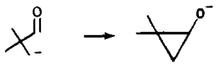
anions such as **1** and **2** make the application of eq 2 only semiquantitative.

The calculations for the acyl anions show different relative acidities at the different levels. Both MNDO and the ab initio methods predict that a formyl ester should be more acidic than an aldehyde at the formyl site by about 20 kcal/mol. The absolute MNDO values, and the ab initio ones relative to methane,[27] indicate that the acyl anion from the aldehyde should be comparable in basicity to hydroxide ion, consistent with experiment, and that the formate ester should be 1 to 9 kcal/mol more acidic than methanol. This acidity for the ester is reasonable in terms of the proposed mechanism of the Riveros reaction involving a hydrogen-bonded acyl anion as an intermediate. The position of the formamide in this series differs, however; the ab initio results place it only 2 to 4 kcal/mol more acidic than the aldehyde, while MNDO indicates that it is 10 to 18 kcal/mol more acidic, or two-thirds of the way to the ester. While our experiments indicate that the formamide is more acidic than ammonia at the formyl site, we cannot place a comparable lower limit on its acidity because of the wide range over which bases can cause the Riveros reaction to occur.[14,17] Nevertheless, the fact that methoxide and other alkoxide bases up to 15 kcal/mol weaker than it can cause formate esters to undergo the Riveros reaction, while none of these are reactive in this fashion with the formamide, is indicative that the amide is considerably less acidic at the formyl site than the ester. This agrees with the ab initio calculations.

Schleyer and co-workers[27] have proposed that the alkyl carbanion observed on reaction of hydroxide ion with 2,2-dimethylpropanal may actually exist as the cyclopropoxide **9**, the cyclic form being more stable by 11 kcal/mole by both MNDO and 4-31+G calculations. Our estimates of $\Delta H_{f,298}$ for this isomerization, based on group additivity[31] for the neutral acids and reasonable estimates of their acidity, agree with the thermochemistry from the MO calculations. It is known from solution-phase experiments, however, that the base-catalyzed isomerization favors the opposite direction: trimethylcyclopropanol opens to pinacolone.[32] This may reflect the neutral stability where the acyclic form is more stable by ca. 16 kcal/mol since the reaction with the hydroxide catalyst is endothermic. Even if the isomerization of the anion does favor the cyclic form in the gas phase, the lack of solvent to dispose of excess energy will result in the more stable cyclic anion being formed in a vibrationally excited state and quickly reverting to the open isomer. Considering the number of deuterium exchanges seen and the limited time window of the ICR, a few hundred neutral collisions, then if the proton-transfer reaction is at all slower than the collision rate,[33] the anion must spend most of its time in the open form. There is no precedent for an alkoxide exchanging protons with D_2O.[34] Thus, the cyclic ion may lie on the reaction surface but is probably not an intermediate in the exchange reaction.



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Acknowledgment. We thank the National Institutes of Health, Grant GM-27743-01, for support of this work.

Registry No. 3, 872-50-4; **4**, 5370-33-2; **8a**, 23314-06-9; **8b**, 84073-77-8; **8c**, 84073-78-9; **8d**, 81763-88-4; $HCONMe_2$, 68-12-2; $DCONMe_2$, 2914-27-4; $HCONEt_2$, 617-84-5; $HCON(n\text{-}Bu)_2$, 761-65-9; Me_3CCHO, 630-19-3; $(Me_3C)_2CO$, 815-24-7.

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Low-Pressure Oxidation Mechanism and Reactivity of Propylene on Ag(110) and Relation to Gas-Phase Acidity

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Received April 12, 1982

Abstract: The reaction of propylene with adsorbed oxygen atoms was examined on the Ag(110) surface by means of thermal desorption and surface titration experiments. The presence of oxygen was observed to enhance the adsorption of propylene at 140 K. Propylene reacted facilely with adsorbed oxygen at 140 K to produce H_2O and CO_2 which desorbed from the surface upon heating. Adsorbed carbon atoms were also deposited on the surface following thermal desorption of the volatile products. At 300 K the probability for the reaction of propylene with adsorbed oxygen atoms was two to three orders of magnitude less than at 140 K, suggesting the involvement of a weakly chemisorbed precursor state in the reaction. Surface titration experiments with acetic acid demonstrate that the reaction of propylene with oxygen reduces the number of Brønsted base sites on the surface by a factor of 2; these data were interpreted in terms of a mechanism by which propylene reacts irreversibly to form hydroxyl groups plus adsorbed carbon on the surface. A portion of the carbon is subsequently oxidized by oxygen atoms liberated by the disproportionation of adsorbed hydroxyl species. These results indicate that propylene is more reactive than ethylene toward adsorbed oxygen atoms; this observation is interpreted on the basis of relative hydrocarbon acidities in the gas phase.

Introduction

The heterogeneous selective oxidation of hydrocarbons is an area of immense industrial importance, and as such has received long and extensive study. Most of these processes are carried out over various composite metal oxides;[1,2] however, a few, such as the partial oxidation of ethylene over silver, utilize supported metal catalysts. While a number of questions remain to be answered about the properties of composite oxide systems, particularly with regard to the catalytic role of the various oxide components, the

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hydrocarbon chemistry is relatively well understood for processes such as propylene oxidation to acrolein over bismuth molybdate.[1] It is somewhat ironic, however, that the mechanisms of partial oxidation processes on a single-component catalyst such as silver remain elusive. Several reviews[1,3-6] of studies of the partial oxidation of ethylene to ethylene oxide on silver have recently appeared, yet it is safe to say that this process is still not understood. Neither the mechanism of the epoxidation reaction nor that of the competing combustion to CO_2 plus H_2O, nor, indeed, the nature of the active oxygen on the catalyst surface for either of these reactions has been conclusively demonstrated. Most of the mechanisms suggested for this reaction have attributed the epoxidation reaction to O_2 species and the combustion reaction to oxygen atoms on the catalyst surface.[1,3,7] However, several workers[8-10] have suggested reaction schemes in which the roles of these two oxygen species are reversed, and others[11-14] have suggested that only a single oxygen species may be involved in both reactions.

One particularly interesting aspect of this reaction is its uniqueness: not only is silver a unique catalyst for the epoxidation reaction, but ethylene is the only hydrocarbon which may be epoxidized with high selectivity (up to 80%[3,7]). In contrast, the selectivities reported for formation of propylene oxide from propylene over silver have generally ranged between 0[7] and 5%.[14] Because of the unfavorable selectivity of this reaction, it is of limited utility for the commercial production of propylene oxide, and considerably less attention has been devoted to the oxidation of propylene on silver than to that of ethylene. Previous studies have suggested that the lower epoxidation selectivity for propylene vs. ethylene is due both to a decreased rate for epoxidation of propylene[3,14] and to an increased rate for propylene combustion.[15,16] The increased favorability for propylene combustion has been attributed[17] to a greater reactivity of the allylic hydrogen atoms in propylene compared to that of the vinyl hydrogens in ethylene. This suggestion is consistent with observation of selectivities to propylene oxide as high as 14% for propylene in which the allylic hydrogens have been replaced with deuterium.[14]

The unique properties of silver as an oxidation catalyst are also suggested by the oxidation behavior of propylene. Although propylene may be oxidized to acrolein (CH_2CHCHO) on Cu_2O,[1] no evidence for this product has been reported on silver. It was suggested in one study[18] that acrolein species might be present on the silver catalyst during the oxidation of propylene, but that these could only be removed by further oxidation or decomposition. No product acrolein was therefore observed in the gas phase.

In a series of previous studies[19-23] we have examined the interaction of oxygen adsorbed on the Ag(110) surface with a number of simple hydrocarbons and organic compounds. The results of these studies have consistently demonstrated a pattern of reactivity for oxygen atoms which is strongly analogous to acid–base processes in homogeneous media. It has therefore been suggested[24-26] that relative hydrocarbon reactivities toward atomic oxygen on this surface may be explained in terms of the relative gas-phase acidities of the hydrocarbon molecules. We report here results for the oxidation of propylene on the Ag(110) surface and the utilization of surface acid–base titration reactions to characterize the reactivity of surface species.

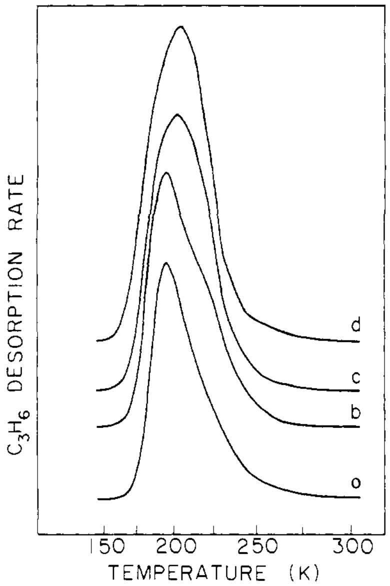

Figure 1. Propylene desorption from clean and oxygen-dosed Ag(110). Exposures: (a) 20 L of C_3H_6 at 140 K; propylene coverage ≈ one-third monolayer; (b) 120 L of O_2 at 170 K plus 20 of L C_3H_6 at 140 K; (c) 240 L of O_2 at 170 K plus 20 L of C_3H_6 at 140 K; (d) 600 L of O_2 at 170 K plus 20 L of C_3H_6 at 140 K.

Experimental Section

The experimental apparatus has been described in detail elsewhere.[27] Oxygen, propylene, and acetic acid were employed in this study. Each was dosed onto the surface via a separate stainless steel needle and leak valve as previously described. Propylene (Matheson 99.0%) was introduced directly from the gas cylinder into the dosing manifold without further purification.

The thermal desorption experiments were conducted as follows. The sample was first dosed with the desired oxygen exposure, and excess oxygen was pumped from the background. The sample was then dosed with propylene and heated following removal of excess propylene from the background. Thermal desorption products were monitored as a function of temperature by means of a UTI 100C mass spectrometer and a chromel–alumel thermocouple press-fitted to the sample. Carbon deposited during thermal desorption was removed by a second oxygen exposure at 300 K or below, followed by heating the sample to 800 K in a second thermal desorption experiment. The CO_2 produced by the clean-off of surface carbon was also monitored with the mass spectrometer. As previously noted[20,23,27,28] surface carbon could be completely removed from the surface provided that a sufficient number of oxygen adsorption/desorption cycles were conducted. A single oxygen exposure of 600 L (1 L = 1 langmuir = 10^{-6} torr·s exposure) was generally sufficient to remove surface carbon deposited by propylene oxidation. Because of the absence of other oxidation products (such as CO) in the oxidation of C(a),[20,23,28] the total amount of CO_2 desorbed from the surface by oxygen clean-off may be equated with the coverage of carbon initially present. This method has previously been shown to yield a quantitative measure of the surface carbon coverage,[23] as neither removal

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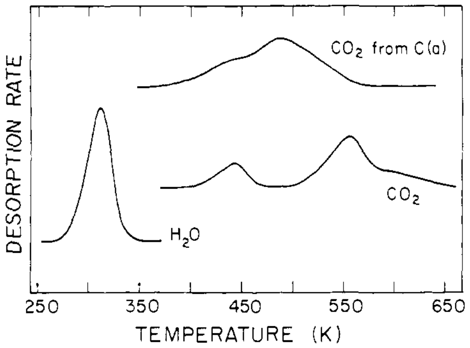

Figure 2. Product desorption spectrum for the reaction of propylene with O(a) on Ag(110). Exposures: 600 L of O_2 at 170 K + 20 L of C_3H_6 at 140 K. The upper CO_2 desorption curve was obtained following a 600-L exposure to O_2 subsequent to the first desorption experiment.

of carbon during oxygen adsorption at 300 K nor diffusion of carbon into the bulk of sample occurs.

Results

Propylene was observed to adsorb on the clean Ag(110) surface at 140 K, with the subsequent desorption peak at 190 K. The adsorption probability at this temperature was of the order of 0.1 or greater, although both the peak shape (see Figure 1) and the small separation of the adsorption and desorption temperatures suggest that the coverage was limited by the temperature of the silver sample. No reaction was observed for exposure of the clean Ag(110) surface to C_3H_6 at either 140 or 300 K.

The presence of oxygen atoms on the Ag(110) surface was found to increase the coverage of propylene which could be adsorbed at 140 K. Oxygen atoms induced adsorption of a second propylene state at 205 K which appeared as a higher temperature shoulder on the 190 K desorption peak for low coverages, and completely enveloped that state at higher coverages (Figure 1). Although the two peaks were difficult to separate, the magnitude of the 205 K state appeared to be roughly proportional to the initial coverage of oxygen atoms.

A similar modification of the adsorption behavior of ethylene by the presence of oxygen atoms on Ag(110) has previously been reported by several authors.[22,26,28-31] Indeed, Backx et al.[31] a 13-fold enhancement in the adsorption of ethylene on Ag(110) at 133 K due to the presence of adsorbed oxygen atoms. "Oxygen-induced adsorption" has also been reported for various oxygen-containing molecules on this surface.[19,20,32] It has been suggested[24] that this effect may be due to a small amount of charge donation from the adsorbates to the silver surface which is rendered slightly electron deficient by the presence of highly electronegative oxygen atoms. In the case of olefins such as ethylene and propylene this interaction would most likely occur with the olefin π system, for alcohols and aldehydes with nonbonding O(2p) electrons.

Propylene was also observed to react with oxygen atoms on the Ag(110) surface, resulting in the formation of H_2O, CO_2, and C(a), completely consuming the adsorbed oxygen atoms. Propylene adsorbed on the oxygen-dosed Ag(110) surface with a sticking probability of order unity at 140 K, and an exposure of 5 to 10 L was sufficient to saturate the surface. Upon heating the sample, the propylene states at 190 and 205 K desorbed first, with H_2O appearing in a single peak at 310 K and CO_2 at 440, 560, and 600 K (see Figure 2). No oxygen was observed to desorb at 590 K, indicating that oxygen atoms were completely removed from the surface reaction with propylene. Further, following the above heating with a second oxygen adsorption/heating experiment showed the formation of CO_2 above 450 K characteristic of the oxidation of adsorbed carbon atoms,[23] indicating that the reaction of propylene resulted in carbon deposition. The absence of formation of other hydrocarbon products was verified by monitoring various cracking fragments of the desorption products with the mass spectrometer. Products with m/e ratios of 2, 15, 28, 29, 40, 41, 42, 43, 44, and 60 were monitored and were not observed other than as cracking fragments of CO_2 or C_3H_6. Desorption products which may be eliminated on this basis include CH_4, C_2H_4, C_2H_6, allene, methylacetylene, acetone, and products containing CHO groups, including acrolein. Isomerization of propylene to cyclopropane may also be ruled out on the basis of the ratio of the m/e 15 to m/e 41 signals.

The reaction probability for propylene with adsorbed oxygen atoms at 300 K was found to be markedly different from that at 140 K. When the oxygen adlayer was exposed to propylene at 300 K, H_2O was not evolved during the adsorption of propylene even though the binding energy of water is sufficiently low to permit desorption at this temperature. The lack of detectable H_2O formation does not, however, indicate the absence of reaction between propylene and oxygen at 300 K. In fact, if no reaction occurred, propylene would simply desorb at room temperature. Provided that the propylene exposure was sufficient, the same levels of the CO_2 and C(a) products were formed at 300 K as at 140 K. At 140 K an exposure of only 5 to 10 L was sufficient to produce the amounts of these products shown in Figure 2; at 300 K a propylene exposure of at least 1500 L was necessary to produce the same levels. These results suggest a decrease of two or three orders of magnitude in the reaction probability with O(a) between 140 and 300 K. In view of the long exposures necessary to consume adsorbed oxygen with propylene at 300 K (of the order of several minutes at the dosing pressures used), it is most probable that the rate of H_2O formation during the reaction was simply too small to be detected. The absence of any hydrogen-containing products in the subsequent thermal desorption experiment indicates that the hydrogen liberated in the reaction of propylene with O(a) at 300 K is removed from the surface during propylene adsorption; the observation of H_2O following this reaction at lower temperature suggests that H_2O formation is the most probable route for hydrogen removal.

It has been previously pointed out[22] that some caution must be exercised in evaluating oxidation reactions on Ag(110) which require extended or high-pressure exposures to hydrocarbons. It was noted, for example, that the presence of 0.1% of C_2H_2 (with unit reaction probability) in C_2H_4 could produce an apparent reaction probability of 10^{-3} for ethylene. Similar impurity levels in the propylene used in this study cannot be ruled out, and the possibility of experimental artifact must be considered due to the clearly lower reactivity of propylene compared with species such as acetylene,[23] alcohols,[32] and carboxylic acids.[19,20] It should be noted, however, that the propylene oxidation data presented here were quite reproducible for both 140 and 300 K exposures. Further, although high exposures of propylene were indeed necessary to completely consume adsorbed oxygen at 300 K, the low exposures necessary at 140 K are the best evidence that significant impurities were not present in these experiments. An exposure of less than 10 L at 140 K was sufficient to (1) saturate the propylene adsorption states, and (2) completely consume O(a) to form H_2O and CO_2 during thermal desorption. In contrast, although similar exposures of C_2H_4 were sufficient to saturate the ethylene adsorption states at this temperature, less than 10% of the adsorbed oxygen was consumed in the subsequent thermal desorption experiment. These results clearly show a higher extent of reaction for O(a) with propylene than with ethylene for comparable exposures of these species at 140 K.

In contrast to the desorption of H_2O produced by the reaction of C_3H_6 with O(a) during thermal desorption, previous studies[19-21] have shown that more reactive species (e.g., carboxylic acids and acetylene) form and displace H_2O from the surface during reaction with O(a) above 160 K. Thus no H_2O is observed during thermal desorption experiments following the reaction of these acidic species with O (a). Similar desorption behavior to that of H_2O produced by oxidation of propylene was, however, observed for

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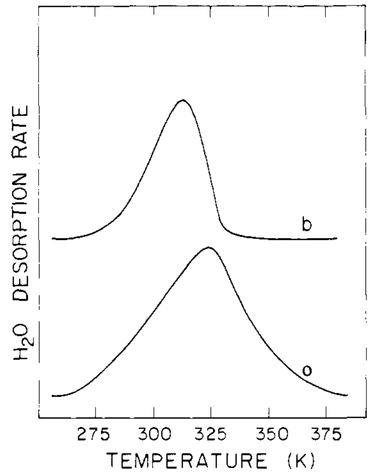

Figure 3. Comparison of H_2O formation from C_3H_6 + O(a) with OH(a) disproportionation on Ag(110): (a) H_2O from the disproportionation of OH(a). Hydroxyl adlayer formed by exposures of 600 L O_2 + 10 L H_2O at 170 K, heated to 270 K; (b) H_2O production from the reaction of C_3H_6 with O(a). Exposures = 600 L O_2 at 170 K + 20 L C_3H_6 at 140 K. These two desorption spectra were obtained for sequential doses of the surface with oxygen. The experimental conditions (pumping speed, heating rate) may therefore be assumed to be identical.

the interaction of H_2O with O(a). Previous studies[27,33] have shown that when H_2O is adsorbed at 140 K in the presence of O(a) on Ag(110), the subsequent thermal desorption spectrum contains four H_2O desorption peaks (170, 200, 240, and 320 K). Of these the peak at lowest temperature (170 K) was also observed for adsorption of H_2O on the clean Ag(110) surface; however, the highest temperature peak (at 320 K) is characteristic of the interaction of H_2O with O(a). It has been conclusively demonstrated[33] that this desorption state is due to the disproportionation of hydroxyl species via

$$2OH(a) \rightarrow H_2O(g) + O(a) \qquad (1)$$

These hydroxyl species are formed at lower temperature by the stoichiometric reaction of H_2O with O(a) (the reverse of eq 1) which produces two hydroxyl species for each oxygen atom initially present.[26,33]

The temperature of H_2O formation from the reaction of C_3H_6 with O(a) is compared favorably with that from the disproportionation of hydroxyl species (formed by the reaction of H_2O with O(a)) in Figure 3. The peak temperatures and the shapes of the two peaks differ slightly, indicating that if hydroxyl species are produced in the oxidation of propylene, the kinetics of their disproportionation on the resulting surface differ somewhat from those of a pure hydroxyl layer. This result is not surprising, as carbon-containing species must also be present on the surface during the oxidation of propylene as demonstrated by the evolution of CO_2 at higher temperature. These species could alter the site distribution as well as the energetics of hydroxyl disproportionation as compared with a pure adlayer.

The amount of H_2O evolved in the two experiments of Figure 3 is also instructive. The ratio of the areas for $H_2O(H_2O + O)/H_2O(C_3H_6 + O)$ in Figure 3 is 1.94 for the same initial oxygen exposure. Since the formation of OH species from the reaction of H_2O with adsorbed oxygen results in twice the number of OH species as the number of oxygen atoms initially adsorbed on the surface,[33] this results suggests that C_3H_6 reacts with O(a) to form a coverage of OH(a) species which is equal to the initial oxygen atom coverage. Since the surface was saturated with C_3H_6 at 140 K, the extent of this reaction cannot be limited by the supply of propylene.

In order to determine the characteristics of the carbon species formed on the surface during the oxidation of propylene, a series of titration reactions was conducted using acetic acid. It has previously been shown,[21,23] for example, that the oxidation of C_2H_2 on Ag(110) results in the formation of surface acetylides (HC_2(a) and C_2(a)) which my be subsequently titrated from the surface with acetic acid to re-form acetylene plus adsorbed acetate intermediates. Further, since both the reaction of C_2H_2 with O(a) and the titration of surface acetylides occur stoichiometrically, the coverage of surface acetates ultimately formed is equal to twice the initial oxygen atom coverage, precisely as in the direct reaction of CH_3COOH with O(a).[20]

Exposure of the propylene–oxygen adlayer to acetic acid was conducted following heating to three different temperatures in an attempt to characterize the surface species at each temperature. If the surface was exposed to CH_3COOH after reaction of C_3H_6 with O(a) at 140 K, propylene was observed to desorb from the surface during exposure to acetic acid, and the number of acetates formed (as determined by subsequent thermal desorption of the acetate decomposition products at 640 K[20]) was equal to one-half that produced by the direct reaction of CH_3COOH with O(a). If the surface was dosed with oxygen and propylene and heated to 250 K (resulting in desorption of the low-temperature C_3H_6 states but none of the H_2O or CO_2 products), no propylene was produced by titration but the acetate coverage was also one-half that expected from the direct reaction of CH_3COOH and O(a). Finally, if the propylene–oxygen adlayer was heated to 350 K to desorb the H_2O product before titration, no acetate formation was observed and the remainder of the thermal desorption spectrum was unchanged by exposure to CH_3COOH. These titration results are summarized as follows:

1. The reaction of C_3H_6 with O(a) irreversibly reduces the number of Brønsted base sites on the surface by a factor of 2.
2. The C_3H_6 formed during titration is simply displaced by acetic acid; the absence of this titration product following heating to 250 K demonstrates that the surface carbon species are not hydrogenated to propylene (or, indeed, to other hydrocarbons).
3. The reaction of C_3H_6 with O(a) thus appears to produce stoichiometrically and irreversibly one hydroxyl group per oxygen atom initially adsorbed, plus surface carbon species which are unreactive toward CH_3COOH.
4. Although the disproportionation of hydroxyl species upon heating to 350 K would be expected to return one-half the initial oxygen coverage to the surface (and provide the oxygen which subsequently appears in the product CO_2), this oxygen is also unreactive toward CH_3COOH.

Discussion

Based upon the thermal desorption and titration results presented above, the following mechanism for the reaction of C_3H_6 with O(a) is proposed:

$$C_3H_6(g) \xrightarrow{140\ K} C_3H_6(a) \qquad (2)$$

$$C_3H_6(a) + O(a) \xrightarrow{slow} OH(a) + C_3H_5(a) \qquad (3)$$

$$C_3H_5(a) + 5O(a) \xrightarrow{fast} 5OH(a) + 3C(a) \qquad (4)$$

$$C_3H_6(a) \xrightarrow{200\ K} C_3H_6(g) \qquad (5)$$

$$2OH(a) \xrightarrow{310\ K} H_2O(g) + O(a) \qquad (6)$$

$$C(a) + 2O(a) \xrightarrow{400-600\ K} CO_2(g) \qquad (7)$$

This sequence is consistent with the results of the previous section although it should be pointed out that direct evidence for some of the steps above is lacking, and these reactions are not meant to imply elementary steps.

Since the reaction of C_3H_6 with O(a) does not appear to proceed beyond formation of OH(a) species, the absence of hydrogen-containing products other than H_2O requires that step 4 be much faster than the initial hydrogen-transfer step 3 in the above mechanism. If this were not the case, substantial formation of H_2 or of hydrocarbons would be expected owing to the excess of hydrogen which would be liberated by decomposition of C_3H_5(a).

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It should be noted that a reverse reaction in step 3 is not precluded by this mechanism; in order to explain the observed stoichiometry, one simply requires that the lifetime of C_3H_5(a) in the presence of O(a) be much shorter than that of C_3H_6(a). The effect of a high ratio of the rates of step 4 to step 3 is to limit the number of propylene molecules which react with oxygen atoms to a level well below the 1:1 ratio which would be predicted by step 3 in the absence of step 4. If the ratio of the rates is very high, the amount of carbon deposited on the surface in step 4 would be limited to one atom for every two oxygen atoms initially present, as steps 3 and 4 require six oxygens and deposit three carbons. In view of the lack of titration activity for these species, it is unlikely that the C_3 framework remains intact, as such species could presumably be titrated in a similar fashion to C_2(a) from C_2H_2. Thus the initial reaction of propylene with O(a) appears to produce hydroxyl species and adsorbed carbon atoms.

As noted above, the stoichiometry of eq 3 and 4 suggests that one carbon atom should be deposited on the surface at 140 K for every two oxygen atoms initially adsorbed. Upon heating above 310 K to desorb H_2O, one-half of the original oxygen would be returned to the surface according to eq 6, thus producing an adlayer with a C/O ratio of 1:1. Heating this layer should therefore produce equal amounts of CO_2 + C(a). The ratio obtained experimentally of CO_2 desorbed to C(a) deposited (determined by subsequent oxidation) was 0.9 ± 0.3. The slightly low value of this ratio and the scatter in the data were most likely due to adsorption of small amounts of hydrocarbons from the background during exposure of the sample to oxygen to remove adsorbed carbon, thus producing slightly larger amounts of CO_2 in the carbon oxidation experiment than would have been produced from the initial carbon coverage. These results are therefore in agreement with the stoichiometries given by eq 3, 4, and 6.

It was also demonstrated by the titration experiments that exposure of the surface to acetic acid following H_2O desorption at 310 K from the propylene–oxygen layer did not result in formation of acetate species. This result indicates that the surface layer following desorption of H_2O from the reaction of propylene did not consist simply of unattached carbon and oxygen atoms, but that the association of these species rendered the oxygen unreactive toward even strong acids. This observation is somewhat similar to those of Rovida et al.[40] and Backx et al.[30,31] who reported formation of a "mixed carbon–oxygen adlayer" and of surface carbonates, respectively, from the reaction of C_2H_4 with O(a), although as noted[22] the source of these products is not unambiguous. The CO_2 desorption spectrum in Figure 2 does not resemble the decomposition of surface carbonates,[27] and it is unlikely that this intermediate is involved in the removal of C(a) from the surface as CO_2. At the least one may conclude that carbon and oxygen may be associated in a mixed adlayer which produces CO_2 upon heating. The absence of LEED patterns indicates that this adlayer has no long-range order. Further, the oxidation of carbon on the Ag(110) surface over a wide range of coverages suggests that the stoichiometry of the carbon–oxygen adlayer is not restricted to that produced by combustion of propylene.

No direct evidence was obtained for the short-lived C_3H_5 species in steps 3 and 4. The formation of OH species equal in number to the initial oxygen coverage clearly indicates that the combustion of propylene involves a hydrogen abstraction process and not attack of the oxygen upon the carbon framework. In such acid–base reactions of propylene the allylic hydrogen is the acidic proton[34,35] because of the resonance stabilization of the negative charge on the allyl anion formed as the conjugate base. Further, π-allyl species have been demonstrated on a number of metal oxides active for propylene oxidation.[36,37] Stable σ-bonded metal–propenyl complexes have also been identified.[38] The apparent lack of stability of this species on the Ag(110) surface is somewhat surprising in view of the stability of other intermediates (e.g., carboxylates, alkoxys, acetylides) formed by hydrogen-transfer reactions on this surface. In this regard the relative heats of reaction for

$$C_2H(g) \rightarrow C_2(g) + H \tag{8}$$

and

$$CH_2CH{=}CH_2 \rightarrow CH_2{=}C{=}CH_2 + H \tag{9}$$

may be relevant, since ΔH is unknown for the surface reactions. Table I lists values of the heat of formation of the appropriate species. Reactions 8 and 9 are endothermic by 116 and 58 kcal/mol, respectively. The analogous reaction 9 on the surface might then be expected to have the lower activation energy, qualitatively, since in both cases C–H bonds are being broken, and the hydrogens should be nearly equally accessible to the surface. This argument is, of course, only tentative, as the actual charge state and orbital energies of the adsorbed states are unknown.

Table I. Heats of Formation of Free Radicals and Stable Hydrocarbons Relevant to Propylene Decomposition on Ag(110)

substance	ΔH_f (kcal/mol)	ref
C_2H	134	39
C_2	198	40
$CH_2CH{=}CH_2$	39.4	41
$CH_2{=}C{=}CH_2$	45.9	42

With regard to the previous suggestion by Freriks et al.[18] of an acrolein intermediate in the oxidation of propylene over silver, the present results do not support such a species on the Ag(110) surface under the temperature and pressure conditions of this study. It should be pointed out, however, that the identification of this species by Freriks et al.[18] was based entirely on the observation of a species giving rise to a carbonyl stretching frequency at 1690 cm^{-1} in an infrared absorption experiment. This result may be consistent with the present observation of an intimate association between carbon and oxygen in the mixed carbon–oxygen adlayer formed by oxidation of propylene. Additional work is necessary in order to further characterize this intermediate state.

The results of the present study are also consistent with previous catalytic studies[15,16] which demonstrated a higher rate of combustion for propylene than for ethylene. Whereas propylene may react completely with O(a) to form OH(a), the extent of the corresponding reaction of ethylene is less than 10%.[22] Because of the lack of epoxidation activity for either hydrocarbon under UHV conditions, it is not possible to verify reports of a lower rate of epoxidation of propylene;[13,14] however, on the basis of thermal desorption results, the interaction of these hydrocarbons with the surface is quite similar.

We have previously suggested[21,24-26] that the reactivity of hydrocarbons toward oxygen adsorbed on Ag(110) may be understood in terms of their gas-phase acidity. The reactivity of propylene observed in the present study is consistent with that suggestion. The failure of C_3H_6 to react with O(a) to form and displace H_2O from the surface at either 140 or 300 K indicates that propylene is far less reactive than acetylene and other strong Brønsted acids previously studied.[19-21] The formation of stable OH species on the surface suggests that the reactivity of propylene is comparable to that of H_2O, and, as noted, propylene is clearly more reactive than ethylene. These trends are consistent with the gas-phase acidities of these species: the free energy of gas-phase heterolytic dissociation is comparable for H_2O and C_3H_6, less favorable than that of C_2H_2 by ~15 kcal/mol, and more favorable

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than that of C_2H_4 by at least 13 kcal/mol.

The application of such acid–base models to hydrocarbon reactivity is by no means restricted to Ag(110). For example, Kokes[35] previously noted that propylene and toluene could be dissociatively adsorbed on zinc oxide whereas ethylene could not. This behavior was explained in terms of a cutoff in the activity for dissociative adsorption between $pK_a = 35$ and 36 based on aqueous dissociation constants. This behavior is also consistent with the gas-phase acidities of these species; indeed, the acidity difference between C_3H_6 and C_2H_4 is much greater in the gas phase than in aqueous solution. These correlations point out the importance of acid–base properties in catalytic processes such as oxidative dehydrogenation which may involve proton-transfer reactions.

Conclusions

1. Propylene reacts facilely with O(a) on Ag(110) at 140 K to yield OH(a) and C(a). 2. The reaction probability for this reaction is higher than that of ethylene with O(a). A propylene precursor state appears involved. 3. Propylene is less reactive than C_2H_2 which can react to form and displace H_2O from the surface at this temperature. 4. Thermal desorption experiments following the reaction of C_3H_6 with O(a) produce H_2O, CO_2, and C(a). There is no evidence for partially hydrogenated carbon species on the surface at any temperature, although there is evidence for association of C and O in the mixed adlayer leading to CO_2 formation.

Acknowledgment. We gratefully acknowledge both the National Science Foundation through NSF Eng 23815 and NSF 12964 and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. Propylene, 115-07-1; silver, 7440-22-4; oxygen, 17778-80-2.

Theoretical Study of Gas-Phase Methylation and Ethylation by Diazonium Ions and Rationalization of Some Aspects of DNA Reactivity[1]

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Abstract: MNDO semiempirical molecular orbital calculations were carried out for the bimolecular reactions of the methyl- and ethyldiazonium ions with formamide, imidazole, pyrimidine, methylamine, and water with complete geometry optimization of all stable species and transition states. The activation barriers for methylation were larger, spanned a wider range, and indicated a greater preference for N- rather than O-alkylation than did those for ethylation. These results were rationalized on the basis of structural and electronic features of the transition states and in turn provided a simple explanation for the parallel behavior observed experimentally when DNA is exposed to diazonium ion precursors and which has been widely discussed in terms of the carcinogenic potency of the latter.

Introduction

Many carcinogenic alkylating agents are believed to owe their activity to conversion to highly reactive diazonium ions (**1**). Among these are the *N*-alkyl-*N*-nitrosoureas,[2a] *N*-alkyl-*N'*-nitro-*N*-nitrosoguanidines,[2b] 1,3,3-trialkyltriazenes,[2c] *N*,*N*-dialkylnitrosamines,[2d] 1-aryl-3,3-dialkyltriazenes,[2e] and probably the dialkylhydrazines.[2f] In vivo and in vitro DNA binding studies, in which sufficiently complete product analyses have been carried out, reveal that a great many of the nucleophilic sites are simultaneously alkylated by these agents.[3] However, a clear distinction exists between the methylating and ethylating agents of this type in that the latter react more extensively with the oxygen, relative to the nitrogen centers, than do the former.[4] This observation is of special significance in the search for meaningful relationships between chemical structure and biological activity since O^6-alkylation of guanine and possibly O^4-alkylation of thymine are believed to be critical mutagenic events, whereas 7-alkylation of guanine (the principal site of methylation) may be innocuous.[5] Thus several workers have sought an explanation for the different reactivities of ethylating and methylating agents of this kind toward the oxygen atoms of nucleic acids and their constituents. Swain–Scott constants,[9] hard–soft acid–base in-

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