

## Formation and Decomposition of Acetate Intermediates on the Ag(110) Surface

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The reactions of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{CHO}$  with oxygen adsorbed on a Ag(110) surface were examined by temperature-programmed reaction spectroscopy. Acetic acid reacted with surface oxygen to form  $\text{H}_2\text{O}$  plus a stable acetate intermediate. Acetaldehyde reacted with surface oxygen to form  $\text{CH}_3\text{CHO}_2(\text{ad})$  which decomposed at 250 K to liberate  $\text{H}_2$  and produce the stable acetate. The role of adsorbed oxygen in these two reactions was that of a strong base and strong nucleophile, respectively. The acetate intermediates formed by these two pathways were indistinguishable. The acetate intermediate decomposed near 640 K to produce  $\text{CO}_2$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{C}=\text{C}=\text{O}$  (and deposit small amounts of surface carbon).

### INTRODUCTION

The partial oxidation of ethylene to form ethylene oxide is perhaps the most well-known industrial process employing silver catalysts. Although this process has been utilized commercially for some time (1), the mechanism of the reaction is still not well understood. A variety of studies have been conducted on this system in order to examine both the nature of the adsorbed oxygen which participates in the reaction (2-6) and the mechanism of the partial oxidation reaction (7-9).

Several workers have proposed that adsorbed acetaldehyde and acetate species participate in the oxidation of ethylene to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  which competes with the partial oxidation to ethylene oxide. Twigg (7) examined the oxidation of ethylene and ethylene oxide and concluded that  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were formed during the partial oxidation of ethylene both by complete oxidation of ethylene and by further oxidation of ethylene oxide. He concluded that the oxidation of ethylene oxide occurred via isom-

erization to form acetaldehyde followed by rapid oxidation to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Other workers have examined these two pathways for  $\text{CO}_2$  formation, and it has been variously reported both that isomerization and oxidation of ethylene oxide is unimportant (10, 11) and, in contrast, that ethylene oxide is indeed oxidized via acetaldehyde (12).

Recent studies appear to support an acetaldehyde intermediate. Kenson and Lapkin (8) examined the isomerization and oxidation of ethylene oxide between 500 and 600 K and concluded that the isomerization to acetaldehyde occurred at a faster rate for chemisorbed  $\text{C}_2\text{H}_4\text{O}$  than for gas-phase molecules, so that the rate of isomerization and oxidation was limited by the rate of chemisorption of  $\text{C}_2\text{H}_4\text{O}$ . They further concluded that the partial oxidation of ethylene to ethylene oxide must involve complexes of multiple oxygen atoms which allow formation of  $\text{C}_2\text{H}_4\text{O}$  which does not go through a chemisorbed state (8). Oxidation of ethylene by single oxygen atoms on the surface would result, according to this model, in the formation of chemisorbed ethylene oxide which would be rapidly isomerized and then oxidized to  $\text{CO}_2$  and water. Kenson and Lapkin thus attributed the pathways for partial and complete oxidation of ethyl-

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ene to the existence of multiple oxygen species on the surface.

Force and Bell (9) also examined surface species present on silver during ethylene oxidation by means of infrared absorption. They observed absorption bands characteristic of  $\text{CH}_3\text{CHO}$  adsorbates, and proposed that the complete oxidation of  $\text{C}_2\text{H}_4$  to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  occurs via  $\text{CH}_3\text{CHO}$  species adsorbed on the surface, which are further oxidized via acetate and oxalate intermediates to the final products (9). They also proposed a mechanism for ethylene oxidation and combustion and the moderation of these reactions by chloride ions which involved the presence of a single atomic oxygen species on the surface (9). As in the model proposed by Kenson and Lapkin (8), Force and Bell proposed that the isomerization of  $\text{C}_2\text{H}_4\text{O}$  on the surface was irreversible. However, in the latter model the adsorption of  $\text{C}_2\text{H}_4\text{O}$  was reversible, allowing for the formation of  $\text{C}_2\text{H}_4\text{O}(\text{g})$  via oxidation of ethylene by a single oxygen atom. The model of Kenson and Lapkin required an oxygen pair in order to prevent rapid isomerization of the  $\text{C}_2\text{H}_4\text{O}$  produced on the surface (8). In any case it is clear that the nature and role of the adsorbed oxygen species and of the various hydrocarbon intermediates remain unresolved for this system.

In this study the reactions of  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$  on the clean Ag(110) surface and on a Ag(110) surface containing adsorbed oxygen were examined. Previous studies have shown both the applicability of temperature-programmed reaction spectroscopy (TPRS) for determination of the reaction mechanisms for such systems (13, 14), and the role of surface oxygen in promoting the reactivity of the Ag(110) surface (15, 16). Studies of reactions of  $\text{HCOOH}$ ,  $\text{H}_2\text{CO}$ , and  $\text{HCOOCH}_3$  (16) indicated that adsorbed oxygen plays three roles in reactions on this surface: those of adsorption promoter, strong base, and strong nucleophile. It was further demonstrated that the stable surface formate

could be formed either by deprotonation of  $\text{HCOOH}$  or by oxidation of  $\text{H}_2\text{CO}$  and  $\text{HCOOCH}_3$  via nucleophilic attack of the acyl carbon by surface oxygen (16). In the present work we have examined the  $\text{C}_2$  homologs of these species,  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{CHO}$ , in order to compare the reaction mechanisms of these species and the decomposition and stabilities of surface carboxylate intermediates.

#### EXPERIMENTAL

The experimental apparatus has been described in detail elsewhere (15). Thermal desorption experiments were conducted as previously described for the study of  $\text{HCOOH}$ ,  $\text{H}_2\text{CO}$ , and  $\text{HCOOCH}_3$  on this surface (16). Carbon deposited on the surface was removed after each thermal desorption experiment by exposure of the surface to 120 Langmuirs  $\text{O}_2$ , followed by heating the sample to 800 K to desorb  $\text{CO}_2$  and the excess oxygen. The sample was then cooled to the desired temperature and a second dose of oxygen was adsorbed on the surface. The excess oxygen in the background was pumped away, and the organic reactant was then dosed onto the surface. Thermally desorbed products were monitored with a UTI 100C quadrupole mass spectrometer. In some of these experiments up to five product masses were monitored simultaneously by rapidly (25 ms) changing the mass selected via control of the mass spectrometer with a PDP-11 computer. Although the signal-to-noise ratio was slightly worse for experiments in which the mass spectrometer was multiplexed, this technique permitted more accurate product ratios to be obtained, as several products could be monitored under exactly the same conditions of initial surface coverage, pumping speed, and heating rate.

#### RESULTS

As previously observed for a variety of other species (13, 16), the clean Ag(110) surface exhibited no reactivity toward either  $\text{CH}_3\text{CHO}$  or  $\text{CH}_3\text{COOH}$ . No adsorp-

tion of  $\text{CH}_3\text{CHO}$  was observed even when the surface was maintained at 160 K.  $\text{CH}_3\text{COOH}$  did adsorb on the clean  $\text{Ag}(110)$  surface at 160 K and yielded a desorption peak at 200 K, but no reaction of the adsorbed  $\text{CH}_3\text{COOH}$  was observed on the clean surface. As the lowest temperature to which the sample could be cooled was near the peak temperature for  $\text{CH}_3\text{COOH}$  desorption, the magnitude of this peak was quite sensitive to the adsorption temperature. The peak temperature was independent of the amount adsorbed. The kinetics of desorption of  $\text{CH}_3\text{COOH}$  from the clean  $\text{Ag}(110)$  surface was determined from analysis of the peak shape (by plotting  $\ln(\text{rate}/\text{coverage})$  vs reciprocal temperature), and a rate law of the form

$$r = 3.3 \times 10^{12} \text{ s}^{-1} \exp(-48 \text{ kJ mol}^{-1}/RT) [\text{CH}_3\text{COOH}(\text{ad})] \quad (1)$$

was obtained. The desorption temperature of  $\text{CH}_3\text{COOH}$  was unaffected by preadsorption of oxygen on the surface, although it was not possible to determine whether the saturation coverages of  $\text{CH}_3\text{COOH}$  were equal on the clean and oxygen-dosed  $\text{Ag}(110)$  surfaces due to the sensitivity of the peak magnitude to the adsorption temperature.

The adsorption of  $\text{CH}_3\text{CHO}$  on the oxygen-dosed  $\text{Ag}(110)$  surface at 160 K resulted in the formation of  $\text{CH}_3\text{CHO}_2(\text{ad})$ , which decomposed at 250 K to liberate  $\text{H}_2$  and produce a stable  $\text{CH}_3\text{COO}(\text{ad})$  intermediate species. Adsorption of  $\text{CH}_3\text{CHO}$  on the oxygen-dosed surface at 300 K directly produced  $\text{CH}_3\text{COO}(\text{ad})$  as the stable surface species with the  $\text{H}_2$  desorbing from the surface at this temperature during adsorption.

Unreacted acetaldehyde desorbed from the oxygen-dosed surface in two peaks at 215 and 233 K following adsorption at 160 K (see Fig. 1). The total coverage of acetaldehyde in these two peaks was  $1.8 \pm 0.2$  times that of the oxygen atoms initially

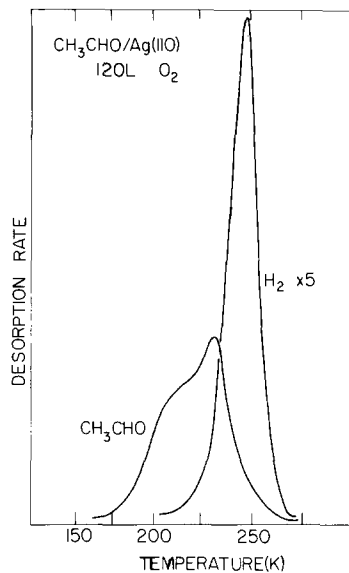


FIG. 1. Low-temperature product desorption spectrum for  $\text{CH}_3\text{CHO}$  adsorption on the oxygen-dosed  $\text{Ag}(110)$  surface: 120 Langmuirs  $\text{O}_2$ .

adsorbed on the surface; thus approximately three acetaldehyde molecules were adsorbed for each oxygen atom on the surface; one acetaldehyde per oxygen was oxidized to  $\text{CH}_3\text{CHO}_2(\text{ad})$ , and the unreacted, adsorbed acetaldehyde desorbed at low temperature. When acetaldehyde was adsorbed on a surface previously dosed with  $^{18}\text{O}_2$ , about 15% of the acetaldehyde desorbed from the surface was  $\text{CH}_3\text{CH}^{18}\text{O}$  (as determined from  $m/e = 31$  and 46 vs 29 and 44 signals); some oxygen atoms were exchanged between the adsorbed acetaldehyde and the surface oxygen. The desorption spectrum for both the labeled and the unlabeled acetaldehyde possessed the same two-peak shape, indicating that the acetaldehyde molecules in the two peaks had an equal probability of exchange. Similar exchange behavior was observed for the oxidation of  $\text{H}_2\text{CO}$  by  $^{18}\text{O}$  on the  $\text{Ag}(110)$  surface (16) and is discussed below.

The adsorption of  $\text{CH}_3\text{COOH}$  on the oxygen-dosed  $\text{Ag}(110)$  surface resulted in the formation of  $\text{CH}_3\text{COO}(\text{ad})$  species plus  $\text{H}_2\text{O}$ . For adsorption of  $\text{CH}_3\text{COOH}$  at 160

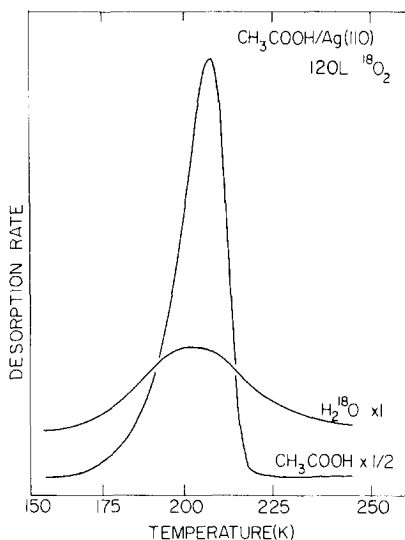


Fig. 2. Low-temperature product desorption spectrum for  $\text{CH}_3\text{COOH}$  adsorption on the oxygen-dosed Ag(110) surface: 120 Langmuirs  $\text{O}_2$ .

K,  $\text{H}_2\text{O}$  desorbed from the surface in a broad peak at 200 K (see Fig. 2). At higher dosing temperatures  $\text{H}_2\text{O}$  desorbed during adsorption of  $\text{CH}_3\text{COOH}$ . The evolution of  $\text{H}_2\text{O}$  during the adsorption of  $\text{CH}_3\text{COOH}$  on the oxygen-dosed surface was qualitatively similar to that produced by adsorption of  $\text{HCOOH}$  on this surface (16); the

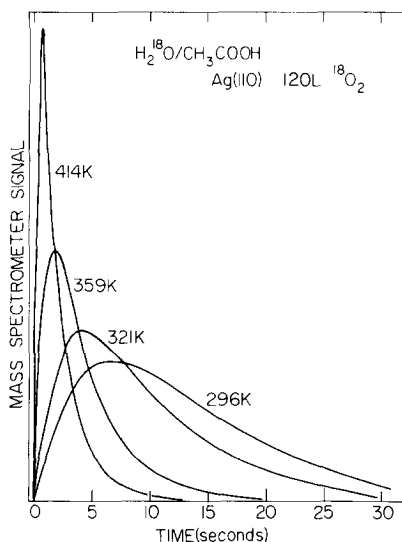


Fig. 3. Isothermal evolution of  $\text{H}_2\text{O}$  during  $\text{CH}_3\text{COOH}$  adsorption on the oxygen-dosed surface.  $\text{CH}_3\text{COOH}$  flux =  $2 \times 10^{14}$  molecules  $\text{s}^{-1}$ .

rate of water production rose to a maximum at nonzero time and then decayed approximately exponentially (see Fig. 3). It was previously shown (16) that such behavior could be explained by successive reaction of two adsorbed acid molecules with surface oxygen to first form adsorbed hydroxyl groups and then  $\text{H}_2\text{O}$ . Thus, as was observed for the adsorption of  $\text{HCOOH}$  on the oxygen-dosed surface, two molecules of  $\text{CH}_3\text{COOH}$  reacted with each surface oxygen atom to yield a pair of carboxylate intermediates on the surface and liberate  $\text{H}_2\text{O}$ . As was also observed for  $\text{HCOOH}$ , no exchange of oxygen occurred between the adsorbed  $\text{CH}_3\text{COOH}$  and the preadsorbed  $^{18}\text{O}$  on the Ag(110) surface.

The adsorbed acetate species formed from  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COOH}$  decomposed at 640 K to yield  $\text{CO}_2$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{C}_2\text{O}$ , and  $\text{C(ad)}$  as major products. The desorption spectra for the major mass fragments observed for decomposition of  $\text{CH}_3\text{COO(ad)}$  are shown in Fig. 4. As illustrated there, the decomposition spectrum for the acetate intermediate consisted of two overlapping peaks with different relative weights of the mass fragments between the two. By application of the cracking patterns for  $\text{CH}_3\text{COOH}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  listed in Table 1 to the relative abundances

TABLE I

Experimentally Determined Mass Spectrometer Cracking Patterns: Acetate Decomposition Products

$m/e$	$\text{CO}_2$	$\text{CH}_3\text{COOH}$	$\text{CH}_4$
60		40	
45		89	
44	100	20	
43		100	
42		29	
41		8	
29		27	
28	22	19	
16	22	32	100
15		70	90
14		43	20
13		15	10

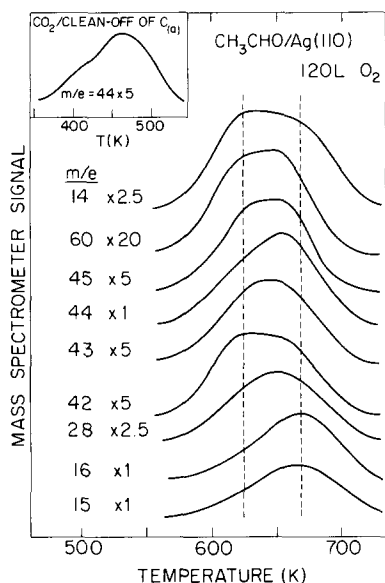


FIG. 4. Product desorption spectrum for the acetate intermediate.  $\text{CH}_3\text{COO}(\text{ad})$  formed in this case by exposure of the oxygen-dosed  $\text{Ag}(110)$  surface (120 Langmuirs  $\text{O}_2$ ) to  $\sim 5$  Langmuirs  $\text{CH}_3\text{CHO}$ .

of the mass fragments for  $\text{CH}_3\text{COO}(\text{ad})$  decomposition the contribution of these species to the product distribution was calculated as shown in Table 2. The cracking patterns for  $\text{CH}_3\text{COOH}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  were applied in succession to the product distribution. Normalizing with respect to

the  $m/e = 43$  product, all of the observed  $m/e = 60, 45, 43,$  and  $29$  products and a portion of all of the remaining masses listed in Table 2 were accounted for by an acetic acid product. Normalizing the the remainder with respect to  $m/e = 44$ , the products with  $m/e = 44$  and  $28$  and a portion of the  $m/e = 16$  product were assigned to  $\text{CO}_2$ . The remaining  $m/e = 15$  and  $16$  products and a portion of the  $m/e = 13$  and  $14$  were then assigned to  $\text{CH}_4$ . An excess of masses  $14$  and  $42$  was detected over that expected from  $\text{CH}_3\text{COOH}$  and  $\text{CH}_4$  alone. These fragments were attributed to the production of ketene,  $\text{H}_2\text{C}_2\text{O}$ . The cracking pattern deduced from the product mass fragments is in reasonable agreement with reported values (17) as shown in Table 3. Other possible products such as acetic anhydride, acetaldehyde, ethane, and ethylene which would yield larger relative amounts of masses such as  $43, 29, 30, 27,$  and  $26$  than were observed, were thus rejected as inconsistent with the distribution of mass fragments produced by  $\text{CH}_3\text{COO}(\text{ad})$  decomposition.

The total coverages of products were determined from the thermal desorption spectra by the method of Ko *et al.* (18) (Table 4). The coverage of the  $\text{H}_2\text{C}_2\text{O}$  product was

TABLE 2  
Mass Spectrometer Signals: Acetate Decomposition Products<sup>a</sup>

$m/e$	Relative area ( $\pm 15\%$ )	$\text{CH}_3\text{COOH}$ product	$\text{CO}_2$ product	$\text{CH}_4$ product	Remainder
60	6	8			
45	17	18			
44	100	4	96		
43	20	20			
42	24	6			18
41	7	1			7
29	6	5			
28	30	4	21		6
16	64	6	21	40	
15	52	14		36	
14	46	9		8	29
13	13	3		4	6

<sup>a</sup> Relative to  $m/e = 44$  signal = 100.

TABLE 3  
Ketene Cracking Patterns

<i>m/e</i>	From remaining mass fragments (Table 2)	Ref. (17)
42	60	94
41	23	27
28	20	11
14	100	100
13	20	13

determined by assuming the derived cracking pattern to be correct and calculating the appropriate mass spectrometer sensitivity (18). The coverages of the surface carbon produced by reaction were determined by dosing the sample with an excess of oxygen after completing the decomposition and cooling to room temperature. Carbon was then easily removed from the surface as CO<sub>2</sub> by heating, primarily by formation of surface carbonate species, which decomposed upon heating to 485 K (15). The small amounts of carbon formed and the overlap of the C(271) and Ag(266) and Ag(301) Auger peaks prevented determination of surface carbon coverages by AES.

As previously mentioned, the decomposition spectrum for the adsorbed acetate species contained two peaks of comparable magnitude near 640 K. Due to the overlap of these peaks the kinetics for the decomposition processes could not accurately be

determined. Some variation in the relative magnitudes of the two peaks was observed, giving rise to a variation of the shape for the overall desorption spectrum; however, no dependence of the peak shape or product selectivity upon coverage was discerned. In addition, no appreciable differences in the product selectivity were observed between acetate species derived from CH<sub>3</sub>COOH and those derived from CH<sub>3</sub>CHO for the same initial concentration of oxygen adsorbed on the surface.

#### DISCUSSION

The reactions of CH<sub>3</sub>CHO and CH<sub>3</sub>COOH with oxygen atoms adsorbed on the Ag(110) surface were quite similar to those of their C<sub>1</sub> homologs, H<sub>2</sub>CO and HCOOH (16). The following common features were observed for these reactions:

1. Both HCOOH and CH<sub>3</sub>COOH underwent deprotonation to form H<sub>2</sub>O and adsorbed carboxylate species. For both acids this reaction occurred at 220 K or below, resulting in the formation of two carboxylate species for each oxygen atom initially adsorbed on the surface.

2. Both H<sub>2</sub>CO and CH<sub>3</sub>CHO were oxidized to yield H<sub>2</sub> and adsorbed carboxylate species. The H<sub>2</sub> produced was reaction limited and desorbed from the surface in a narrow peak below room temperature.

3. The nondissociative adsorption of both H<sub>2</sub>CO and CH<sub>3</sub>CHO was enhanced by

TABLE 4

Product Coverages: Acetate Decomposition (Scaled to CO<sub>2</sub> = 100)

Product	Relative abundance	Basis mass fragment	M.S. sensitivity correction relative to <i>m/e</i> = 28/CO (18)
CO <sub>2</sub>	100	44	1.15
CH <sub>3</sub> COOH	65	43	3.5
CH <sub>4</sub>	74	16	2.0
H <sub>2</sub> C <sub>2</sub> O	49	14	1.8
C(ad)	11	44/CO <sub>2</sub>	1.15

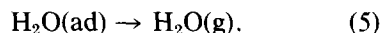
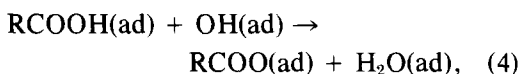
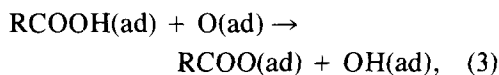
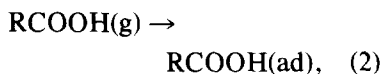
Product stoichiometry = C<sub>2</sub>H<sub>3.2</sub>O<sub>1.8</sub>

For CH<sub>3</sub>COOH,  $\theta_{\text{CO}_2} = 1 \times 10^{14}$  molecules cm<sup>-2</sup>

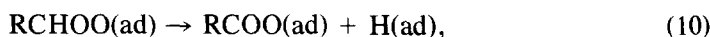
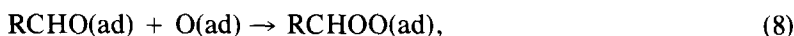
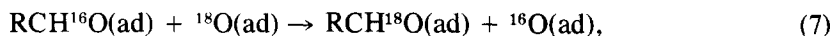
For CH<sub>3</sub>CHO,  $\theta_{\text{CO}_2} = 5 \times 10^{13}$  molecules cm<sup>-2</sup>

preadsorption of oxygen, and both species underwent limited exchange of oxygen when  $^{18}\text{O}$  was adsorbed on the surface.

Common mechanisms for the reaction of homologous species with oxygen may therefore be proposed. For carboxylic acids, this reaction may be written as follows:



For aldehydes the acyl-bound hydrogen atom is much less acidic, and the acyl carbon represents the most electron-deficient center in the molecule. Thus the oxidation of formaldehyde proceeded via nucleophilic attack of the oxygen at the acyl carbon to form a stable  $\text{H}_2\text{CO}_2$  species which decomposed by elimination of a hydrogen atom to yield a formate. As the same behavior, including limited oxygen exchange, was observed for  $\text{CH}_3\text{CHO}$ , the following general mechanism may be written:



The R group in the above mechanisms has not been extended beyond H- and  $\text{CH}_3$ - in the present studies; however, it is reasonable to postulate that the reactions of higher homologs would proceed in a similar fashion. Likewise it has been previously demonstrated that other oxygen-containing species react on the Ag(110) surface via mechanisms similar to those listed above. Wachs and Madix showed that both  $\text{CH}_3\text{OD}$  (13) and  $\text{CH}_3\text{CH}_2\text{OD}$  (14) react by loss of the alcohol proton to surface oxygen to yield  $\text{D}_2\text{O}$  and adsorbed alkoxy species. Likewise  $\text{H}_2^{16}\text{O}$  adsorbed on the surface in the presence of  $^{18}\text{O}$  underwent statistical exchange of oxygen with the surface, presumably by a rapid proton-transfer reaction involving surface OH groups (15). Also analogous to the oxidation of aldehydes shown above, methyl formate reacted via

nucleophilic attack of surface oxygen at the acyl carbon followed by elimination of a  $\text{CH}_3\text{O}$ - group to yield adsorbed formate and methoxy species (16). Thus it is expected that these acid-base and nucleophilic mechanisms may be applied to the reactions of a wide variety of species adsorbed on this surface and, indeed, may be extended to reactions on other metal surfaces, as similar behavior has also been observed for certain of the above-mentioned species on the Cu(110) surface (19-21).

Some qualitative differences were noted in the adsorption and reaction behavior of the  $\text{C}_2$  species in the present study as compared with their  $\text{C}_1$  homologs previously examined (16).  $\text{CH}_3\text{COOH}$  adsorbed nondissociatively on both the clean and the oxygen-dosed Ag(110) surfaces, whereas

such behavior for HCOOH above 150 K was observed on neither. This distinction is most likely due to the temperature of the experiment rather than to any substantial differences in the adsorption behavior of HCOOH and CH<sub>3</sub>COOH. Due to the higher molecular weight and polarizability (22) of CH<sub>3</sub>COOH, this species desorbs at higher temperature than HCOOH. The desorption rate equation for HCOOH obtained from molecular beam experiments (16, 23) predicts a desorption peak temperature of about 170 K for thermal desorption experiments, too near the adsorption temperature for a stable adsorbed state to be observed. The evolution of H<sub>2</sub>O from CH<sub>3</sub>COOH and HCOOH above 250 K was qualitatively similar. The broad thermal desorption curve for H<sub>2</sub>O from CH<sub>3</sub>COOH at low temperature consisted of two peaks, suggesting that at these temperatures the desorption of H<sub>2</sub>O was important. Likewise both aldehydes reacted with oxygen to form intermediates of the form RCHO<sub>2</sub> which decomposed at low temperature to liberate hydrogen. The H<sub>2</sub> peak from both H<sub>2</sub>CO and CH<sub>3</sub>CHO was more narrow than would be expected for a simple unimolecular decomposition ( $\nu = 10^{13} \text{ s}^{-1}$ ) at these temperatures. In the case of H<sub>2</sub>CO this narrow peak has been explained in terms of a coverage-dependent activation energy arising from attractive interactions within an ensemble consisting of an H<sub>2</sub>CO<sub>2</sub> intermediate surrounded by adsorbed formaldehyde molecules. As the surface was heated, formaldehyde desorbed from the surface and the ensembles were destabilized, resulting in a decrease in the attractive interaction and an acceleration of the rate of H<sub>2</sub> evolution. When acetaldehyde was oxidized to CH<sub>3</sub>CHO<sub>2</sub>(ad), only two additional acetaldehyde molecules per ensemble were adsorbed at 150 K, in contrast to the four formaldehyde molecules adsorbed per ensemble for the oxidation of H<sub>2</sub>CO. This result suggested that the net attractive interaction within the ensembles was lower

for acetaldehyde than for formaldehyde, possibly due to steric hindrance by the additional CH<sub>3</sub> groups present. Since the interaction energy was lower in the case of acetaldehyde, less absolute change of the interaction energy occurred upon decomposition of the ensembles, and the perturbation of the kinetics for H<sub>2</sub> evolution was therefore less for CH<sub>3</sub>CHO oxidation than for H<sub>2</sub>CO oxidation. The result of this diminished interaction energy was a somewhat broader peak for H<sub>2</sub>/CH<sub>3</sub>CHO (full width at half-maximum for H<sub>2</sub>/CH<sub>3</sub>CHO = 16 K, for H<sub>2</sub>/H<sub>2</sub>CO = 12 K, at heating rates of 17 K s<sup>-1</sup>). The detailed kinetics for H<sub>2</sub> evolution from CH<sub>3</sub>CHO were not, however, determined.

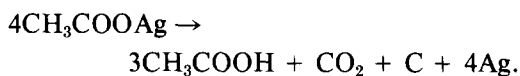
While the reactions of these homologous species to form stable surface intermediates were clearly similar, the decomposition behavior of the homologous intermediates was not so in all cases. Wachs and Madix demonstrated that alkoxy species such as CH<sub>3</sub>O (13) and CH<sub>3</sub>CH<sub>2</sub>O (14) reacted to form the corresponding C<sub>1</sub> or C<sub>2</sub> alcohols and aldehydes. The CH<sub>3</sub>O intermediate also gave rise to HCOOCH<sub>3</sub>; however, no CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub> was observed from the reactions at CH<sub>3</sub>CH<sub>2</sub>O species (14). Likewise the decomposition of CH<sub>3</sub>COO(ad) species produced on the Ag(110) surface was quite different from that of HCOO(ad). It was previously demonstrated (16) that HCOO(ad) species decomposed at 410 K to yield H<sub>2</sub> and CO<sub>2</sub>. The analogous behavior for CH<sub>3</sub>COO(ad) would produce CO<sub>2</sub> and CH<sub>3</sub>CH<sub>3</sub>; the latter product was not observed in this study, although a variety of other C<sub>1</sub> and C<sub>2</sub> products were observed.

It is clear from both the presence of two decomposition peaks and the variety of products observed that the decomposition of the CH<sub>3</sub>COO(ad) species is not a simple process. In order to form products such as H<sub>2</sub>C<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub>, it was necessary not only to break and reform C-H bonds as in the decomposition of adsorbed HCOO species, but C-O and C-C bonds as well. The mechanism of this reaction may best be

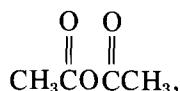


understood by examination of the pyrolysis of bulk silver acetate.

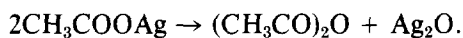
Early workers (24–28) proposed the following overall reaction for the decomposition of silver acetate:



Later studies by Kanevskaya and Schemyakin (29) revealed small amounts of acetic anhydride,



which was taken to be the major product, giving rise to much larger yields of  $\text{CH}_3\text{COOH}$  due to hydrolysis by small amounts of  $\text{H}_2\text{O}$  present. Under rigorously anhydrous conditions Kirshenbaum *et al.* (30) obtained high yields of the anhydride and verified that the principal reaction was indeed



Small amounts of  $\text{CO}_2$  and metallic silver were also detected (30). More recent thermodynamic studies (31) have indicated that Cu and Ag are unique among the Group IA & B and IIA & B metals in the thermodynamic favorability of the pyrolysis of their acetates to form acetic anhydride plus a metal oxide rather than acetone plus a metal carbonate as for the other metals. Further, Yakerson (31) has shown that the pyrolysis of  $\text{CH}_3\text{COOAg}$  to acetic anhydride becomes thermodynamically favorable at  $\sim 614$  K, in reasonable agreement with the temperatures for pyrolysis reported by other workers (29, 30) and with the decomposition temperature observed for the surface acetate in the present study.

Since no acetic anhydride was detected in the present study, the thermal stability and decomposition products of that species are also of interest. Several workers (32,33) have examined the thermal decomposition of gaseous acetic anhydride. Blake and Speis (33), for example, have reported that

acetic anhydride decomposed entirely to  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{C}_2\text{O}$  and obtained a first-order rate constant for this reaction of the form

$$k = 10^{11.27} \text{ s}^{-1} \exp(-137.4 \text{ kJ mol}^{-1}/RT). \quad (12)$$

If this rate law is applied to a reaction observed by TPRS assuming a heating rate of  $25 \text{ K s}^{-1}$ , the peak temperature predicted is 625 K, quite near that observed for the acetate decomposition. Thus if either "hot" gaseous anhydride molecules or anhydrides which interacted further with the surface were produced by pyrolysis of the acetate species, one would expect substantial decomposition of the anhydride to yield  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{C}_2\text{O}$ . As previously shown, these species were indeed two of the major products observed for the decomposition of adsorbed acetate species on the Ag(110) surface.

It remains to account for the other products. In order to understand the mechanism by which  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{C(ad)}$  were produced, let us first examine the differences between acetate species adsorbed on a silver surface and bulk silver acetate. If one assumes the silver–acetate bond to be the same in both cases (which in the light of the above evidence appears to be a good assumption), the most obvious difference is that of density; the adsorbed acetate species, at least at low coverages, are much less densely packed than the bulk compound, and a substantial free silver surface is also present which may promote further decomposition of the products, e.g., the anhydride. Ignoring the latter point for a moment, at low coverages the surface species might be too widely separated to interact to form the anhydride as in the bulk case, and an additional "unimolecular" decomposition path would be required. The most obvious model system for such a case would be gaseous species; however, as  $\text{AgOAc}$  cannot be vaporized without decomposing, an alternate model is required. A preferable model is thus acetic acid,

which can be vaporized without decomposition.

It is well known that acetic anhydride may be formed by pyrolysis of acetic acid. It has been proposed (34) that this reaction occurs first by dehydration to form ketene followed by reaction of the ketene with additional acetic acid to form the anhydride. This pathway is analogous to that observed for bulk silver acetate. In addition,  $\text{CH}_3\text{COOH}$  may be pyrolyzed via a second path to form  $\text{CH}_4$  and  $\text{CO}_2$  (34). In the case of  $\text{CH}_3\text{COOH}$ , such a reaction would require only internal rearrangement and bond cleavage; however,  $\text{AgOAc}$  is deficient in hydrogen for this reaction. If stable adsorbed  $\text{CH}_3$  species are not formed, and no recombination of  $\text{CH}_3$  groups is allowed, the formation of  $\text{CH}_4$  plus  $\text{CO}_2$  from adsorbed acetate species would also require the formation of carbon on the surface in order to liberate hydrogen atoms for  $\text{CH}_4$  formation. Thus by analogy with the pyrolysis of acetic acid, one would expect "isolated" surface acetate species to decompose to yield  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{C(ad)}$ . All of the products observed for the decomposition of  $\text{CH}_3\text{COO(ad)}$  species on the  $\text{Ag(110)}$  surface may thus be explained by reactions analogous to the pyrolysis of bulk  $\text{AgOAc}$  and gaseous acetic acid.

As can be seen from the previous discussion, one important point to be considered in comparing surface to bulk decomposition is the distribution of species on the surface. The oxygen initially adsorbed on the surface is not randomly distributed, but, as shown by Engelhardt and Menzel (35), forms long chains due to attractive interactions along the (100) direction on the (110) surface. At low coverages these chains are widely separated from one another due to repulsive interactions along the close-packed direction on the surface. However, there is no evidence that the adsorbed organic intermediates formed by reaction with surface oxygen maintain this configuration: no LEED patterns other

than the  $(1 \times 1)$  were observed for adsorbed  $\text{HCOO}$  and  $\text{CH}_3\text{COO}$  intermediates, although this may have been due to electron-stimulated decomposition in the electron beam. Previous studies (13, 16) have suggested that intermediates such as  $\text{CH}_3\text{O}$  and  $\text{HCOO}$  are mobile on the surface well below their respective decomposition temperatures; thus the interactions between  $\text{CH}_3\text{O(ad)}$  species appear to be dependent only upon the *total* coverage, and not upon the local differences in distribution which would be expected for different parent reactants. The lack of a coverage dependence upon the product distribution of  $\text{CH}_3\text{COO}$  species suggests that these species may indeed be ordered on the surface in a manner which reduces concentration effects. For example, if  $\text{CH}_3\text{COO(ad)}$  intermediates were arranged in long, one-dimensional chains on the surface as are observed for  $\text{O(ad)}$ , the local distribution of intermediates would not be affected by increasing concentration which manifested itself in increasing chain length. The complexity of this reaction and the evidence of interactions to form anhydride species both suggest that a mechanism based upon the decomposition of individual acetate species is insufficient to explain all of the reaction behavior observed.

#### CONCLUSION

It has been shown that acetaldehyde and acetic acid react in similar fashion to their  $\text{C}_1$  homologs with oxygen adsorbed on the  $\text{Ag(110)}$  surface. Carboxylate intermediates are formed from the aldehydes via nucleophilic attack of the surface oxygen at the acyl carbon followed by elimination of hydrogen and from carboxylic acids via deprotonation of a pair of acid molecules to form water. The acetate species thus formed undergo a complex decomposition at 640 K to form  $\text{CO}_2$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{C}_2\text{O}$ , and  $\text{C(ad)}$ . This decomposition involved two reaction pathways which have been accounted for by comparison with the pyrolysis of bulk silver acetate, acetic an-

hydride, and acetic acid. The  $\text{H}_2\text{C}_2\text{O}$  and  $\text{CH}_3\text{COOH}$  are formed via a surface anhydride and  $\text{CH}_4$  and  $\text{CO}_2$  via decomposition of individual acetate species. The acetate intermediates observed in this study were found to exhibit thermal stability well above temperatures (150 to 280°C) at which the oxidation of ethylene is typically conducted (1). No other reactive intermediates resulting from further oxidation of acetate species were observed even though in the initial stages of exposure of the surface to  $\text{CH}_3\text{COOH}$  or  $\text{CH}_3\text{CHO}$ , a large excess of oxygen atoms was present on the surface with respect to the number of acetates. Thus these results do not appear to support acetate intermediates as active species in the oxidation of ethylene.

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#### REFERENCES

- Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, New York/London, 1974.
- Czanderna, A. W., *J. Chem. Phys.* **68**, 2765 (1964).
- Meisenheimer, R. G., Ritchie, A. W., Schissler, D. O., Stevenson, D. P., Voge, H. H., and Wilson, J. N., in "Proc., 2nd Int. Congr. Surface Activity," Vol. 2, p. 299 (1957).
- Sandler, Y. L., and Durigon, D. D., *J. Phys. Chem.* **69**, 4211 (1965).
- Smeltzer, W. W., Tollefson, E. L., and Cambron, A., *Canad. J. Chem.* **34**, 1046 (1956).
- Kummer, J. T., *J. Phys. Chem.* **63**, 460 (1959).
- Twigg, G. H., *Proc. Roy. Soc. Lond. Ser. A* **188**, 92 (1946); *Trans. Faraday Soc.* **42**, 284 (1946).
- Kenson, R. E., and Lapkin, M., *J. Phys. Chem.* **74**, 1493 (1970).
- Force, E. L., and Bell, A. T., *J. Catal.* **38**, 440 (1975); **40**, 356 (1975); **44**, 175 (1976).
- Orzechowski, A., and MacCormack, K. E., *Canad. J. Chem.* **32**, 388 (1954).
- Margolis, L. Ya., and Roginski, S. Z., *Probl. Kinet. Katal. Akad. Nauk SSR* **9**, 107 (1957).
- Ide, Y., Takagi, T., and Keii, T., *Nippon Kagaku Zasshi* **86**, 1249 (1965).
- Wachs, I. E., and Madix, R. J., *Surface Sci.* **76**, 531 (1978).
- Wachs, I. E., and Madix, R. J., *Appl. Surface Sci.* **1**, 303 (1978).
- Bowker, M., Barreau, M. A., and Madix, R. J., *Surface Sci.* **92**, 528 (1980).
- Barreau, M. A., Bowker, M., and Madix, R. J., *Surface Sci.* **94**, 303 (1980).
- "Eight Peak Index of Mass Spectra," 2nd ed. Mass Spectrometry Data Centre, Aldermaston, Reading, U.K., 1974.
- Ko, E. I., Benziger, J. B., and Madix, R. J., *J. Catal.* **62**, 264 (1980).
- Wachs, I. E., and Madix, R. J., *J. Catal.* **53**, 208 (1978).
- Wachs, I. E., and Madix, R. J., *Surface Sci.* **84**, 375 (1979).
- Bowker, M., and Madix, R. J., *Surface Sci.* **95**, 190 (1980).
- Weast, R. (Ed.), "Handbook of Chemistry and Physics." Chem. Rubber Co., Cleveland, 1972.
- Fair, J. A., and Madix, R. J., to be published.
- Iwig, F., and Hecht, O., *Ber.* **19**, 238 (1886).
- Kachler, J., *Monatsch.* **12**, 338 (1891).
- Koenigs, W., *Ber.* **24**, 3589 (1892).
- Lieben, A., *Ber.* **25**, 1188 (1892).
- Kronig, W. Z., *Angew. Chem.* **37**, 667 (1925).
- Kanevskaya, S. G., and Schemyakin, M. M., *Ber.* **69**, 2152 (1936).
- Kirshenbaum, A. D., Streng, A. G., and Hauptschein, M., *J. Amer. Chem. Soc.* **75**, 3141 (1953).
- Yakerson, V. I., *Izv. Akad. Nauk SSSR. Otd. Khim. Nauk* **6**, 1003 (1963).
- Sezwarc, M., and Murawski, J., *Trans. Faraday Soc.* **47**, 269 (1951).
- Blake, P. G., and Speis, A., *J. Chem. Soc. B*, 1877 (1971).
- Hurd, C. D., "The Pyrolysis of Carbon Compounds," Amer. Chem. Soc. Monogr. Ser. No. 50. Amer. Chem. Soc., Washington, D.C., 1929.
- Engelhardt, H. A., and Menzel, D., *Surface Sci.* **57**, 591 (1976).