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The Relationship of Adsorbed Species Observed by Infrared Spectroscopy to the Mechanism of Ethylene Oxidation over Silver

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A combined infrared and kinetic investigation was performed on the oxidation of ethylene over a silver catalyst. Based upon the surface structures deduced from the spectra and additional information taken from the literature, a mechanism was developed to interpret both the epoxidation and combustion processes. The proposed mechanism explains qualitatively the kinetics observed in the present investigation and the variations in selectivity as a function of reactant and product concentrations reported in the literature by previous investigators.

INTRODUCTION

Numerous reports have been published concerning the kinetics of ethylene oxidation over a silver catalyst (*1-5*). From these studies and complementary ones devoted to the adsorption of reactants and products, attempts have been made to explain the formation of the products, ethylene oxide, carbon dioxide, and water. To date, however, generally accepted mechanisms for the epoxidation and combustion reactions have not been established and considerable differences of interpretation still exist. Critical questions which are yet to be resolved include: the extent to which oxygen is adsorbed as atoms versus molecules; the relationship of atomically and molecularly adsorbed oxygen to the final products; and the form in which ethylene reacts with adsorbed oxygen, i.e., gaseous or adsorbed.

While a number of surface species have been postulated to explain the mechanism of ethylene oxidation, only limited experimental observations of the surface structures have been reported. Gerei *et al.* (*6*) have used infrared spectroscopy to determine the adsorbed species formed when ethylene is adsorbed on a silver surface partially covered by oxygen. From the spectra it was concluded that ethylene adsorption, at a temperature (95°C) below which oxidation takes place, occurs through a rupture of the double bond to form a peroxide structure. The existence of such a structure has been confirmed by Kilty *et al.* (*7*) by examination of the isotopic shifts produced when $^{18}O_2$ and its mixtures with $^{16}O_2$ are used. It was noted, however, that the peroxide structure is not stable at higher temperatures (> 100°C) and that only an alkoxide-type structure is observed. Similar structures were observed by Gerei *et al.* (*6*) when ethylene oxide was adsorbed on silver indicating that adsorption is accompanied by a rupture of the epoxide ring.

In an earlier paper (*8*) we discussed the use of infrared spectroscopy to characterize the adsorbed species present on the surface of a silver catalyst during the oxidation of ethylene. Through a comparison of the spectra obtained under reaction conditions with those observed when individual reactants or products were adsorbed, identification could be made of a number of surface structures. Thus, it was determined that ethylene adsorbs with the assistance of oxygen coadsorption to form an olefinic structure similar to that known for complexes of ethylene with individual silver ions. Ethylene oxide adsorbtion was observed both in the absence and presence of oxygen. In the former case two ring-open structures were identified, viz., $-O-CH_2CH_2\cdot$ and $-O-\dot{C}HCH_3$. The second structure was also observed for adsorbed acetaldehyde indicating that a part of the adsorbed ethylene oxide undergoes isomerization. In the presence of oxygen a ring-closed form of adsorbed ethylene oxide could also be observed but this form was not present under reaction conditions. Carbon dioxide was found to absorb in two forms. In the first the axis of the molecule is parallel to the surface and the bonding weak enough to allow rotation. In the second form the carbon dioxide interacts with adsorbed oxygen atoms to form mono- and bidentate carbonates.

Under reaction conditions, two bands were observed which were not directly relatable to the adsorption of reactants or products. The first was a carbonyl band most likely due to carbonyl groups present in the partially oxidized intermediates which precede the formation of carbon dioxide and water. The second band occurred at a frequency only slightly downscale from that for carbon dioxide. This was assigned to a carbon dioxide molecule adsorbed through one of its oxygen atoms. This structure was not observed when carbon dioxide was adsorbed by itself and hence is believed to be derived from the oxidation of ethylene.

The purpose of the present work was to explore further the relationship between the structures identified by infrared spectroscopy and the mechanisms of the epoxidation and combustion reactions. In particular it was desired to deduce the role played by adsorbed ethylene. To this end experiments were carried out in which the rates of reaction and the spectra of adsorbed species were obtained as a function of temperature and reactant concentrations. The effects of product inhibition were also explored.

EXPERIMENTAL

The catalyst used in this work was identical to that prepared for our previous studies (*8*) and consisted of a 6.6% loading of silver on Cab-O-Sil M-5. About 200 mg of this material was pressed into a circular disk $1\frac{1}{8}$ in. in diameter. To allow for a measurement of the disk temperature, a copper-constantan thermocouple with wires 0.002 in. in diameter was embedded into the disk. Further details concerning catalyst preparation and pretreatment can be found in Ref. (*8*).

The experimental apparatus was essentially the same as that described by London and Bell (*9–10*). The central component is a heated infrared cell located in the sample compartment of a Perkin-Elmer 457 spectrometer. The catalyst disk is held within the cell so that it is aligned with the sample beam of the spectrometer. A second disk, consisting of pure Cabosil, is held in the reference beam. Using this technique it is possible to record the spectrum of only those species adsorbed on the catalyst and to subtract the spectrum of the silica support and of reactants and products present in the gas phase (*10*).

In all of the runs described here the cell was used in a batch recycle mode, recirculation being provided by a stainless steel bellows pump. Once filled with a reactant mixture, the recirculation loop and cell were operated continuously for periods lasting up to 18 hr. Periodic analyses of the gas composition in the loop were performed using a Varian Aerograph 90P3 gas chromatograph fitted with a 24-ft-long, $\frac{1}{4}$-in.-diameter column packed with Porapak Q. Infrared spectra were recorded at the same time that gas analyses were being performed.

Between runs the catalyst was reduced using the following procedure. The cell and recirculation loop were first purged with helium at 220°C for 6 hr. At this point a 1-atm mixture containing 12% hydrogen in helium was introduced and the catalyst was reduced at 250°C for 6 hr. After reduction, the cell was evacuated to less than 10^{-6} Torr, at which point the catalyst was ready for the start of a new run. The use of this procedure was found to yield reproducible results (*8*).

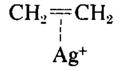
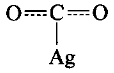
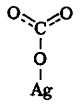
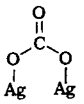
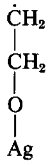
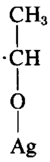
RESULTS

A representative sequence of spectra obtained during a run is shown in Fig. 1. The bands observed in these spectra can be related to the surface structures shown in Table 1 based on the assignments reported previously (*8*). In the absence of products in the gas phase the only features present are those for adsorbed ethylene. With increasing time, bands appear which can be identified with adsorbed ethylene oxide and carbon dioxide. Bands are also seen for species containing carbonyl groups and for mono- and bidentate carbonate structures.

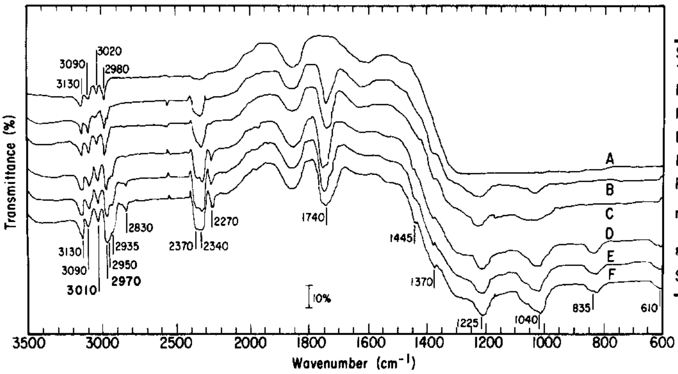
As noted in the previous section, the recirculation loop was flushed with helium at the end of each run and prior to the reduction of the catalyst. Attempts were

TABLE 1

Assignment of Infrared Bands to Surface Structures[a]

ν (cm^{-1})	Structure	
3130 3090 3020 2980	 $CH_2{=}CH_2 \cdot Ag^+$	(I)
2270	 $O{=}C{=}O{-}Ag$	(II)
2350	 $O{=}C{=}O \cdot Ag$	(III)
1365 1230 1035 810 605	 $O_2C{-}O{-}Ag$ (IV) and  $O{=}C(OAg)_2$	(V)
2970 2920 2890 2820 1080 860	 $\dot{C}H_2{-}CH_2{-}O{-}Ag$ (VI) and  $CH_3{-}\dot{C}H{-}O{-}Ag$	(VII)

[a] See Ref. (*8*) for a detailed discussion of the assignment of each band.



Spectrum	A	B	C	D	E	F
Time (hr)	0	1	3	6	10	13
P_{O_2} (atm)	0.236	0.230	0.213	0.188	0.166	0.154
$P_{C_2H_4}$ (atm)	0.099	0.094	0.085	0.073	0.065	0.054
P_{CO_2} (atm)	0.0	0.005	0.013	0.025	0.036	0.041
P_{H_2O} (atm)	0.0	0.005	0.013	0.025	0.036	0.041
$P_{C_2H_4O}$ (atm)	0.0	0.002	0.007	0.012	0.017	0.020
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	77.0	74.0	70.5	63.3	35.1	22.0
$r_{CO_2}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	162.0	151.0	147.2	125.8	76.6	51.8
$S_{C_2H_4O}$ (%)	48.7	49.5	48.9	49.8	47.8	45.9

Fig. 1. Sequential spectra taken during a run at T = 220°C.

TABLE 2

REACTION RATES AND SELECTIVITY AS A FUNCTION OF GAS COMPOSITION AND TEMPERATURE

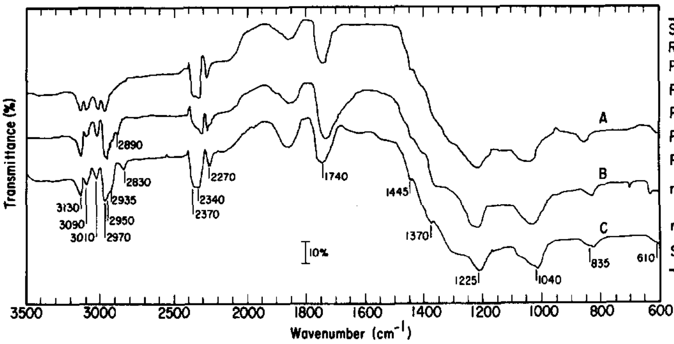
Run no.	T (°C)	t (hr)	P_{O_2} (atm)	$P_{C_2H_4}$ (atm)	$P_{C_2H_4O}$ (atm)	P_{CO_2} (atm)	P_{H_2O} (atm)	$r_{C_2H_4O}$ (μmol/g Ag min)	r_{CO_2} (μmol/g Ag min)	$S_{C_2H_4O}$ (%)
R-8	220	0	0.236	0.099	0.0	0.0	0.0	77.0	162.0	48.7
		1	0.230	0.094	0.002	0.005	0.005	74.0	151.0	49.5
		3	0.213	0.085	0.007	0.013	0.013	70.5	147.2	48.9
		6	0.188	0.073	0.012	0.025	0.025	63.3	125.8	49.8
		10	0.166	0.061	0.017	0.036	0.036	35.1	76.6	47.8
		13	0.154	0.054	0.020	0.041	0.041	22.0	51.8	45.9
R-7	220	0	0.287	0.118	0.0	0.0	0.0	104.0	225.0	48.0
		1	0.273	0.113	0.003	0.006	0.006	94.4	197.5	48.9
		3	0.255	0.101	0.008	0.017	0.017	89.4	177.3	50.2
		6	0.227	0.089	0.016	0.031	0.031	82.6	146.2	53.1
		10	0.200	0.074	0.022	0.045	0.045	31.6	107.0	37.1
		13	0.184	0.067	0.024	0.053	0.053	18.6	64.6	36.5
R-4	220	0	0.383	0.177	0.0	0.0	0.0	155.3	332.6	48.3
		1	0.375	0.170	0.005	0.010	0.010	147.2	332.2	47.0
		5	0.313	0.136	0.020	0.042	0.042	105.3	196.4	51.7
		9	0.280	0.116	0.030	0.060	0.060	71.4	118.7	54.6
		14	0.259	0.103	0.038	0.073	0.073	33.3	57.4	53.7
		18	0.244	0.096	0.040	0.077	0.077	17.4	21.0	62.4
R-3	220	0	0.393	0.180	0.0	0.036	0.0	155.3	332.6	48.3
		2	0.370	0.170	0.007	0.051	0.015	97.8	212.6	47.9
		5	0.330	0.150	0.015	0.068	0.033	80.0	166.0	49.1
		9	0.295	0.130	0.022	0.084	0.050	41.1	101.5	44.7
		14	0.270	0.110	0.027	0.096	0.062	22.3	56.7	44.0
		18	0.250	0.107	0.029	0.100	0.067	10.1	30.0	40.3
R-5	220	0	0.385	0.177	0.035	0.0	0.0	51.0	126.2	44.7
		1	0.383	0.174	0.037	0.003	0.003	42.6	81.4	51.1
		3	0.378	0.172	0.039	0.007	0.007	25.7	32.4	61.4
		5	0.367	0.167	0.038	0.007	0.007	3.8	5.2	59.3
		7	0.358	0.164	0.036	0.011	0.010	—	—	—
R-6	220	0	0.385	0.177	0.035	0.035	0.0	59.6	174.4	40.6
		1	0.383	0.175	0.038	0.040	0.004	58.1	89.7	56.4
		3	0.376	0.170	0.040	0.043	0.007	38.8	57.6	57.4
		5	0.367	0.165	0.042	0.045	0.010	24.4	36.4	57.3
		7	0.358	0.160	0.043	0.046	0.010	2.3	10.1	31.1
		9	0.348	0.157	0.040	0.049	0.013	—	—	—
R-11	170	0	0.236	0.099	0.0	0.0	0.0	—	—	—
		2	0.230	0.092	0.002	0.004	0.004	36.1	77.8	48.1
		4	0.215	0.088	0.005	0.008	0.008	30.5	64.8	48.5
		6	0.208	0.083	0.007	0.013	0.013	22.8	40.2	53.4
		8	0.193	0.078	0.009	0.018	0.018	15.4	24.4	56.0
		11	0.189	0.075	0.105	0.022	0.022	7.2	11.6	55.4
R-13	200	0	0.236	0.099	0.0	0.0	0.0	—	—	—
		3	0.226	0.089	0.002	0.005	0.005	46.3	95.8	48.6
		7	0.203	0.079	0.006	0.019	0.019	27.2	42.2	56.3
		11	0.180	0.062	0.013	0.024	0.024	14.0	23.0	55.0

made to record spectra during this period to determine whether any of the spectral features were retained in the absence of reactants and products. In every case it was found that, as soon as the reacting mixture had been eluted, the spectrum became devoid of features and coincident with that obtained prior to the initiation of the run. These results clearly indicate that none of the adsorbed species that could be observed are strongly chemisorbed to the surface.

The effects of changes in the initial concentration of reactants on the rates of epoxidation and combustion and the selectivity to ethylene oxide are tabulated in Table 2 for the case of reaction at 220°C. For each of these three runs the rates of both reactions are highest at the beginning of the run and decline sharply with increasing time. For run R-4 the selectivity increases steadily while for runs R-7 and R-8 the selectivity increases initially but then passes through a maximum. Comparison of runs R-4, R-7, and R-8 shows that the rates of both the epoxidation and combustion reactions are increased with increased reactant concentrations but that the selectivity is essentially unaffected.

A comparison of the spectra obtained during runs R-4, R-7, and R-8 is shown in Fig. 2. The particular spectra illustrated correspond to nearly identical product concentrations and thus reflect only the effects of changes in reactant concentrations. Several features are to be noted. The first is that the intensities of the bands corresponding to adsorbed ethylene are nearly the same in all three spectra despite the fact that there is over a twofold reduction in ethylene partial pressure going from run R-4 to R-8. This suggests that the surface concentration of ethylene is essentially independent of ethylene partial pressure for the indicated range of partial pressures. Second, it is noted that the bands associated with adsorbed ethylene oxide are not noticeable in the spectrum for run R-4 at the same time that they are quite pronounced in the spectra for runs R-7 and R-8. Since the partial pressure of ethylene oxide is essentially the same for all three cases, only the ratio of ethylene to ethylene oxide changes. This ratio is 6.96 for run R-4, 3.28 for run R-7, and 2.77 for run R-8. It is therefore suggested that ethylene and ethylene oxide compete for similar types of sites and that the absence of spectral features associated with adsorbed ethylene oxide in the spectrum for run R-4 is due to the larger ratio of ethylene to ethylene oxide partial pressures. These conclusions are consistent with those reported earlier (*8*) concerning the effects of ethylene oxide on the adsorption of ethylene.

The effects of adding products to the initial reaction mixture were investigated in runs R-3, R-5, and R-6. The product com-



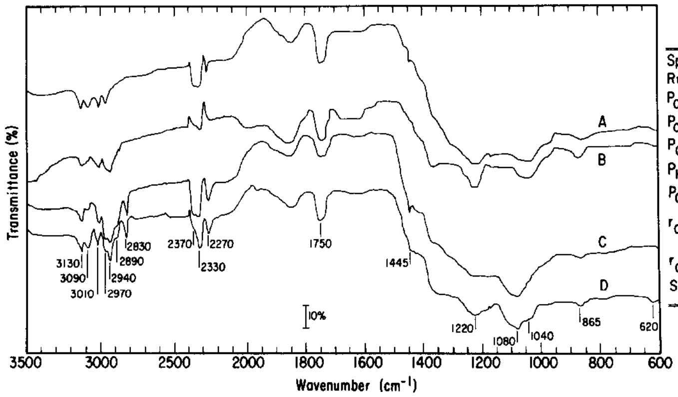
Spectrum	A	B	C
Run	R-4	R-7	R-8
P_{O_2} (atm)	0.313	0.200	0.154
$P_{C_2H_4}$ (atm)	0.136	0.074	0.054
P_{CO_2} (atm)	0.042	0.045	0.041
P_{H_2O} (atm)	0.042	0.045	0.041
$P_{C_2H_4O}$ (atm)	0.020	0.022	0.020
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	105.3	31.6	22.0
$r_{CO_2}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	196.4	107.0	51.8
$S_{C_2H_4O}$ (%)	51.7	37.1	45.9

FIG. 2. Comparison of spectra taken at constant product concentration and varying reactant concentration; $T = 220°C$.

position, reaction rates, and selectivities are listed in Table 2 for these runs. Addition of carbon dioxide alone, run R-3, causes a decrease in both the epoxidation and combustion rates relative to those in run R-4 for which the initial reactant concentrations are the same. The selectivity for run R-3 increases slightly at the beginning of the run but then declines steadily. As shown by the data for run R-5, ethylene oxide addition causes a strong reduction in reaction rates and produces a more rapid decline of the rates with time. After 7 hr of reaction it is evident that while ethylene is still being oxidized the ethylene oxide present is also undergoing oxidation. In sharp contrast to the effect of carbon dioxide, ethylene oxide causes a significant rise in the selectivity. This increase is not permanent, however, and declines sharply as the ethylene oxide starts to be consumed. Run R-6 shows the results of the simultaneous addition of carbon dioxide and ethylene oxide in equivalent amounts. The curious effect noted here is that the reaction rates are somewhat higher than in run R-5. Nevertheless, the decline in rate with time is still quite strong. Here again the selectivity shows an initial increase at the start of the run and then declines sharply after 7 hr, as ethylene oxide begins to be oxidized.

Representative spectra recorded during runs R-3, R-4, R-5, and R-6 are shown in Fig. 3. In this instance the spectra have been chosen to correspond to conditions for which the reactant concentrations are essentially the same. Comparison of spectra A and B shows the effects of increased carbon dioxide partial pressure. It is noted that the intensities of the ethylene derived bonds in the vicinity of 3000 cm^{-1} are essentially the same suggesting that the adsorption of carbon dioxide does not have a strong influence on the adsorption of ethylene. The extent of carbon dioxide adsorption cannot be judged on the basis of the intensity of the band centered at 2350 cm^{-1} due to the fact that in the presence of more than a few percent of carbon dioxide in the gas phase the subtraction of the gas phase spectrum is incomplete. However, it is observed that at higher partial pressures of carbon dioxide the bands associated with carbonate species are intensified which indicates that a greater portion of the adsorbed oxygen is tied up in this form.

The influence of added ethylene oxide may be seen by comparison of spectra A and C. The bands for adsorbed ethylene oxide are strongly intensified in spectrum C relative to spectrum A. At the same time the band for adsorbed carbon dioxide is enhanced while the bands for carbonate species are reduced. While the latter effect



Spectrum	A	B	C	D
Run	R-4	R-3	R-5	R-6
P_{O_2} (atm)	0.375	0.370	0.378	0.376
$P_{C_2H_4}$ (atm)	0.170	0.170	0.172	0.170
P_{CO_2} (atm)	0.010	0.051	0.007	0.043
P_{H_2O} (atm)	0.010	0.015	0.007	0.007
$P_{C_2H_4O}$ (atm)	0.005	0.007	0.039	0.040
$r_{C_2H_4O}$ $\left(\frac{\mu mole}{min\ g\ Ag}\right)$	147.2	97.8	25.7	38.8
r_{CO_2} $\left(\frac{\mu mole}{min\ g\ Ag}\right)$	332.2	212.6	32.4	57.6
$S_{C_2H_4O}$ (%)	47.0	47.9	61.4	57.4

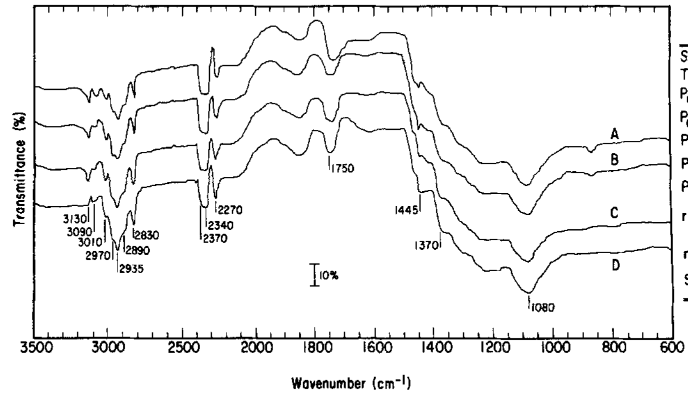
FIG. 3. Comparison of spectra taken at constant reactant concentrations and varying product concentrations; T = 220°C.

might be explained by the lower partial pressure of carbon dioxide associated with spectrum C the former effect suggests that the adsorption of ethylene oxide in some way enhances the adsorption of carbon dioxide. Of particular interest is the effect of adsorbed ethylene oxide on the adsorption of ethylene. The bands at 3130 and 3090 cm^{-1} which are both associated with adsorbed ethylene are weaker in spectrum C than in spectrum A. Furthermore, the relative intensities of these two bands are altered, the band at 3090 cm^{-1} being more strongly attenuated than that at 3130 cm^{-1}.

Spectrum D illustrates the influence of simultaneously increasing the partial pressures of ethylene oxide and carbon dioxide. Bands for adsorbed ethylene oxide and carbonate-type species are clearly evident. Comparison of spectra C and D shows that the intensities of the bands for adsorbed ethylene oxide in spectrum D are less than in spectrum C which suggests that the presence of carbon dioxide interferes with the adsorption of ethylene oxide. The combined presence of moderate concentrations of carbon dioxide and ethylene oxide has two effects on the adsorption of ethylene. These may be identified by comparing spectrum D with spectra A and C. First it is seen that while the absolute intensities of the bands at 3130 and 3090 cm^{-1} in spectrum D are not quite as large as in spectrum A, they are greater than those in spectrum C. Second, the relative intensities of the two bands are nearly the same in spectra A and D in contrast to what is observed in spectrum C.

Further details concerning the influence of ethylene oxide on the adsorption of ethylene are shown by the spectra in Fig. 4. This sequence of spectra taken from run R-5 shows that the bands characteristic of adsorbed ethylene oxide are present from the outset of the run and increase in intensity with prolonged reaction time. By contrast, the band at 3090 cm^{-1} which is associated with adsorbed ethylene shows a steady decrease in intensity with time. The band at 3130 cm^{-1} which is also associated with adsorbed ethylene remains at constant intensity and is diminished only in the spectrum recorded at 7 hr into the run. The observed variations in band intensities are somewhat surprising when one notices by reference to Table 2 that the gas phase concentrations of both ethylene and ethylene oxide vary by no more than about 10% in the course of the run. This observation together with the observed decline in reaction rates with time noted earlier may be associated with the gradual formation of a fairly stable surface species which occludes the catalyst surface and thereby prevents the further adsorption of reactants. This idea is pursued further in the discussion presented below.

Runs R-11 and R-13 were carried out at



Spectrum	A	B	C	D
Time (hr)	1	3	5	7
P_{O_2} (atm)	0.383	0.378	0.367	0.358
$P_{C_2H_4}$ (atm)	0.174	0.172	0.167	0.164
P_{CO_2} (atm)	0.003	0.007	0.007	0.011
P_{H_2O} (atm)	0.003	0.007	0.007	0.011
$P_{C_2H_4O}$ (atm)	0.037	0.039	0.038	0.036
$r_{C_2H_4O}\left(\frac{\mu mole}{min\ g\ Ag}\right)$	42.6	25.7	3.8	-
$r_{CO_2}\left(\frac{\mu mole}{min\ g\ Ag}\right)$	81.4	32.4	5.2	-
$S_{C_2H_4O}$ (%)	51.1	61.4	59.3	-

FIG. 4. Sequential spectra showing the effects of ethylene oxide addition to the reactants; $T = 220°C$.

temperatures of 170 and 200°C with the same initial reactant composition as in run R-8. The reaction rates and selectivities as a function of time for these two runs are listed in Table 2. Comparison of the rates for runs R-11, R-13, and R-8 shows a continual increase in both the rates of epoxidation and combustion with increasing temperature. The selectivities, on the other hand, show a negligible effect of temperature.

A series of spectra for run R-11 is shown in Fig. 5. The general features of these spectra are identical to those illustrated in Fig. 1 for run R-8. The evolution of the features is more gradual here than in Fig. 1 because of the lower temperature and correspondingly lower reaction rates. Here again we observe that the band at 3090 cm^{-1} diminishes gradually with time while that at 3130 cm^{-1} remains constant in intensity. It is also noted that the intensity of the carbonyl band at 1740 cm^{-1} is significantly smaller at the lower temperature.

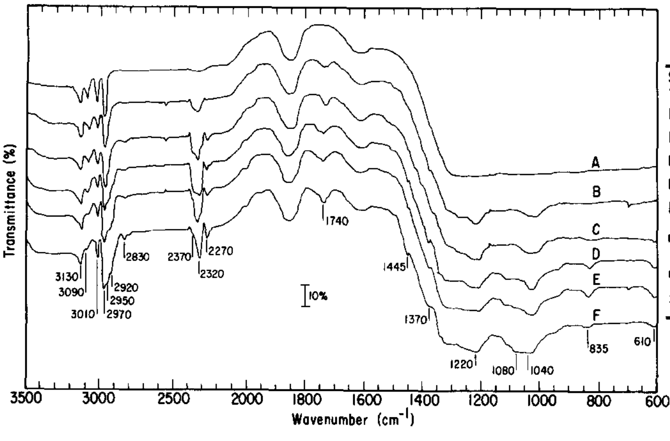
DISCUSSION

The spectra presented in Figs. 1–5 clearly demonstrate the presence of adsorbed ethylene under reaction conditions. As was discussed in our previous paper (*8*), this adsorption occurs only in the presence of oxygen and the spectrum obtained strongly resembles that for ethylene coordinated to isolated silver ions. Correspondingly, we have postulated the structure of adsorbed ethylene to be that shown below.

$$\underset{\displaystyle Ag^+}{H_2C{=}CH_2} \qquad \text{(I)}$$

The necessary Ag^+ sites are presumed to be formed through the adsorption of oxygen on the silver surface.

Structure I can be assigned to the C_{2V} point group and an application of group theory leads to the conclusion that three, rather than four, infrared active bands should be observed. While it is possible to explain this inconsistency by proposing an alternative to structure I, possessing fewer symmetry elements, we believe that a more satisfactory interpretation can be provided by assuming that structure I occurs on two types of ionized silver sites which differ in their degree of interaction with the adsorbed ethylene. A careful examination of the spectra taken at early reaction times reveals weak bands at 3000 and 2950 cm^{-1} in addition to the more intense bands at 3130, 3090, 3020, and 2980 cm^{-1}. These six bands could be associated with two forms of adsorbed ethylene, attributing the bands at 3090, 3000, and



Spectrum	A	B	C	D	E	F
Time (hr)	0	2	4	6	8	11
P_{O_2} (atm)	0.236	0.230	0.215	0.208	0.193	0.189
$P_{C_2H_4}$ (atm)	0.099	0.092	0.088	0.083	0.078	0.075
P_{CO_2} (atm)	0.0	0.004	0.008	0.013	0.018	0.022
P_{H_2O} (atm)	0.0	0.004	0.008	0.013	0.018	0.022
$P_{C_2H_4O}$ (atm)	0.0	0.002	0.005	0.007	0.009	0.011
$r_{C_2H_4O}\left(\frac{\mu mole}{min\ g\ Ag}\right)$	48.0	36.1	30.5	22.8	15.4	7.2
$r_{CO_2}\left(\frac{\mu mole}{min\ g\ Ag}\right)$	97.0	77.8	64.8	40.2	24.4	11.6
$S_{C_2H_4O}$ (%)	49.7	48.1	48.5	53.4	56.0	55.4

FIG. 5. Sequential spectra taken during a run at $T = 170°C$.

2950 cm^{-1} to one form and the bands at 3130, 3020, and 2980 cm^{-1} to another.

The major question to be answered is whether either or both of the postulated forms of adsorbed ethylene participate in the oxidation of ethylene. Of the two forms it is anticipated that the one characterized by the lower set of frequencies (i.e., 3090, 3000, and 2950 cm^{-1}) will be more reactive since a lowering of the C–H stretching frequencies can be associated with a weakening of the carbon–carbon double bond due to a stronger interaction with the adsorption site. It would appear, therefore, that a reasonable criterion for establishing the participation of adsorbed ethylene would be the observation of a correlation between the relative intensities of the bands associated with the two forms of adsorbed ethylene and the reaction rates and selectivities. Since the bands at 3000 and 2950 cm^{-1} are very weak and the formation of ethylene oxide leads to the appearance of bands in the range between 3000 and 2800 cm^{-1} which mask those associated with ethylene, the proposed test can only be applied by comparing the relative intensities of the bands at 3130 and 3090 cm^{-1}.

In the presentation of the spectra appearing in Figs. 3 and 4 it was noted that the relative intensities of the bands at 3130 and 3090 cm^{-1} change with changes in the gas phase composition and the extent of reaction. The general trend observed there was that conditions which lead to a reduction in the rates of epoxidation and combustion also lead to a reduction in the intensity of the band at 3090 cm^{-1} relative to that at 3130 cm^{-1}. Furthermore the intensity of the band at 3130 cm^{-1} is essentially constant for the duration of most runs and shows a decline only toward the end of a run or after a prolonged exposure of the catalyst to ethylene oxide.

On the basis of these observations we believe that adsorbed ethylene does participate in the oxidation processes. Consequently, any mechanism developed to explain the epoxidation and combustion reactions must include steps to account for the reactions of adsorbed ethylene.

The following mechanism can be proposed to explain the kinetic data obtained in this study and to illustrate the relationship of the structures observed by infrared spectroscopy to the elementary processes occurring on the catalyst surface.

1. $O_2 + 2Ag \text{ (or } Ag^{\delta+}) \rightleftarrows 2Ag^+O^-$
2. $O_2 + Ag \text{ (or } Ag^{\delta+}) \rightleftarrows Ag^+O_2^-$
3. $Ag^+O_2^- + Ag \text{ (or } Ag^{\delta+}) \rightleftarrows 2Ag^+O^-$
4. $Ag^+O^- + Ag \text{ (or } Ag^{\delta+}) \rightleftarrows Ag_2{}^+O^{2-}$
5. $C_2H_4 + Ag^{\delta+} \rightleftarrows Ag^{\delta+}C_2H_4$ (I)

6a. $C_2H_4 + Ag^+O^- \rightarrow Ag^+O^-CH_2CH_2\cdot$ (VI)

6b. $C_2H_4 + Ag^+O^- \rightarrow Ag^+O^-\dot{C}HCH_3$ (VII)

7a. $Ag^{\delta+}C_2H_4 + Ag^+O^- \rightarrow Ag^+O^-CH_2CH_2\cdot + Ag^{\delta+}$

7b. $Ag^{\delta+}C_2H_4 + Ag^+O^- \rightarrow Ag^+O^-\dot{C}HCH_3 + Ag^{\delta+}$

8. $Ag^+O^-CH_2CH_2\cdot \rightarrow Ag^+O^-\dot{C}HCH_3$
9. $Ag^+O^-\dot{C}HCH_3 + 5Ag^+O^- \rightarrow 6Ag^+ + 2CO_2 + 2H_2O$
10. $C_2H_4O + Ag \text{ (or } Ag^{\delta+}) \rightleftarrows Ag^+O^-CH_2CH_2\cdot$
11. $CO_2 + Ag^{\delta+} \rightleftarrows Ag^{\delta+}CO_2$ (III)
12. $CO_2 + Ag^+O^- \rightleftarrows Ag^+CO_3^-$ (IV)
13. $CO_2 + Ag^+O^- + Ag \text{ (or} Ag^{\delta+}) \rightarrow Ag_2{}^+CO_2{}^{2-}$ (V)
14. $H_2O + Ag^+O^- + Ag^{\delta+} \rightleftarrows 2Ag^+OH^-$

Two types of adsorption sites are identified. These are designated by Ag if the site is totally uncharged and by Ag$^{\delta+}$ if the site carries a partial positive charge. The value of δ is assumed to vary between 0 and 1. The Roman numerals appearing next to certain of the surface structures designate those species for which infrared bands have been observed. The numbering sequence is the same as that used in Table 1.

Steps 1–4 represent a summary of the reactions which have been proposed to occur during the adsorption of oxygen on silver (*11,12*). In accord with Czanderna's interpretation (*11*), it is assumed that above 150°C oxygen adsorbs principally as the anions O_2^-, O^-, and O^{2-}. The first two of these species are formed by interaction of an oxygen molecule with either a single site or an adjacent pair of sites. Subsequent to their formation O_2^- and O^- can react with an additional site to form O^- and O^{2-}, respectively. The free site required for these reactions may be provided by unoccupied sites adjacent to the original adsorption site or by migration of a site from other parts of the surface, a phenomenon which is expected to occur at temperatures above 100°C (*11*).

The adsorption of oxygen is shown as occurring on both uncharged and charged sites. It is believed that initial adsorption occurs on uncharged metal atoms and results in the formation of a negative oxygen ion. The counterbalancing positive charge is expected to be distributed between the silver atom on which adsorption has taken place and those in its immediate vicinity. This results in the formation of unoccupied silver sites bearing a partial positive charge. Subsequent adsorption can then occur on these sites as well as on other uncharged sites.

While surface conductivity measurements have established that oxygen adsorption takes place with a transfer of negative charge to the oxygen, the distribution of different anionic species has not been established clearly. Studies by Czanderna (*11*) and by Sato and Seo (*12*) support the existence of at least two forms of reversibly adsorbed oxygen differing in binding energies and a third form which is irreversibly adsorbed and can be removed only by chemical reaction. It is postulated that reversible forms of adsorption involve O_2^- and O^- species while the irreversible form is associated with O^{2-}.

Positive identification of O_2^- on the surface of silver has been established by Clarkson and Cirillo (*13,14*) by means of ESR. Their results have shown that at 25°C and in the presence of 0.6 Torr of oxygen, 0.44 of a monolayer is obtained, of which 0.02% is in the form of O_2^- anions. An increase in the temperature to 200°C causes a reduction in the surface concentration of O_2^- by almost two orders of magnitude. These results suggest that only a small fraction of the total adsorbed oxygen would be expected to be present as O_2^- at the temperatures normally used for the catalytic oxidation of ethylene (150–250°C). Furthermore, it would be anticipated that even if O_2^- could be formed it would be rapidly decomposed in the presence of water vapor and carbon dioxide since metal superoxides (in which the anion is O_2^-) are readily decomposed by these compounds (*15*).

Since O^- does not possess a net electron spin it cannot be detected by ESR and hence its existence on a silver surface has not been confirmed experimentally. Evidence for O^{2-} does exist, however, and is derived from LEED observations (*17*) of an ordered structure resembling Ag_2O formed after exposure of a silver crystal to oxygen. If it is assumed that the irreversibly adsorbed oxygen noted during adsorption studies (*11,12*) corresponds to O^{2-} then it may be concluded that over the temperature range of 100–250°C about 0.25–0.5 of the adsorbed oxygen is present as O^{2-}. One may therefore presume that the balance is O^-.

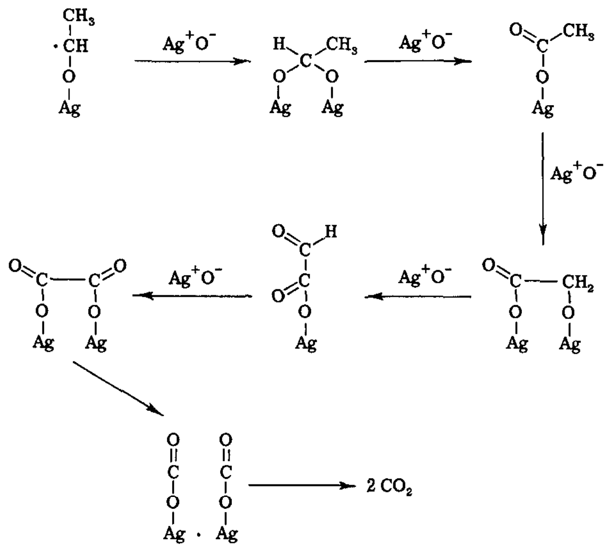
Thus the available evidence concerning oxygen chemisorption suggests that O^- and O^{2-} are the predominant species present on the surface of a silver catalyst at the temperatures used for ethylene oxidation. While both O^- and O^{2-} might be expected to participate in the oxidation of ethylene, it is anticipated that O^-, being the more labile ion, will be the principal oxidizing species. Consequently, only reactions involving O^- have been included in the proposed mechanism. It is recognized that the postulation of O^- as the sole form of adsorbed oxygen participating in the oxidation mechanism is in conflict with the interpretation given recently by Kilty and Sachtler (*5*). However, as will be shown below, a satisfactory interpretation of selectivity trends as a function of reactant and product concentrations can be obtained on the basis of the present postulate.

The reversible adsorption of ethylene, reaction 5, is shown to occur only on the partially charged silver sites produced through the adsorption of oxygen. The selection of these sites is based on the observation that the spectra for ethylene adsorbed in the presence of oxygen (see Figs. 1 and 5) closely resemble those for ethylene coordinated with isolated Ag^+ ions (*8*). In the absence of oxygen it has been observed in the current studies as well as in those carried out previously that ethylene does not adsorb on a fully reduced silver surface. Both of these observations are brought together in the work of Gerei ET AL. (*17*) in which it is shown that maximum ethylene adsorption occurs when the silver surface contains free sites as well as adsorbed oxygen. No ethylene adsorption was detected either in the absence of oxygen adsorption or in the presence of a monolayer of adsorbed oxygen. The explanation proposed for these results is that adsorbed oxygen serves to create positively charged surface sites which then act as adsorption sites for ethylene. Such an interpretation is consistent with the observation that ethylene acts as an electron donor upon adsorption (*18*).

It is assumed that ethylene can react with the adsorbed O^- ions by both Rideal–Eley and Langmuir–Hinshelwood processes, reactions 6 and 7 of the mechanism. While there is no direct evidence for the participation of gaseous ethylene, interpretation of the infrared spectra presented here suggests that adsorbed ethylene does participate in the oxidation reactions, as was discussed above. Two exit channels are shown for each of the reactions and it is postulated that reaction 6a proceeds in preference to reaction 6b and that reaction 7b proceeds in preference to reaction 7a. The selection of the preferred exit channels is based on the need to interpret the effects of reaction conditions upon selectivity. This point is discussed more fully below.

The formation of ethylene oxide is postulated to occur through the intermediate designated as structure VI which is formed as a product in reactions 6a and 7a. The reverse of reaction 10 shows that this species is converted to gaseous ethylene oxide by closure of the epoxide ring and desorption of C_2H_4O. The proposed sequence of reactions is strongly supported by the recent work of Hall (*19*) in which it was found that a nearly equimolar mixture of *cis* and *trans* 1-2 dideuteroethylene oxide was formed when either *cis* or *trans* 1-2 dideuteroethylene was oxidized over silver. Furthermore, experiments with 1-1 dideuteroethylene showed that no intra- or intermolecular exchange occurred. This was interpreted to mean that in the course of forming ethylene oxide the carbon–carbon double bond opens allowing the CH_2 groups to rotate relative to each other. The spectra recorded during the present study showed no evidence for structure VI at the beginning of a run when the gas phase concentration of ethylene oxide was very low, which suggests that the desorption of ethylene oxide, the reverse of reaction 10, occurs very rapidly by comparison to the sum of the rates of reactions 6a and 7a.

Reactions 6b and 7b produce an intermediate, structure VII, believed to be the precursor for the complete combustion of ethylene to carbon dioxide and water. This initial structure is undoubtedly oxidized via a sequence of steps which might be represented as follows.



Whereas the details of the combustion sequence cannot be verified, the presence of a strong band at 1740 cm^{-1} in the spectra does indicate that the intermediates contain carbonyl groups. The position of this band corresponds most closely to that found in esters and supports the occurrence of groups such as $-\overset{O}{\overset{\|}{C}}-O-$. In some of the spectra additional bands can be observed as shoulders on the main band at 1740 cm^{-1}. These weak bands appear in the range of 1710–1730 cm^{-1} and can be associated with structures such as $-\overset{O}{\overset{\|}{C}}H$, $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$, and $-\overset{O}{\overset{\|}{C}}-$. Some support may also be found for the oxalate formation of carbon dioxide adsorbed in this manner can readily be explained by the decomposition of an oxalate-type structure shown to precede the formation of carbon dioxide immediately. In this instance we note that the band at 2270 cm^{-1} can be identified with a perpendicularly adsorbed form of carbon dioxide present only under reaction conditions (*8*). The structure.

The adsorption of ethylene oxide is represented by reaction 10 and is shown to take place with rupture of the epoxide ring. Our previous study of the infrared spectra for adsorbed ethylene oxide (*8*) supports this form of adsorption. In that work it was shown that under reaction conditions the infrared spectra showed no bands which could be identified with a ring intact form of adsorption. A similar conclusion was reached by Gerei *et al.* (*6*).

Reaction 8 shows an isomerization of the structure formed by adsorbed ethylene oxide to the structure which acts as the precursor to complete combustion. This reaction has been included to account for the observation that at high concentrations ethylene oxide is oxidized to carbon dioxide and water. Three observations support the occurrence of reaction 8. The first is that the infrared spectra for adsorbed ethylene oxide and acetaldehyde bear strong resemblance (*8*). For both adsorbates the spectra suggest that a mixture of structures VI and VII are present on the catalyst surface. The second observation is that silver will catalyze the isomerization of ethylene oxide to acetaldehyde when carried out in the absence of oxygen (*20*). Finally it is noted that the passage of ethylene oxide and oxygen over a silver catalyst produces only carbon dioxide and water. This observation suggests that any acetaldehyde formed through the adsorption and isomerization of ethylene oxide is rapidly oxidized.

While not shown as a part of the reaction mechanism, it is conceivable that the free radicals formed by reactions 6 and 7 could react among themselves to form dimers and possibly even higher oligomers. Such processes would be expected to occur when the surface concentrations of structures VI and VII were high and hence would be favored by high concentrations of ethylene oxide in the gas phase. No direct evidence for oligomerization was found in the present study. However, it may be recalled that the variations in band intensity observed during run R-5 (see Fig. 4), in which a moderate concentration of ethylene oxide was included with the initial reactants, could be interpreted in terms of the gradual formation of a surface oligomer which occludes the catalyst surface. A similar interpretation of the effects of ethylene oxide on ethylene oxidation has been proposed by Metcalf and Harriott (*21*).

As shown in Table 1 the adsorption of carbon dioxide produces several surface structures. The adsorption sites for this product include both the $Ag^{\delta+}$ sites and the O^- sites. The occurrence of these forms of adsorption is accounted for by reactions 11–13.

Little is known about the adsorption of water on silver or silver oxide. The work of Benton and Elgin (*22*) indicates, however, that the adsorption of water requires a partial oxidation of the surface but the form of the adsorbed water is not known. In reaction 14 the adsorption of water has been shown to occur dissociatively, forming two hydroxyl groups. While we have not observed the presence of hydroxyl groups, it seems likely that the formation of water occurs by the reverse of reaction 14.

The mechanism outlined above proposes that the initial steps of the epoxidation and combustion pathways are essentially identical. The nature of the final products is dictated by whether structures VI or VII is formed. In view of the similarity of the proposed initial steps, it is anticipated that the rates of epoxidation and combustion should respond in very similar manners to changes in reactant concentrations and temperature. To test this expectation as well as other features of the mechanism we have plotted, in Fig. 6, initial rates of epoxidation and combustion divided by the product $P_{C_2H_4}P_{O_2}{}^{1/2}$ versus $1/T$. The ordinate thus represents an effective rate coefficient.

The data shown in Fig. 6 can be described by two curves, one corresponding to epoxidation, the other to combustion. It is to be noted that for each temperature the data for runs carried out with different

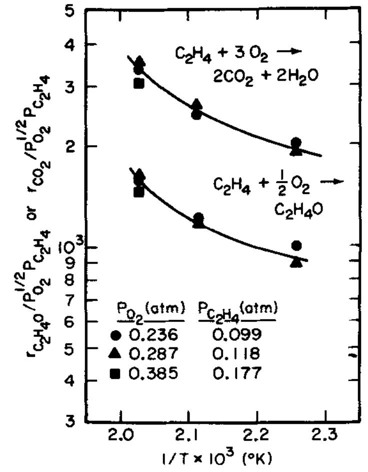


FIG. 6. $r_{C_2H_4O}/P_{O_2}{}^{1/2}P_{C_2H_4}$ and $r_{CO_2}/P_{O_2}{}^{1/2}P_{C_2H_4}$ versus $1/T$.

starting concentrations of reactants all lie on the same line. Furthermore, the extent to which the data are reduced to a common curve by dividing by $P_{C_2H_4}P_{O_2}^{1/2}$ is the same for the two reactions. This leads us to the conclusions that the rates of both epoxidation and combustion are first order in ethylene and half order in oxygen. These conclusions are consistent with the proposed mechanism. Thus both reactions 6 and 7 predict a first-order dependence in ethylene. A half-order dependence on oxygen implies that oxygen adsorption occurs dissociatively in a single step rather than by a sequence of two steps.

With increasing temperature the magnitude of the effective rate coefficient appearing in Fig. 6 increases. For neither reaction is the curve linear. The most likely reason for this is the failure to account for the adsorption terms normally present in the denominator of rate expressions for catalyzed reaction. Certainly the direction of the curvature is consistent with this interpretation. It is worth noting that while the plots do not exhibit a true Arrhenius behavior, the two curves are essentially parallel. This leads us to conclude that the selectivity of the initial rates is very little affected by changes in temperature. A similar point can be made based upon the data presented in Table 2. These observations are consistent with those made previously (*2*) and further support the contention that the rate limiting steps in the epoxidation and combustion mechanisms are nearly identical as has been proposed here.

The effects of reactants and product concentrations on the selectivity toward ethylene oxide can also be interpreted in terms of the proposed mechanism. Inspection shows that reaction 6a, the primary path to ethylene oxide, involves the surface concentration of only one species, while reaction 7a, the primary path to carbon dioxide and water involves the product of two surface concentrations. Consequently, the rate of reaction 7a will rise less rapidly than that of reaction 6a as the concentration of reactants is increased. The predicted trend is an increase in selectivity toward ethylene oxide as the concentration of reactants is increased. In the present work the concentrations of ethylene and oxygen were not varied over a sufficiently broad range to observe significant changes in selectivity. Such an effect can be established, however, from an evaluation of the data presented by Klugherz and Harriott (*23*). From their work we have calculated that the selectivity rises from about 50 to 66% as the partial pressure of ethylene is varied from 0.026 to 1.32 atm for a constant oxygen partial pressure of 0.263 atm. Similar calculations show that the selectivity rises from 53 to 57% as the partial pressure of oxygen is varied from 0.061 to 1.32 atm for a constant ethylene partial pressure of 0.2 atm.

The adsorption of ethylene oxide that can occur on both charged and uncharged silver sites causes a loss of sites required for the adsorption of oxygen and ethylene. The result is a decrease in the rates of both epoxidation and combustion. However, since, as noted earlier, the rate of combustion is more strongly sensitive to surface coverage, the decline in rates is expected to be accompanied by an increase in selectivity. The data in Table 2 for runs R-5 and R-6 in which ethylene oxide was added to the initial charge of reactants clearly demonstrates that such an effect is observed during the early portion of the run. A similar trend is observed for runs R-4, R-7, and R-8, in which the selectivity increases as ethylene oxide is produced in the course of the reaction.

In each of the runs just noted it is observed that the selectivity eventually reaches a maximum and declines thereafter. The decline in selectivity can be explained by the onset of ethylene oxide combustion via reactions 10, 8, and 9. As observed in the spectra shown in Figs. 1

and 5, increasing gas phase concentrations of ethylene oxide produce an intensification of the bands ascribed to adsorbed ethylene oxide, structure VI, and its isomerization product, structure VII. The latter structure is believed to be the precursor to complete combustion as is suggested by reaction 9. Further evidence in support of the combustion of ethylene oxide is the observation that the partial pressure of ethylene oxide shows a notable decline toward the end of runs R-5 and R-6 even though ethylene is still being converted to products during this period. Hence it may be concluded that carbon dioxide and water are produced by both parallel and sequential paths.

The effects of adsorbed carbon dioxide on the selectivity differ from those for ethylene oxide. Table 1 shows that this product can adsorb directly on the silver surface as structure III as well as by interaction with adsorbed O^- ions to form mono- and bidentate carbonate structures such as IV and V. If it is assumed, as proposed by Czanderna (*24*), that the primary mode of adsorption is through the O^- ion, then it may be concluded that the adsorption of carbon dioxide will bring about a decrease in the rates of both the epoxidation and the combustion reactions without a change in the selectivity. This conclusion is based on the fact that reactions 6 and 7 both depend on the surface concentration of O^- to the first power. Reference to the results of run R-3 shown in Table 2 indicate that the selectivity is not altered relative to that for run R-4 by the addition of moderate amounts of carbon dioxide. At higher carbon dioxide partial pressures it is anticipated that adsorption onto silver sites to form structures III and V via reactions 11 and 13 will become more significant. Under these circumstances an increase in selectivity would be expected for reasons identical to those presented earlier for ethylene oxide adsorption. While this effect was not explored in the course of this work, the predicted trend can be observed by evaluation of the data presented by Metcalf and Harriott (*21*). In this case, the selectivity increased from 57 to 75% as the partial pressure of carbon dioxide was increased from 0.004 to 0.36 atm, while the partial pressures of the reactants were held constant.

CONCLUSIONS

In conclusion, the present work has shown that infrared spectroscopy is an effective tool for identifying the structures present on the surface of a silver catalyst during the oxidation of ethylene. Based upon these structures and additional information taken from the literature a mechanism has been proposed for both the expoxidation and combustion process. One assumption of this mechanism is that O^- ions present on the silver surface are the primary oxidizing agent for both processes. A second assumption is that oxidation proceeds through both gaseous and adsorbed ethylene, the former yielding primarily ethylene oxide and the latter yielding primarily carbon dioxide and water. The proposed mechanism explains qualitatively the kinetics observed in the present investigation and the variations in selectivity as a function of reactant and product concentrations reported in the literature by previous investigators.

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