcohols via the adsorption of the strong gas-phase acid acetylene, C_2H_2, via the following reaction (*16*):

$$RO_{(a)} + C_2H_{2(a)} \rightarrow ROH_{(a)} + C_2H_{(a)}. \quad (3)$$

Formation of the alcohol ROH, if it occurs, can be detected in a subsequent temperature-programmed reaction experiment. Displacement of the intermediate(s) formed during propylene oxidation on Ag(110) was attempted in the following way. The Ag(110) surface was precovered with 0.50 monolayers of adsorbed oxygen atoms and then exposed to propylene at 100 K. The propylene exposure was sufficient to saturate the chemisorbed state. The Ag(110) surface was subsequently annealed to temperatures up to 350 K, cooled to 100 K, and then exposed to deuterated acetylene, C_2D_2. A temperature-programmed reaction experiment was then conducted. Displacement was attempted for six annealing temperatures: 100 (no anneal), 150, 200, 250, 300, and 350 K. In every case, attempted displacement of the propylene-derived intermediate(s) by C_2D_2 was entirely unsuccessful; unreacted C_2D_2 desorbed from the surface, and no alcohol desorption could be detected. The lack of *any* alcohol formation in the attempted displacement of the propylene oxidation intermediate(s) by C_2D_2 provides strong exidence that alkoxides are not formed during the reaction of propylene and $O_{(a)}$ on silver.

DISCUSSION

Any valid mechanism for olefin combustion must account for the fact that ethylene (*1*, *2*), styrene (2) (*3*, *6*), 3,3-dimethylbutene (3) (*7*), and norbornene (4) (*8*) are the only olefins which have been observed to undergo epoxidation with high selectivity (>50%) over silver. Other olefins such as propylene, 1-butene, and 2-butene are epoxidized over silver but with extremely poor selectivity (*17–19*). Carter and Goddard explained this observation by correctly pointing out that the allylic C–H bonds in propylene, 1-butene, and 2-butene are weaker than any of the C–H bonds in ethylene, styrene, 3,3-dimethylbutene, and norbornene. They proposed that epoxidation can compete with olefin combustion only due to radical-like reactions between a chemisorbed oxyradical (for $\theta_0 > 0.5$ ML on Ag(110)) and the alkene. Although this mechanism certainly rationalizes the low epoxidation selectivities of linear alkenes, it is inconsistent with experiments, since epoxidation of norbornene and styrene occur readily on Ag(110). It could be argued that the $-OCH_2CHCH_3$ radical proposed to be produced initially by the attack of the oxyradical on propylene reacts with a second oxyradical to form 1,2-propane dialkoxide, rather that suffer γC–H bond activation to form allyl alkoxide, rendering our measurements invalid. In fact, this dialkoxide reacts at low oxygen coverages to form the expected aldehydes and at moderate oxygen coverages to liberate formaldehyde and acetaldehyde (*20*), none of which are observed in propylene oxidation over the range of oxygen coverages studied. Further, Carter and Goddard state that for $\theta_0 \leq 0.5$ ML on Ag(110) only combustion will occur. If the combustion mechanism proposed by Carter and Goddard is *general*, 1-butene should combust readily. Instead, it reacts with adsorbed oxygen to butadiene via an acid–base reaction of the allylic hydrogen to yield predominantly butadiene (*21*). We therefore propose an alternative combustion mechanism.

We assert that the dominant rate-limiting step and dominant mechanism for olefin *combustion* over silver is the activation of a C–H bond by atomically chemisorbed oxygen ($O_{(a)}$). First, clean silver surfaces without chemisorbed oxygen are completely unreactive toward C–H bond activation. For instance, ethylene (*22*), propylene (*12*), 1- and 2-butene (9), cyclohexene (*23*), styrene (*24*), and 2-methylpropene (*20*) all quantitatively desorb from clean silver without reaction. This fact establishes either that (i) chemisorbed oxygen atoms themselves react with C–H bonds in the rate-limiting step, or

(ii) chemisorbed oxygen atoms perturb the electronic structure of silver to such an extent that silver becomes reactive for C–H bond activation. The latter possibility may be excluded since the hydrogen released to the surface from C–H bond activation inevitably evolves into the gas phase as water, even if C–H bond scission occurs well above the characteristic desorption temperature of dihydrogen. Second, we have been unable to react *either* $CH_2{=}CHCD_3$ or $CD_2{=}CDCD_3$ with absorbed oxygen on Ag(110). This pronounced isotope effect eliminates the possibility that oxygen attack at the double bond initiates the combustion. Furthermore, there is a pronounced kinetic isotope effect for ethylene combustion over a silver catalyst ($k_H/k_D \approx 2$ at 500 K) (*25*), indicating C–H bond activation as the rate limiting step.

What distinguishes those olefins which are epoxidized over silver from those which are not are the thermodynamic properties of C–H bonds. Propylene and all isomers of butene possess allylic C–H bonds which are both homolytically (ΔH_{bond}) and heterolytically (ΔH_{acid}) weak compared to any of the C–H bonds in ethylene, norbornene (*4*), styrene (2) and 3,3-dimethylbutene (3). For example the gas-phase acidity of an allylic C–H bond in propylene is 391 kcal/mol (*26*), while the gas-phase acidity of ethylene is 406 kcal/mol (*27*). The homolytic C–H bond dissociation energy of propylene is 88 kcal/mol (*28*), while that of ethylene is 106 kcal/mol (*29*). The origin of the lower heterolytic and homolytic bond enthalpies in propylene and 1- and 2-butene can be traced to the stabilization of the radicals and anions, respectively, relative to those derived from other alkenes. Ethylene, styrene and 3,3-dimethylbutene contain no allylic C–H bonds. There can be no resonance-induced stabilization of the norbornene-derived allylic radical and anion. Therefore, the gas-phase acidity of norbornene (402 kcal/mol) (*30*) is much closer to that of ethylene (406 kcal/mol (*28*) than that of propylene (391 kcal/mol) (*27*).

TABLE 1

Comparison of the Heterolytic and Homolytic C-H Bond Dissociation Enthalpies of Ethane and Acetylene

	ΔH_{acid} (kcal/mol)	$\Delta H_{\text{homolytic}}$ (kcal/mol)
C_2H_6	421(26)	100.3 ± 1.0(33)
C_2H_2	375.4(32)	132 ± 5(28)

Examination of the available experimental evidence makes it clear that the C–H gas-phase acidity, *not* C–H homolytic dissociation enthalpy, determines the energetics for C–H bond activation by atomically chemisorbed oxygen on silver. The strongest evidence for this differentiation has been derived from the reaction of methylacetylene (CH_3CCH) with atomically adsorbed oxygen ($O_{(a)}$) on Ag(110), which reacts according to (*31*)

$$H_3CCH_{(g)} + O_{(a)} \rightarrow CH_3CC_{(a)} + OH_{(a)}. \quad (4)$$

Deuterium labeling studies unambiguously show that it is the *acetylenic* C–H bond exclusively which breaks in this reaction. Acetylenic C–H bonds are not only good gas-phase acids, and hence weak towards heterolytic cleavage (*32*), but also strong with respect to homolytic cleavage (*28*). In contrast, relative to acetylenic C–H bonds, sp^3-hybridized bonds, such as those in a methyl group, are strong with respect to heterolytic cleavage (*27*) but weak towards homolytic cleavage (*33*) (Table 1). Because the acetylenic C–H bond cleaves when methylacetylene is reacted with $O_{(a)}$ on Ag(110) (*34*), it follows that heterolytic bond dissociation controls the energetics of the reaction.

Other evidence points to the fact that bond activation on silver is controlled by the gas-phase acidity of the reacting bond. For instance, if ethanol is adsorbed on $O_{(a)}$-precovered Ag(110) at 300 K, cleavage of the acidic O–H bond occurs to give a surface ethoxide and gaseous water (*34*):

$$2C_2H_5OH_{(g)} + O_{(a)} \rightarrow 2C_2H_5O_{(a)} + OH_{(a)}. \quad (5)$$

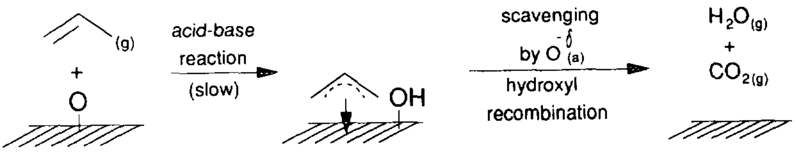


FIG. 3. Pathway proposed for the complete oxidation of propylene over a silver catalyst.

Subsequent adsorption of formic acid-d_1 (HCOOD), a stronger gas-phase acid then ethanol (*35*), on the ethoxide covered surface leads to quantitative displacement of the ethoxide (*32*):

$$HCOOD_{(g)} + C_2H_5O_{(a)} \rightarrow HCOO_{(a)} + C_2H_5OD_{(g)}. \quad (6)$$

Importantly, displacement occurs via reaction of the acidic O–D bond in formic acid; the C–H bond is completely unreactive at 300 K. Furthermore, displacement occurs despite the fact that the homolytic dissociation energy of the O–H bond in formic acid is larger than that in ethanol (107 vs 104 kcal/mol, respectively) (*36*). The displacement is best understood as an acid–base reaction between a strong acid ($HCOOH_{(g)}$) and strong base ($C_2H_5O_{(a)}$) to form a weak acid ($C_2H_5OD_{(g)}$) and weak base ($HCOO_{(a)}$). Many displacement reactions have now been observed on Ag(110), including displacement by C_2H_2 to form $C_2H_{(a)}$. The ability of a molecule to act as a displacing agent toward an absorbed base is directly related to its gas-phase acidity. Displacement occurs only if the gas-phase acidity of the displacing agent is greater than that of the acid formed upon displacement (*34*).

Because the energetics for C–H bond activation on silver appear to be determined by the C–H bond acidity, it is extremely likely that the *mechanism* for C–H bond activation on silver involves an acid–base reaction between the reacting C–H bond (an acid) and $O_{(a)}$ (a Brønsted base). Such a process implies the existence of intermediates which are at least partly ionic in nature. There is both experimental and theoretical evidence that ionic intermediates can be formed on silver. For example, surface carbonate ($CO_{3(a)}$) on Ag(110) has been the subject of intense experimental and theoretical scrutiny. Near edge X-ray adsorption fine structure (NEXAFS) studies of the electronic structure of $CO_{3(a)}$ strongly suggest that it is anionic in nature (*37*), as do X-ray photoelectron spectroscopy (XPS) measurements (*38*). Quantum mechanical claculations are in agreement with these results (*39*). Hence, the electronic structure of some species on silver can best be understood in terms of chemisorbed anions. This fact has important implications on the mechanism for olefin combustion over silver because it provides support for the assertion that C–H bond activation occurs via an acid–base reaction.

SUMMARY

The overwhelming majority of experimental evidence for oxidation of higher olefins on silver, including that reported herein, suggests that: (i) the rate-limiting step for combustion is C–H bond activation of acidic C–H bonds, and (ii) the C–H bond activation proceeds via direct reaction with chemisorbed oxygen atoms ($O_{(a)}$). Taken together, these facts suggest a pathway for olefin combustion on silver like that shown in Fig. 3 for the reaction of $O_{(a)}$ and propylene. The initial step is an acid–base reaction between $O_{(a)}$ and an allylic C–H bond, resulting in the formation of a surface hydroxyl group ($OH_{(a)}$) and a chemisorbed allyl species. $OH_{(a)}$ can subsequently react with a second hydroxyl via disproportionation to form gaseous water and regenerated $O_{(a)}$. The surface allyl group need not be stable with respect to further reaction. Indeed, if the rate-limiting step for reaction is activation of the allyl C–H bond, then further reaction should be rapid, with formation of combustion products carbon dioxide and water proceeding via a pathway that is yet unknown. $O_{(a)}$ addition to the double bond does not appear to be a dominant step on the combustion pathway. We propose that $O_{(a)}$ acts as a scavenging agent for the hydrocarbon fragment, stripping it of hydrogen (perhaps by way of acid–base reactions), and oxidizing the surface carbonaceous species CO_2, it remains open to question whether or not the reactive oxygen is radical-like.

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