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Infrared Spectra of Adsorbed Species Present During the Oxidation of Ethylene over Silver

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Infrared spectra are presented of the adsorbed species present on the surface of a silver catalyst during the oxidation of ethylene. These spectra, recorded as a function of time using a batch recirculation reactor, show significant changes as the reaction proceeds. The interpretation of the spectra recorded under reaction conditions is facilitated by comparison of these spectra with those obtained during the individual adsorption of reactants and products, both in the presence and absence of oxygen. Surface structures are proposed for each of the adsorbed species.

INTRODUCTION

Considerable attention has been given to understanding the mechanism by which ethylene is oxidized to ethylene oxide over a silver catalyst (*1–3*). For the most part, these studies have focused on determining the form in which oxygen adsorbs on silver or the changes in the physical properties of silver when first oxygen and then ethylene is adsorbed. Mechanistic inferences have also been drawn from a variety of kinetic investigations.

Only a limited amount of work has been reported concerning the direct observation of surface structures which might relate to the progress of the oxidation reaction. In a study by Gerei *et al.* (*4*) infrared spectroscopy was used to observe the adsorbed species formed when ethylene is adsorbed on a silver surface partially covered by preadsorbed oxygen. From the spectra it was concluded that ethylene adsorption occurred with rupture of the double bond to form a peroxide structure $-CH_2-CH_2-O-O-$. Primary evidence for this structure was the absence of olefinic C–H stretching vibrations and the presence of a band at 870 cm^{-1} which was assigned to the vibration of the peroxide group. More recent work by Kilty *et al.* (*5*) has conclusively confirmed the formation of the structure proposed by Gerei *et al.* and their interpretation of the band at 870 cm^{-1}. It was noted, however, that this structure is not stable at temperatures above 100°C and most likely rearranges to form an alkoxide type surface structure, $-CH_2-CH_2-O-$. By observing the spectra obtained when ethylene oxide is adsorbed on silver, Gerei *et al.* (*4*) also concluded that adsorption causes the epoxide ring to rupture leading to an alkoxide type surface structure.

The present work was undertaken with the aim of studying simultaneously the kinetics of ethylene oxidation and the structure of the adsorbed species present on the catalyst surface under reaction conditions. The latter investigation was performed by the use of infrared spectroscopy. Separate studies were also performed in which spectra were recorded for ethylene, ethylene oxide, acetaldehyde, and carbon dioxide adsorbed with and without the coadsorption of oxygen. Comparisons are made between the spectra observed under both adsorption and reaction conditions, and structures are proposed for each of the adsorbed species. The relationship of the species identified here to the mechanism of oxidation will be discussed in a subsequent paper (*6*).

EXPERIMENTAL METHODS

The catalyst used for the present work was prepared by depositing silver on Cab-O-Sil M-5. The first step in the preparation procedure was the removal of residual chlorine from the Cab-O-Sil to avoid unintentional moderation of the catalyst. The chlorine content of the solid was reduced from 2000 ppm to less than 50 ppm by weight by heating it in a vacuum oven at 150°C and 0.5 Torr for a period of 48 hr.

An 8 g charge of pretreated Cab-O-Sil was slowly added to 300 ml of distilled water maintained at 85°C and stirred. Once a uniform slurry had been obtained, 160 ml of a silver nitrate solution (0.5 g Ag/100 ml) was added slowly over a period of 1 hr. To reduce the silver nitrate to metallic silver, a 10-fold excess of aqueous formaldehyde solution was added slowly over a period of 2 hr. When the formaldehyde addition had been completed, the slurry was observed to have a light-grey color. Agitation was continued for several hours more at a temperature of 90–95°C to assure completion of the reduction and to begin evaporation of water. After the slurry volume had been reduced to about 200 ml, it was transferred to a crystallizing dish placed on a hot plate. Evaporation was continued until a thick paste had formed. At this point the paste was transferred to an aluminum boat and placed in a helium-purged oven for 24 hr. The final product was grey-brown in color and showed no tendency to segregate into silver and support particles. The dried solid was ground in a mortar with a pestle, both of which had been cleaned with hot nitric acid. By following a sequence of grinding and sieving, a free flowing powder of sub-300 mesh size was finally achieved. The silver content of this product was analyzed at about 8.5% by weight.

The catalyst prepared as described above was mixed with fresh Cab-O-Sil in the proportions of 1:4 of fresh Cab-O-Sil to catalyst. This step proved necessary to obtain a product of acceptable optical transparency. A homogeneous blend was achieved by mixing and resieving. The diluted material gave a silver analysis of 6.6% by weight.

A circular disc 1.125 in. in diameter was formed by pressing about 200 mg of the diluted powder in a die at 8000 psi. To allow for a measurement of the disc temperature, a copper–constantan thermocouple with wires 0.002 in. in diameter was placed into the powder and embedded into the disc. In the course of time it was discovered that under reaction conditions the copper wire of the thermocouple became amalgamated with the silver leading to the disintegration of the wire. As a result, it was necessary to press three catalyst discs in order to complete the work. The weights of these discs, all of which were prepared from the same batch of diluted catalyst, are indicated in Table 1.

The apparatus used to obtain the spectral and kinetic data reported here was the same as that described previously by London and Bell (*7,8*). The central component of this apparatus is a heated infrared cell which is connected to a gas recirculation loop. The catalyst disc is held within the cell so that it is aligned with the sample beam of the spectrometer (Perkin-Elmer, Model 457). A second disc, consisting of pure Cab-O-Sil, is held in the reference

TABLE 1
MASSES OF CATALYST AND REFERENCE DISCS

No.	Catalyst disc mass (g)	Reference disc mass (g)
1	0.204	0.211
2	0.194	0.225
3	0.198	0.226

beam. The weights of the reference discs used with each of the three catalyst discs are listed in Table 1. Using this technique it is possible to record the spectrum of only those species adsorbed on the catalyst and to subtract out the spectrum of silica and of species present in the gas phase (*7*).

Analysis of the gas in the recirculation loop was carried out on a Varian Aerograph 9OP3 gas chromatograph fitted with a 24 ft long 0.25 in. diameter column packed with Porapak Q. To achieve a complete separation of all reactants and products the following sequence of steps was used. First, a stable base line was established at a column temperature of 82°C and a helium gas flow rate of 28 cm^3/min. A sample was then injected and the peaks for oxygen, carbon dioxide and ethylene were recorded. This part of the analysis was completed within 10 min after sample injection. At this point the column temperature was rapidly raised to a final level of 171°C and the helium flow rate was increased to 50 cm^3/min. Two additional peaks corresponding to ethylene oxide and water were then recorded. A complete analysis could be obtained by this procedure in about 35 min and a complete cycle repeated every 50–55 min.

Prior to beginning experiments with a freshly prepared catalyst disc, the disc and its companion reference disc were placed in the reactor and evacuated to less than 10^{-6} Torr at 250°C for a period of 18 hr. A gas mixture containing 12% hydrogen in helium was then passed over the discs in order to completely reduce the catalyst. During this period which lasted 6 hr, the catalyst temperature was 250°C and the total gas pressure was 1 atm.

Between runs the catalyst was reduced again using the following procedure. The reactor and recirculation loop were first purged with helium at 220°C for 6 hr. At this point a mixture of 12% hydrogen in helium was introduced and the catalyst reduced under the same conditions used for a fresh disc. After reduction, the reactor was again evacuated, at which point the catalyst was ready for the start of a new run.

Two sets of experiments were performed. The first, identified as reaction runs, were carried out by filling the recirculation loop with a reactant mixture with or without products and then recirculating the mixture over the catalyst. During these batch runs spectra were recorded and gas analyses were performed every few hours. The second set of experiments were identified as adsorption runs. For these runs, a continuous flow of helium containing the adsorbate alone or the adsorbate plus oxygen was passed into and out of the recirculation loop. The total gas flow rate was maintained high enough to avoid any measurable degree of conversion.

RESULTS

As noted in the previous section, it was necessary to use three catalyst discs in the course of this work to collect sufficient kinetic and spectral data. To ascertain that these three discs were catalytically equivalent, the first run on each disc was carried out under an identical set of conditions, noted in Table 2. During the course of these runs, which lasted 18 hr, the composition of the recirculating gas was analyzed and infrared spectra of the disc were recorded at fixed intervals of time. These

TABLE 2

STANDARD CONDITIONS USED TO TEST CATALYST ACTIVITY AND THE OBSERVED INITIAL REACTION RATES[a]

Run	Disc No.	$r_{C_2H_4O}$ (μmol/g min)	r_{CO} (μmol/g min)	$S_{C_2H_4O}$[b]
R-1	1	148.0	333.2	47.0
R-2	1	148.1	333.0	47.0
R-4	2	147.2	332.2	47.0
R-9	3	155.6	221.2	48.4

[a] $T = 220°C$; $p_{O_2} = 0.39$ atm; $p_{C_2H_4} = 0.18$ atm; $p_{He} = 0.43$ atm.

[b] $S_{C_2H_4O} = r_{C_2H_4O} + 1/2r_{CO_2})$.

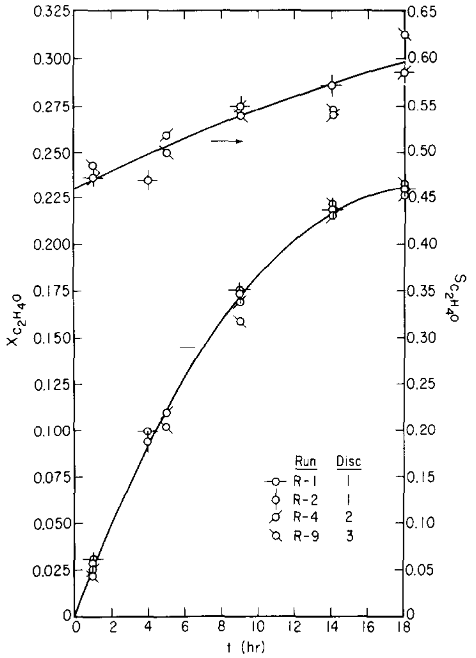


FIG. 1. Conversion and selectivity to ethylene oxide for batch runs over catalyst discs 1, 2 and 3: $T = 220°C$.

data allowed a comparison to be made of the performance of each catalyst disc.

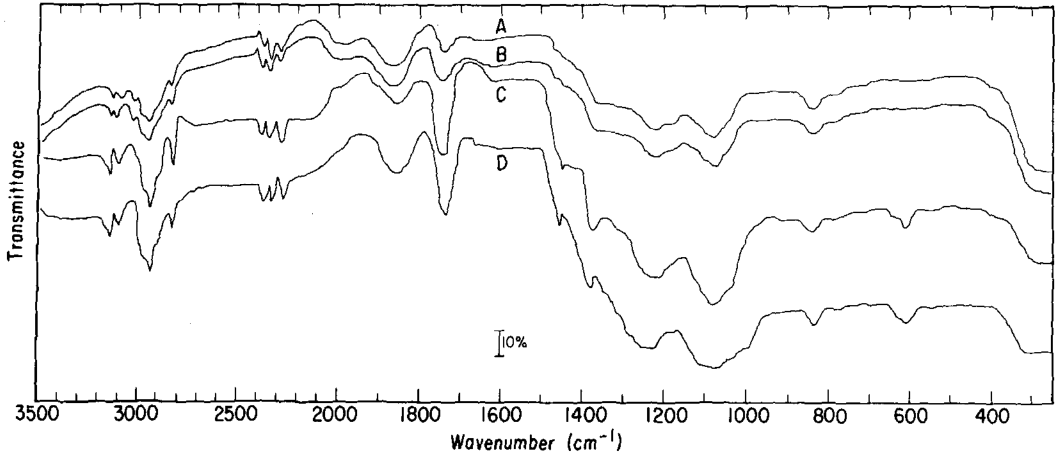
Figure 1 illustrates the extent of conversion of ethylene to ethylene oxide and the selectivity for ethylene oxide for each disc as a function of reaction time. The data for all three discs are nearly identical, and any differences can be accounted for by differences in the masses of the catalyst discs and the exact starting concentration of reactants. Also shown in Fig. 1 is a comparison of the data for two standard runs carried out over disc No. 1. Between these two runs the catalyst was reduced in hydrogen following the procedures noted earlier. The data for these two runs are less than the uncertainties in the data themselves. As shown in Fig. 1, the selectivity and fractional conversion data for runs R-1, R-2, R-4, and R-9 can be described by a single pair of curves.

A comparison of the spectra obtained after 14 hr of reaction is shown in Fig. 2 for each of the three discs. Examination shows that the spectra for runs R-4 and R-9 are nearly identical. The spectrum for run R-1 exhibits essentially all of the bands observed in the spectra for runs R-4 and R-9, but with significantly reduced intensity. The reduction in intensity of the spectrum for run R-1 can be explained in terms of the difference in mass between the catalyst disc and the companion reference disc. The use of a reference disc which is heavier (and hence thicker for a fixed die size and pressing force) than the catalyst disc, aids in intensifying the bands due to species adsorbed on the catalyst. For runs R-4 and R-9, the mass differences are 28 and 31 mg, respectively, while for runs R-1 the mass difference is 7 mg. Consequently, it is expected that the spectra for runs R-4 and R-9 should be comparable but more intense than the spectrum for run R-1. Interestingly, the effect of mass difference between catalyst and reference discs overrides the effect of the mass of the catalyst disc itself.

Figure 2 also provides a comparison of the spectra for runs R-1 and R-2. In this case the two spectra are completely identical indicating that the hydrogen reduction between these two runs restores the catalyst surface to the same initial state.

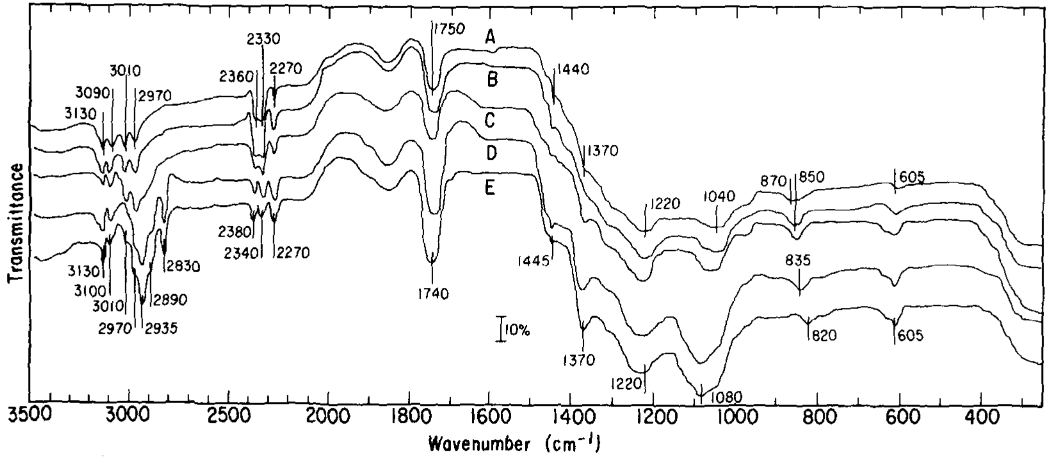
The rates of ethylene oxide and carbon dioxide production and the selectivity for ethylene oxide are listed in Table 2 for each disc. The reaction rates and selectivites for runs R-1 and R-2 are identical, indicating that hydrogen reduction returns the catalyst to its original activity. Likewise, a comparison of runs R-1, R-4, and R-9 shows that the reaction rates and selectivities for all three discs are comparable which further confirms that all three discs have essentially equivalent activities.

During the course of a batch run it was observed that the spectrum of adsorbed species changed. A representative sequence of spectra illustrating these changes is shown in Fig. 3. The reactant and product partial pressures, the reaction rates, and the selectivities are listed in Fig.



Spectrum	A	B	C	D
Run	R-1	R-2	R-4	R-9
Disc	1	1	2	3
P_{O_2} (atm)	0.250	0.250	0.259	0.254
$P_{C_2H_4}$ (atm)	0.099	0.099	0.103	0.101
P_{CO_2} (atm)	0.075	0.075	0.073	0.074
P_{H_2O} (atm)	0.075	0.075	0.073	0.074
$P_{C_2H_4O}$ (atm)	0.039	0.039	0.038	0.038
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	37	37	33	32
r_{CO_2} $\frac{\mu\text{mole}}{\text{min g Ag}}$	56	56	57	54
$S_{C_2H_4O}$ (%)	57	57	54	54

FIG. 2. Comparison of the spectra taken from catalyst discs 1, 2 and 3: $T = 220°C$; $t = 14$ hr.



Spectrum	A	B	C	D	E
Time (hr)	1	5	9	14	18
P_{O_2} (atm)	0.375	0.313	0.280	0.259	0.244
$P_{C_2H_4}$ (atm)	0.170	0.136	0.116	0.103	0.096
P_{CO_2} (atm)	0.010	0.042	0.060	0.073	0.077
P_{H_2O} (atm)	0.010	0.042	0.060	0.073	0.077
$P_{C_2H_4O}$ (atm)	0.004	0.020	0.030	0.038	0.040
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	147	105	71	33	17
$r_{CO_2}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	332	196	119	57	21
$S_{C_2H_4O}$ (%)	47	52	55	54	62

FIG. 3. Sequential spectra taken during a reaction run: $T = 220°C$.

3 as a function of time. Frequency shifts and intensity variations of individual bands can best be summarized by dividing the spectrum into the following four regions: 3200–2800, 2400–2200, 1800–1700, and 1600–600 cm^{-1}.

The portion of the spectra between 3200 and 2800 cm^{-1} contains two groups of bands. The first group appears in the spectrum recorded after 1 hr of reaction and contains four well-defined bands at 3130, 3090, 3010 and 2970 cm^{-1}. As the reaction proceeds, the band at 3130 cm^{-1} grows while the band at 3090 cm^{-1} diminishes and is shifted gradually to 3100 cm^{-1}. The band at 3010 cm^{-1} grows during the first 9 hr of reaction but then decreases in intensity, becoming a shoulder on the large new band at 2935 cm^{-1}. A reduction in intensity accompanies the shift. The band at 2970 cm^{-1} also increases during the first 9 hr of reaction, ultimately becoming a large shoulder on the band at 2935 cm^{-1}.

A second distinct group of bands comprised of peaks at 2935 and 2830 cm^{-1} and a shoulder at 2890–2900 cm^{-1} appears as the reaction proceeds. The band at 2935 cm^{-1} first appears as a shoulder on the band at 2970 cm^{-1} after 9 hr of reaction and grows to become the most intense peak in the spectrum. The sharp band at 2830 cm^{-1} and the shoulder at 2890–2900 cm^{-1} also emerge after 9 hr of reaction.

In the region between 2400 and 2200 cm^{-1}, three bands are observed at 2360, 2330 and 2270 cm^{-1}. The bands occurring at 2360 and 2330 cm^{-1} overlap each other at low reaction times and grow steadily up to a reaction time of 5 hr. For longer reaction times, the positions of the two bands are shifted to 2380 and 2340 cm^{-1}, respectively, causing a complete resolution of the bands. Accompanying the separation into two bands there is a noticeable reduction in intensity. By contrast, the intensity of the band at 2270 cm^{-1} increases continuously throughout the run.

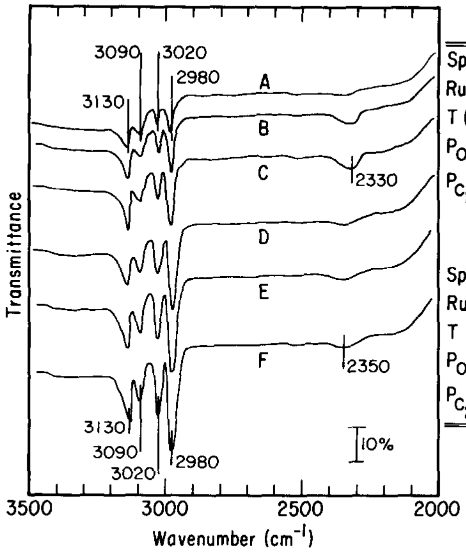
Only a single band at 1740 cm^{-1} is observed in the region between 1800 and 1700 cm^{-1}. This band is present after 1 hr of reaction and grows steadily with increasing reaction time.

In the region between 1600 and 600 cm^{-1}, six bands are observed after 1 hr of reaction. These are located at 1445, 1370, 1220, 1040, 870 and 605 cm^{-1}. With the exception of the band at 1445 cm^{-1}, the intensity of these bands increases with increasing reaction time. As the run proceeds, the band at 870 cm^{-1} shifts downscale gradually appearing at 820 cm^{-1} after 18 hr of reaction. Finally, a broad peak is observed to emerge at 1080 cm^{-1} between 9 and 14 hr into the run.

From the kinetic data given in Fig. 3 it is apparent that the presence of reaction products in the recirculated gases causes a reduction in the rates of both the epoxidation and the combustion reactions. The decline in rates is accompanied, however, by an increase in the selectivity towards ethylene oxide.

The association of the spectral features shown in Fig. 3 with individual reactants and products, was carried out by comparing spectra taken under reaction conditions with those obtained by individually adsorbing ethylene, ethylene oxide, acetaldehyde, and carbon dioxide on the catalyst, both in the presence and absence of oxygen. In performing the adsorption studies the gas phase concentration of the adsorbates and the catalyst temperature were selected to be the same as those observed during reaction. In addition to this method of comparison, reaction runs were also performed in which either carbon dioxide or ethylene oxide was added to the original reactor charge. The spectra obtained from these runs were compared to those obtained from runs in which no products were present at the start of the run.

No spectra could be obtained when a mixture of ethylene and helium was passed



Spectrum	A	B	C
Run	A-4	A-4	A-4
T (°C)	220	220	220
P_{O_2} (atm)	0.230	0.270	0.370
$P_{C_2H_4}$ (atm)	0.094	0.110	0.170

Spectrum	D	E	F
Run	A-5	A-5	A-5
T (°C)	170	170	170
P_{O_2} (atm)	0.230	0.270	0.370
$P_{C_2H_4}$ (atm)	0.094	0.110	0.170

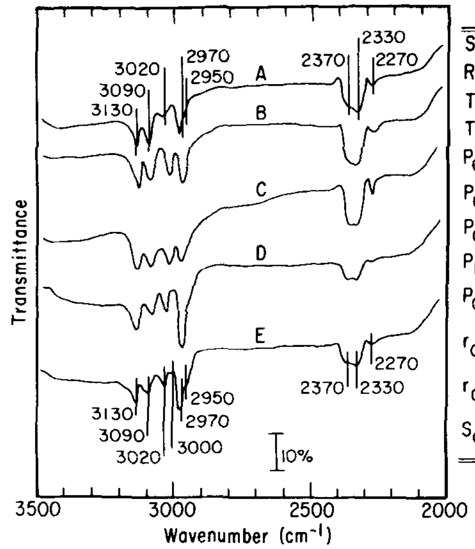
FIG. 4. Spectra of ethylene adsorbed in the presence of oxygen: T = 220°C; and T = 170°C.

over the catalyst. However, when oxygen was added to the mixture, well-defined spectra were recorded. Figure 4 illustrates the spectra for coadsorbed oxygen and ethylene at temperatures of 220 and 170°C. Four bands are observed at 3130, 3090, 3020, and 2980 cm^{-1}. The intensities of these bands increase with increasing partial pressures of ethylene and oxygen for a given temperature and with decreasing temperature for a given gas composition. Both of these observations conform to the expected behavior for an adsorption process.

The only other peak observed in the spectra for adsorbed ethylene is a very weak one at 230–50 cm^{-1}. As discussed below, this peak can be associated with the adsorption of carbon dioxide produced by oxidation of a small portion of the ethylene fed to the reactor. It is noted that the intensity of this peak increases with increasing partial pressures of ethylene and oxygen for a given temperature and with increasing temperature for a given gas composition.

In the discussion of Fig. 3, it was noted that the spectra obtained at low reaction times exhibit a group of four bands at frequencies which are very close or identical to those observed during the adsorption of ethylene. To emphasize this comparison further, Fig. 5 illustrates the high frequency portions of the spectra from five reaction runs. These five spectra were taken at the same partial pressures of ethylene and oxygen as the correspondingly labeled spectra in Fig. 4.

Examination of Figs. 4 and 5 brings out a number of observations. The first is that the correspondence in frequency for the four bands occurring in both adsorption and reaction runs is sufficiently close to support the existence of adsorbed ethylene on the catalyst surface under reaction conditions. Secondly, there are some small differences in individual band positions between the two types of experiments. In particular, the band which appears at 3020 cm^{-1} in the adsorption studies appears at frequencies between 3010 and 3020 cm^{-1} in the reaction studies. This difference in band position does not appear to be related in a straightforward manner to either gas composition or reaction rate. Thirdly, the spectra recorded under reaction conditions show the presence of two additional bands (see spectra A, D and E in Fig. 5). These

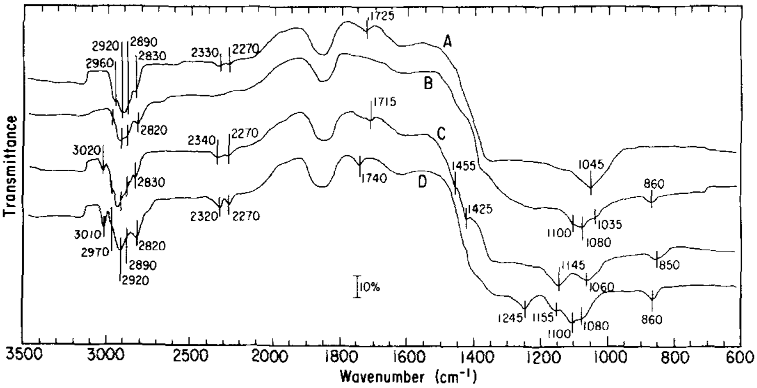


Spectrum	A	B	C	D	E
Run	R-8	R-7	R-4	R-11	R-10
Time (hr)	1	1	1	2	2
T (°C)	220	220	220	170	170
P_{O_2} (atm)	0.230	0.270	0.370	0.230	0.270
$P_{C_2H_4}$ (atm)	0.094	0.110	0.170	0.092	0.110
P_{CO_2} (atm)	0.005	0.006	0.010	0.004	0.007
P_{H_2O} (atm)	0.005	0.006	0.010	0.004	0.007
$P_{C_2H_4O}$ (atm)	0.002	0.003	0.004	0.002	0.003
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	74	94	147	36	47
$r_{CO_2}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	151	198	332	78	107
$S_{C_2H_4O}$ (%)	50	49	47	48	48

FIG. 5. Comparison of the spectra taken from reaction runs: T = 220°C; and T = 170°C.

bands appear as a low frequency shoulder on the 2970–80 cm^{-1} band and as a very weak peak at approximately 3000 cm^{-1}. Fourthly, the intensities of the four major bands appearing in the spectra for reaction runs, Fig. 5, do not show the same regular behavior with ethylene partial pressure and temperature noted in the spectra for adsorption runs presented in Fig. 4. The observed differences between the reaction and adsorption runs are believed to be due to the presence of reaction products in the former case. The specific influences of carbon dioxide and ethylene oxide on the adsorption of ethylene are examined below.

By contrast to ethylene, ethylene oxide is found to adsorb both with and without oxygen. Spectra for both cases are shown in Fig. 6. In the absence of oxygen, four bands are seen in the vicinity of 3000 cm^{-1}, occurring at 2970, 2920, 2890 and 2820 cm^{-1}. Another four bands at 1100, 1080, 1035 and 860 cm^{-1} are found in the low frequency portion of the spectrum. When oxygen is added to the system, new bands appear at 3010, 2320, 2270 and 1740 cm^{-1} and the bands at 2920 and 2820



Spectrum	A	B	C	D
Run	A-10	A-3	A-11	A-6
P_{O_2} (atm)	-	-	0.370	0.380
$P_{C_2H_4O}$ (atm)	-	0.035	-	0.038
P_{CH_3CHO} (atm)	0.035	-	0.038	-
T (°C)	220	220	220	220

FIG. 6. Spectra of acetaldehyde and ethylene oxide adsorbed in the absence and presence of oxygen: T = 220°C.

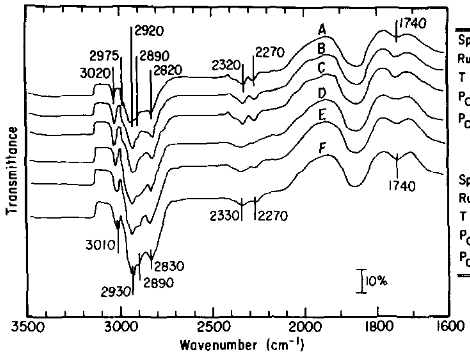
cm^{-1} are intensified. In the low frequency portion of the spectrum, the addition of oxygen causes an intensification of the bands at 1100 and 860 cm^{-1} and the appearance of new bands at 1245, 1155 and 605 cm^{-1}.

Figure 7 illustrates a series of spectra obtained for ethylene oxide adsorbed with oxygen at 220 and 170°C. It is noted that the intensity of the bands near 3000 cm^{-1} increases with increasing partial pressures of ethylene oxide and oxygen for a given temperature and with decreasing temperature for a given gas composition consistent with the behavior expected for an adsorption process. The weak bands present at 2330 and 2270 cm^{-1} are intensified by increasing temperature which suggests that they are derived from the products of ethylene oxide oxidation. A similar deduction cannot be made for the band at 1740 cm^{-1} since its intensity is independent of temperature for a given gas composition.

While acetaldehyde was not observed as a product of ethylene oxidation its adsorption was investigated because it is an isomer of ethylene oxide and because it has been postulated as an intermediate in the reaction mechanism (*9*). Figure 6 shows the spectra for acetaldehyde adsorbed with and without oxygen at 220°C. The partial pressures of acetaldehyde and oxygen used in these experiments were identical to the partial pressures of ethylene oxide and oxygen used for the adsorption of ethylene oxide. These conditions were chosen to facilitate a comparison of the spectra for adsorbed acetaldehyde and ethylene dioxide.

The spectrum of acetaldehyde adsorbed in the absence of oxygen exhibits four overlapping bands in the vicinity of 3000 cm^{-1}. These bands are located at 2960, 2920, 2890 and 2830 cm^{-1} which corresponds very closely to the positions of similar bands observed for adsorbed ethylene oxide. The appearance of bands at 2330, 2270 and 1725 cm^{-1} for adsorbed acetaldehyde contrasts sharply with the spectrum for adsorbed ethylene oxide and suggests that a portion of the adsorbed acetaldehyde decomposes to release oxygen which can then oxidize a portion of the remaining adsorbed acetaldhyde. In the low frequency portion of the spectrum, shown in Fig. 6, only a single band is observed at 1045 cm^{-1}. The position of this band is close to that occurring at 1035 cm^{-1} for adsorbed ethylene oxide.

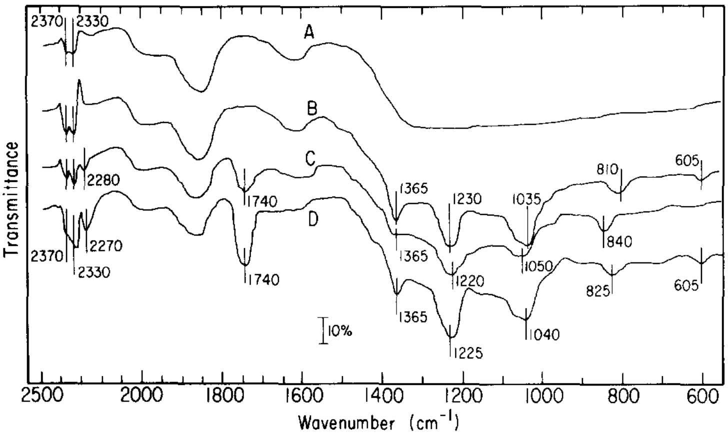
When oxygen is added to acetaldehyde the band at 2960 cm^{-1} shifts to 2970 cm^{-1} and both this band and the band at 2830 cm^{-1} are reduced in intensity. The presence of oxygen also causes a new band to appear at 3020 cm^{-1}. Comparison of the spectrum for adsorbed acetaldehyde with that for adsorbed ethylene oxide shows that both spectra exhibit a series of four bands near 3000 cm^{-1}. The primary differences are that the bands at 3020 and 2830 cm^{-1} are less intense and the band at



Spectrum	A	B	C
Run	A-6	A-6	A-6
T (°C)	220	220	220
P_{O_2} (atm)	0.200	0.270	0.376
$P_{C_2H_4O}$ (atm)	0.022	0.027	0.038

Spectrum	D	E	F
Run	A-7	A-7	A-7
T (°C)	170	170	170
P_{O_2} (atm)	0.200	0.270	0.376
$P_{C_2H_4O}$ (atm)	0.022	0.027	0.038

FIG. 7. Spectra of ethylene oxide adsorbed in the presence of oxygen: $T = 220°C$; and $T = 170°C$.



Spectrum	A	B	C	D
Run	A-1	A-2	R-2	R-3
Time (hr)	—	—	9	14
P_{O_2} (atm)	—	0.270	0.270	0.270
$P_{C_2H_4}$ (atm)	—	—	0.110	0.110
P_{CO_2} (atm)	0.096	0.096	0.060	0.096
P_{H_2O} (atm)	—	—	0.060	0.062
$P_{C_2H_4O}$ (atm)	—	—	0.031	0.027
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	—	—	69	22
$r_{CO_2}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	—	—	115	57
$S_{C_2H_4O}$ (%)	—	—	55	44

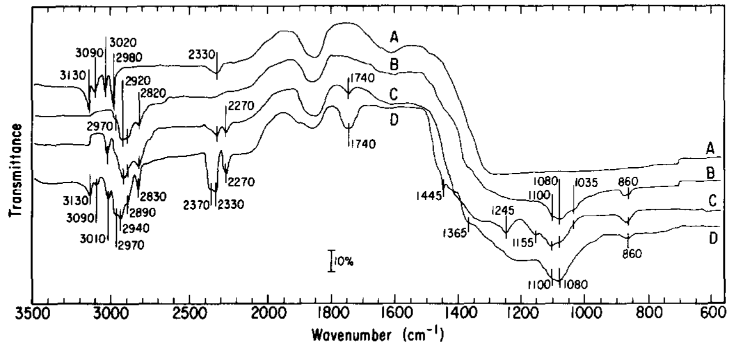
FIG. 8. Comparison of the spectra for carbon dioxide adsorbed in the absence and presence of oxygen with spectra taken under reaction conditions: $T = 220°C$.

2970 cm^{-1} is more intense for adsorbed acetaldehyde than for adsorbed ethylene oxide. The presence of oxygen during the adsorption of acetaldehyde causes the appearance of five new bands at 1455, 1425, 1145, 1060 and 850 cm^{-1}. Of these bands the ones at 1145, 1060 and 850 cm^{-1} closely resemble similar bands observed during the adsorption of ethylene oxide with oxygen.

Figure 8 compares spectra obtained for the adsorption of carbon dioxide with spectra obtained under reaction conditions. Spectrum A corresponds to the adsorption of carbon dioxide in the absence of oxygen. Only a single pair of overlapping bands appearing at 2370 and 2330 cm^{-1} is observed in this case. When oxygen is added, spectrum B is obtained. Although the partial pressures used in producing spectra A and B are the same, the intensities of the bands at 2370 and 2330 cm^{-1} are significantly stronger in spectrum B than in spectrum A. Reference to spectra C and D indicates that the same two bands are observed under reaction conditions and that their intensity is enhanced by an increased partial pressure of carbon dioxide. It is also noted that while the intensities of the two bands are equivalent under adsorption conditions, the band at 2330 cm^{-1} is more intense than that at 2370 cm^{-1} under reaction conditions.

Spectrum B in Fig. 8 also illustrates that the adsorption of carbon dioxide in the presence of oxygen causes the appearance of five new bands at 1365, 1230, 1035, 810 and 605 cm^{-1}, which are not present in spectrum A. These five bands correspond very closely to the five bands indicated in spectra C and D, taken under reaction conditions. Comparison of spectra C and D shows further that when the partial pressure of carbon dioxide is increased while maintaining the partial pressures of the remaining components essentially constant that the intensities of the five bands attributed to adsorbed carbon dioxide increase.

Finally, it is noted that the band appearing in the 800 cm^{-1} region of the spectra shown in Fig. 9 shifts depending on the composition of the gas in the reactor. Under adsorption conditions this band appears at 810 cm^{-1} as seen in spectrum B. In spectrum D, taken under reaction conditions, this band is shifted to 825 cm^{-1} even though the partial pressures of carbon dioxide and oxygen are the same as for spectrum B. When the partial pressure of carbon dioxide is reduced keeping the partial pressures of all other components



Spectrum	A	B	C	D
Run	A-4	A-3	A-6	R-5
P_{O_2} (atm)	0.370	–	0.376	0.378
$P_{C_2H_4}$ (atm)	0.170	–	–	0.172
P_{CO_2} (atm)	–	–	–	0.007
P_{H_2O} (atm)	–	–	–	0.007
$P_{C_2H_4O}$ (atm)	–	0.035	0.038	0.039
$r_{C_2H_4O}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	–	–	–	26
$r_{CO_2}\left(\frac{\mu\text{mole}}{\text{min g Ag}}\right)$	–	–	–	32
$S_{C_2H_4O}$ (%)	–	–	–	61
T (°C)	220	220	220	220

FIG. 9. Comparison of the spectra for adsorbed ethylene and ethylene oxide with a spectrum taken under reaction conditions: $T = 220°C$.

the same, the band position moves upscale to 840 cm^{-1} as seen in spectrum C. The observed shift in the position of this band is similar to that noted in the discussion of Fig. 3. In both cases the band moves downscale with increasing partial pressure of carbon dioxide.

The relationship of the spectra of individual adsorbed components to the spectrum of adsorbed species taken under reaction conditions is illustrated in Fig. 9. Spectra A, B, and C correspond to the adsorption of ethylene, ethylene oxide, and carbon dioxide, each in the presence of oxygen, and spectrum D corresponds to reaction run R-6. The partial pressures of each adsorbate used in performing the adsorption runs were chosen to correspond as closely as possible to the partial pressures of the identical components observed at a point 3 hr into run R-5.

The bands at 3130, 3090, 3010, 2970, 2940, 2890 and 2830 cm^{-1} appearing in spectrum D of Fig. 9 are seen to correspond very closely to similar peaks in spectra A and B for adsorbed ethylene and ethylene oxide. Similarly, the pair of bands at 2370 and 2330 cm^{-1} can be identified with adsorbed carbon dioxide. The remaining two bands at 2270 and 1740 cm^{-1} occur at identical positions to the corresponding bands observed in spectrum B but are considerably less intense. This observation suggests that these two bands are due to an intermediate species which is present both under reaction conditions and when ethylene oxide is adsorbed in the presence of oxygen.

Further inspection of Fig. 9 shows that the bands appearing at 1365, 1225 and 1040 cm^{-1} in spectrum D correspond exactly to bands located at the same frequencies in spectrum C for adsorbed carbon dioxide. Likewise the band occurring at 1080 cm^{-1} can be definitely associated with adsorbed ethylene oxide by reference to spectrum B. The two bands at 865 and 620 cm^{-1} in spectrum D correspond most closely to the bands at 865 and 610 cm^{-1} observed for adsorbed ethylene oxide. It should be noted, however, that adsorbed carbon dioxide also exhibits two such bands, but these are shifted to 810 and 605 cm^{-1}. Finally, it is noted that a band located at 1445 cm^{-1} is observed only under reaction conditions. Adsorbed ethylene oxide also produces bands at 1245 and 1155 cm^{-1}. While it is possible that a band corresponding to the one at 1245 cm^{-1} is masked by the broad band at 1225 cm^{-1} in spectrum D, no band is observed at 1155 cm^{-1} in spectrum D. This may suggest that the form of adsorbed ethylene oxide present under reaction conditions is more nearly similar to that corresponding to ethylene oxide adsorbed on silver in the absence of oxygen (see spectrum A in Fig. 6).

DISCUSSION

As noted in the previous section, the majority of the bands observed under reaction conditions can be ascribed to the adsorption of reactants or products. Consequently the interpretation of these bands can proceed through an examination of the spectra obtained from adsorption runs. The elucidation of explicit surface structures proceeds by comparison of the observed spectra with those for the adsorbate molecule, transition metal complexes of the adsorbate, and related compounds or structures derived from the original adsorbate.

The spectrum of ethylene adsorbed in the presence of oxygen contains four strong bands in the vicinity of 3000 cm^{-1}. The positions of these bands are listed in Table 3 and compared with the position of bands observed for gaseous ethylene (*10*). Also noted in Table 3 are the band positions taken from the spectra of ethylene adsorbed on silver ions present in an ion-exchanged zeolite (*11*), silver ions present in an aqueous solution of silver tetrafluoroborate (*12*), and oxygen-covered silver dispersed on a silica support (*4,5*). The four bands observed in this work correlate very closely with the four bands assigned to C–H stretching vibrations for gaseous ethylene which suggests that the adsorption of ethylene on silver occurs without rupture of the C=C bond. The positions of the ν_2 and ν_3 vibrations in both of these studies agree very closely. Furthermore it is evident that both of these modes, which are normally only Raman active, become infrared active upon interaction of ethylene with silver ions. The ν_{12} vibration which is normally infrared active is observed only in the spectrum ethylene adsorbed on the silver-exchanged zeolite. Bands corresponding to ν_2, ν_3, or ν_{12} vibrations were not observed in the present work. Two reasons can be offered to account for this. The first is that the symmetry of the adsorbed ethylene molecule did not change sufficiently to cause the ν_2 and ν_3 vibrations to become infrared active. The second, and perhaps more likely explanation, is that the transmission of the discs in the vicinity of 1600 to 1400 cm^{-1} is so poor, due to strong adsorption by the silica support, that it is impos-

TABLE 3

COMPARISON OF THE VIBRATIONAL FREQUENCIES FOR ETHYLENE IN DIFFERENT ENVIRONMENTS

	Gaseous C_2H_4 (*10*)		C_2H_4 adsorbed on Ag-Zeolite (*11*)		C_2H_4 adsorbed on $AgBF_4$ (*12*)	$C_2H_4 + O_2$ adsorbed on Ag (this work)	C_2H_4 adsorbed on Ag containing preadsorbed O_2 (*4*)	C_2H_4 adsorbed on Ag containing preadsorbed O_2 (*5*)
Band	ν(cm^{-1})	Sym. species	ν(cm^{-1})	Sym. species^a	ν(cm^{-1})	ν(cm^{-1})	ν(cm^{-1})	ν(cm^{-1})
ν_9	3105	B_{2u}	3140	B_2	—	3130	—	—
ν_5	3086^b	B_{1g}	3086	A_2	—	3090	—	—
ν_1	3026^b	A_g	3060	A_1	—	3020	—	—
ν_{11}	2989	B_{3u}	2985	B_1	—	2980	2958,2850	2940,2840
ν_2	1623^b	A_g	1570	A_1	1579^b	—	—	—
ν_{12}	1444	B_{3u}	1425	B_2	—	—	1460,1440	1458,1440
ν_3	1342^b	A_g	1310	A_1	1320^b	—	—	—
ν_6	1217^b	B_{1g}	—	—	—	—	—	—
ν_4	1023^c	A_u	—	—	—	—	—	—
ν_7	949	B_{1u}	—	—	—	—	—	—
ν_8	940^b	B_{2g}	—	—	—	—	—	—
ν_{10}	826	B_{2u}	—	—	—	—	870	870

[a] Symmetry species for an assumed C_{2v} point group.

[b] Raman active.

[c] Both Raman and infrared inactive.

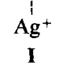
sible to observe the ν_{12} vibration or the ν_2 vibration even if the latter were infrared active.

It is important to note that the spectra for adsorbed ethylene bear closer resemblance to those for ethylene complexed with a silver ion than to those for ethylene adsorbed on silver containing preadsorbed oxygen, columns 5 and 6 of Table 3. The latter spectra, obtained by Gerei *et al.* (*4*) and by Kilty *et al.* (*5*) are similar to each other but show no evidence for ethylene adsorbed on the surface in an undissociated form. Instead, the work of these two groups support the presence of a peroxide structure, $-CH_2-CH_2-O-O-$, as discussed in the introduction. The reason for the differences between the spectra published by Gerei *et al.* and Kilty *et al.* and those presented here are likely due to the means by which the former spectra were obtained. In both cases oxygen was adsorbed onto silver at 95°C. The oxygen in the gas phase was then removed and replaced by ethylene which was adsorbed at 95°C. Before recording a spectrum the sample cell was evacuated and the sample temperature, was brought down to room temperature. Because of this procedure the spectra presented by Gerei *et al.* and Kilty *et al.* show features only for those species which are strongly chemisorbed. The procedure of the present work differs in that the spectra are recorded in the presence of both gas phase components and at the temperature at which adsorption has occurred.

The nature of the sites on which ethylene adsorption occurs can now be considered. As noted above, no spectrum could be obtained when the catalyst was exposed to ethylene in the absence of oxygen. Thus it may be concluded, in agreement with previous studies (*13–19*), that a completely reduced silver surface does not contain sites suitable for the adsorption of ethylene. In the presence of oxygen ethylene is adsorbed and the spectrum obtained bears close resemblance to that for ethylene coordinated with individual silver ions (*11*). This observation suggests that the adsorption sites are individual silver ions present in a silver oxide surface layer. Strong support for the existence of a surface oxide layer on silver at temperatures above which bulk Ag_2O is unstable has been given by a number of recent studies (*6,20–27*).

Ethylene adsorption studies on oxygenated silver (*15,17,18*) and silver oxide (*28*) offer additional evidence supporting the selection of silver ions as the proper adsorption site. The work of Gerei *et al.* (*15*) showed that ethylene would adsorb on silver previously exposed to oxygen provided that the adsorbed oxygen did not cover the surface completely. Based on this observation it was proposed that both adsorbed oxygen and free surface sites are required for ethylene adsorption. It was further postulated that the adsorbed oxygen forms negative ions which are counter-balanced by positive silver ion sites on which ethylene adsorption occurs. This interpretation is consistent with work function measurements performed earlier by Einkeev *et al.* (*29*) which showed that ethylene acts as an electron donor upon adsorption. Also consistent with this interpretation is Seo and Sato's work (*18*) which shows that the differential heat of reversible ethylene adsorption on oxygenated silver is approximately the same as that for adsorption on bulk silver oxide (*28*).

A proposed structure for the adsorbed ethylene molecule is shown below,



$$\underset{Ag^+}{H_2C{=}CH_2}$$

I

and is identical to that proposed by Carter *et al.* (*11*) to explain the spectrum of ethylene adsorbed on silver ions substituted into a zeolite lattice. The bonding of this structure consists of two components. These are the overlap of the filled π orbitals of the olefin with the partially vacant 5*sp* hybrid orbital of the silver ion, and the overlap of the filled 4*d* orbitals of the silver ion with vacant π^* orbitals of the olefin. While admittedly hypothetical, this bonding concept was used to explain successfully a number of the spectral features observed for ethylene coordinated to a silver ion.

It is important to note, however, that the proposed structure may not be entirely correct in explaining either the spectrum reported by Carter *et al.* (*11*) or the present results. The seven atom configuration represented by structure **I** is characterized by three symmetry elements in addition to the identity element E, a C_2 axis of rotation, a σ_v plane of reflection, and a σ_v' plane of reflection. These symmetry elements place structure **I** into the C_{2v} point group. Application of group theory shows that of the 15 fundamental vibrational modes 5 have A_1 symmetry (totally symmetric), three have A_2 symmetry (symmetric with respect to the C_2 axis only), three have B_1 symmetry (symmetric with respect to the σ_v plane only), and four have B_2 symmetry (symmetric to the σ_v' plane only). Of these, the A_2 modes are infrared inactive. The problem arises upon consideration of the C–H stretching modes. Analysis of the symmetry characteristics of the four C–H modes for structure **I** requires a distribution of one mode to each symmetry species. Correspondingly we should expect to observe three infrared bands related to C–H stretching rather than four. The mode with A_2 symmetry should be absent.

Since the coordinated ethylene shown in structure **I** is presumed to retain the planar geometry of gaseous ethylene, the individual stretching modes should be very similar to those in the molecule itself. Using this analogy it is possible to identify each band with a particular symmetry species. This has been done in Table 3. Thus we conclude that if adsorbed ethylene possesses C_{2v} symmetry, then the band at 3090 cm^{-1} should not be observable in the infrared spectrum.

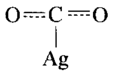
At least two possible explanations can be offered for the presence of four rather than three C–H stretching vibrations. The first is that, while the π-bonding scheme proposed by structure **I** is essentially correct, the symmetry of the complex is sufficiently distorted so that it no longer falls into the C_{2v} point group. A possible source of distortion would be interactions of next nearest neighbors with atoms in the adsorbed ethylene molecule. A second possibility is that one of the bands in the 3000 cm^{-1} region is not associated with C–H stretching vibrations but instead is due to a combination of bands or an overtone of vibrations occuring at lower frequencies.

The infrared bands associated with the adsorption of carbon dioxide are shown in Table 4 and compared with the bands observed for gaseous CO_2 (*30*), bulk Ag_2CO_3 (*31*), and Ag_2CO_3 films formed by reaction of CO_2 with Ag_2O (*32*). Also shown in Table 4 are the frequency ranges for the vibrations of monodentate and bidentate carbonate coordination complexes of transition metals (*33*). It is immediately apparent that the doublet band centered at 2350 cm^{-1} produced when carbon dioxide is adsorbed in the absence of oxygen is identical to the ν_3 stretching vibration of gaseous CO_2. Such close agreement suggests that this form of adsorbed carbon dioxide is loosely bonded to the surface so that the bonds in the molecule are unaltered. Two structures can be proposed, viz,

$O{=}C{=}O{-}Ag$

II

or



$O{=}\underset{\underset{Ag}{|}}{C}{=}O$

III

The fact that the band centered at 2350 cm^{-1} is a doublet composed of two bands whose maxima occur at 2330 and 2370

TABLE 4

COMPARISON OF THE VIBRATIONAL FREQUENCIES OF CO_2 ADSORBED ON Ag WITH THOSE FOR CARBONATE STRUCTURES AND GASEOUS CO_2

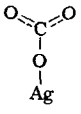
Band	Gaseous CO_2 (*31*) ν(cm^{-1})	$CO_2 + O_2$ adsorbed on Ag (this work) ν(cm^{-1})	$AgCO_3$ (*32*) ν(cm^{-1})	CO_2 adsorbed on Ag_2O (*33*)	Monodentate carbonate (*34*) ν(cm^{-1})	Bidentate carbonate (*34*) ν(cm^{-1})
ν_3	2349	2350	—	—	—	—
	—	—	1790	—	—	—
	—	—	—	—	—	1630–1590
	—	—	—	—	1530–1470	—
	—	—	1449	1410	—	—
ν_1	1337[a]	1365	—	—	1370–1300	—
	—	1230	—	—	—	1270–1260
	—	1035	1072	1020	1080–1040	1030–1020
	—	810	802,785	880	880–850	840–830
	—	—	720,705	820	820–750	760–740
ν_2	667	605	—	690	690–670	680–660

[a] Raman active.

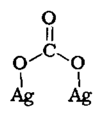
cm^{-1} (see Fig. 8) suggests that the adsorbed CO_2 molecule is free to rotate. This interpretation is consistent with the observation that the rotation of gaseous carbon dioxide leads to a doublet composed of the *P* and *R* branches of the band. The positions of the maxima of the *P* and *R* branches are 2330 and 2370 cm^{-1} (*30*), respectively. Consequently, it is contended that structure **III** properly represents the form of carbon dioxide adsorbed in the absence of oxygen.

The rather peculiar changes in band intensity and shape of the doublet centered at 2350 cm^{-1} can be interpreted in terms of carbon dioxide adsorption on the silica support material. In preliminary tests it was observed that a silica disc would adsorb carbon dioxide and give rise to a doublet band centered at 2350 cm^{-1}. For a given partial pressure of carbon dioxide the intensity of this spectrum was weaker than that for carbon dioxide adsorbed on silver. Since there is a greater mass of silica in the reference disc than in the catalyst disc, it is expected that more carbon dioxide will be adsorbed by the silica of the reference disc than that of the catalyst disc. This situation would give rise to a weak negative band which would be superimposed on the positive band formed by carbon dioxide adsorbed on silver. It is proposed that with increasing carbon dioxide partial pressures the interference of the bands from the two sources becomes more significant and contributes to the apparent reduction in band intensity and the division of the doublet into two fully resolved bands.

When oxygen is present, five additional bands appear in the spectrum of adsorbed carbon dioxide. These new bands occurring at 1365, 1230, 1035, 810 and 605 cm^{-1} can be associated with various forms of carbonate structures as shown in Table 4. In view of the positions of these bands we expect that both monodentate and bidentate type carbonates will exist as indicated by structures **IV** and **V**.



IV



V

It is important to comment further on the role of oxygen in the adsorption of carbon dioxide. Czanderna (*34*) has reported that carbon dioxide will not adsorb on fully reduced silver and that adsorption will occur only after oxygen has been preadsorbed onto the surface of the silver. The present observations appear to contradict Czanderna's results inasmuch as a spectrum of adsorbed carbon dioxide was obtained on reduced silver. The absence of any carbonate type bands in these spectra suggests that very little if any residual oxygen was present on the reduced silver surface. For a common partial pressure of carbon dioxide, the presence of oxygen causes the band at 2350 cm^{-1} to be intensified over the level when oxygen is absent. This observation indicates that the adsorption of oxygen enhances the adsorption of carbon dioxide in the form of structure **III**. The presence of oxygen also contributes to the formation of carbonate structures such as **IV** and **V** as noted above.

The interpretation of the spectra for adsorbed ethylene oxide and acetaldehyde can be examined together since their spectra bear many similarities. Table 5 lists the bands observed for ethylene oxide and acetaldehyde adsorbed in presence and absence of oxygen. These bands are compared with those for gaseous ethylene oxide (*35*) and acetaldehyde (*36*) and with the bands for ethylene oxide adsorbed on silver reported by Gerei *et al.* (*4*).

In the absence of oxygen, the spectrum of adsorbed ethylene oxide contains four C–H stretching frequencies which correlate most closely with the asymmetric and symmetric vibrations of CH_2 and CH_3 groups occurring in aliphatic molecules. This fact, plus the absence of any bands above 3000 cm^{-1}, as found in gaseous ethylene oxide, strongly suggests that ethylene oxide adsorbs in a form in which the epoxide ring is open. It is proposed, therefore, that initial adsorption produces a structure such as **VI** shown below. Subsequent migration of a hydrogen atom

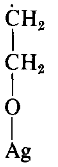
TABLE 5

COMPARISON OF THE VIBRATIONAL FREQUENCIES FOR GASEOUS AND ADSORBED ETHYLENE OXIDE AND ACETALDEHYDE

Band	Gaseous C_2H_4O (*35*) $\nu(cm^{-1})$	C_2H_4O adsorbed on Ag (this work) $\nu(cm^{-1})$	$C_2H_4O + O_2$ adsorbed on Ag (this work) $\nu(cm^{-1})$	C_2H_4O adsorbed on Ag (*4*) $\nu(cm^{-1})$	Band	Gaseous CH_3CHO (*36*) $\nu(cm^{-1})$	CH_3CHO adsorbed on Ag (this work) $\nu(cm^{-1})$	$CH_3CHO + O_2$ adsorbed on Ag (this work) $\nu(cm^{-1})$
ν_{13}	3079	—	—	—	ν_1	3014	—	3020
ν_6	3063[a]	—	—	—	ν_{11}	2966	2960	2975
ν_9	3019	—	3010	—	ν_2	2923	2920	2940
ν_1	3005	—	—	—	$2\nu_6$	2830,2809	2890,2830	2890,2830
—	—	2970	2970	2960	ν_3	2716	—	—
—	—	2920	2920	—	ν_4	1743	—	—
—	—	2890	2890	2800	ν_{12},ν_5	1433	—	1455,1425
—	—	2820	2820	2850	ν_6	1395	—	—
ν_2	1490	—	—	1460	ν_7	1352	—	—
ν_{10}	1470	—	—	1440	ν_8	1114	—	1145
ν_7	1345[a]	—	—	—	ν_{13}	1111	—	—
ν_3	1266	—	1245	—	—	—	1045	1060
ν_{11}	1153	—	1155	—	ν_9	867	—	850
ν_{14}	1120	—	1100	—	ν_{14}	764	—	—
—	—	1080	1080	—	ν_{10}	509	—	—
—	—	1035	—	—	ν_{15}	150	—	—
ν_4	892	—	—	—	—	—	—	—
ν_5	877	860	860	860	—	—	—	—
ν_{15}	821	—	—	—	—	—	—	—
ν_8	807[a]	—	—	—	—	—	—	—

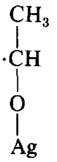
[a] Raman active.

would produce structure **VII** thereby explaining the presence of C–H vibrations associated with CH_3 groups. Structures **VI** and **VII**,



$$\begin{array}{c}\dot{C}H_2\\ |\\ CH_2\\ |\\ O\\ |\\ Ag\end{array}$$

VI



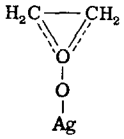
$$\begin{array}{c}CH_3\\ |\\ \cdot CH\\ |\\ O\\ |\\ Ag\end{array}$$

VII

are supported by the presence of the band at 1080 cm^{-1}. This band, which does not appear in the spectrum of gaseous ethylene oxide, can be assigned to the C–O stretching vibrations in compounds having terminal alkoxide groups (*37*).

The remaining band appearing at 860 cm^{-1} is only slightly displaced from the band at 865 cm^{-1} which is ascribed to an epoxide ring vibration of gaseous ethylene oxide. The band at 860 cm^{-1} cannot, however, be assigned to this type of vibration since, as described above, the remaining portions of the spectrum do not support the adsorption of ethylene oxide in a ring-closed form. Instead, it is believed that this band is also due to vibrations associated with either structure **VI** or **VII**. A similar interpretation has been given by Kilty *et al.* (*5*) for a band observed at 864 cm^{-1} for ethylene adsorbed on oxygenated silver. Finally, Barraclough *et al.* (*37*) reported the observation of bands in this frequency range for various metal alkoxides.

The coadsorption of ethylene oxide and oxygen introduces bands at 3010, 1245, 1155 and 1100 cm^{-1} in addition to those observed when ethylene oxide is adsorbed by itself. Furthermore, there is an intensification of the band at 860 cm^{-1}. All five of these features correlate very closely with the spectrum for gaseous ethylene oxide, leading to the suggestion that in the presence of oxygen, ethylene oxide can adsorb in both a ring-closed and a ring-open manner. A possible form for the ring-closed structure is shown (**VIII**).



VIII

The adsorption of acetaldehyde by itself produces four bands in the C–H stretching region of the spectrum and a single band at 1045 cm^{-1}. Comparison with the tabulated bands for gaseous acetaldehyde shows the complete absence of strong bands at 2716 and 1743 cm^{-1} characteristic of the C–H and C=O stretching vibrations associated with the acyl carbon. These observations suggest that acetaldehyde adsorbs initially as an alkoxide similar to structure **VII** which may subsequently isomerize to structure **VI.** The postulation of structures **VI** and **VII** is further supported by the similarities between the bands observed for ethanol and for adsorbed ethylene oxide. The major differences between the spectra of adsorbed acetaldehyde and ethylene oxide are the absence of a band at 860 cm^{-1} from the spectrum of adsorbed acetaldehyde and the position of the band in the region of 1000 to 1100 cm^{-1} (i.e., 1045 cm^{-1} for acetaldehyde and 1080 cm^{-1} for ethylene oxide). These differences may be attributable to the predominance of structure **VII** for adsorbed acetaldehyde and structure **VI** for adsorbed ethylene oxide.

The coadsorption of acetaldehyde and oxygen introduces new bands at 3020, 1455, 1425, 1145 and 850 cm^{-1} and causes a shift of the band at 1045 to 1060 cm^{-1}. The assignment of this spectrum to a definite structure is considerably more difficult than for the species discussed previously. The presence of bands at 3020, 1145 and 850 cm^{-1} could be used to argue for a structure like **VIII** by analogy with the spectrum for ethylene oxide adsorbed in the presence of oxygen. Arguing against such an interpretation is the absence of bands near 1245 and 1100 cm^{-1}. Nevertheless, the possibility of forming structure **VIII** cannot be ruled out completely since it is known that ethylene oxide and acetaldehyde will isomerize over silver (*9*). Furthermore, if structure **VIII** were excluded it would be very difficult to explain the occurrence of a C-H stretching frequency of 3020 cm^{-1} inasmuch as this frequency level implies the presence of either a strained ring or unsaturation.

The two bands at 1455 and 1425 cm^{-1} appear to be unique to acetaldehyde coadsorption with oxygen. The most reasonable assignment of these bands is to CH_2 or CH_3 deformation vibrations (*38*). However, if this assignment is correct, then similar bands would be expected in the spectra of ethylene oxide adsorbed with an without oxygen. An explanation for the absence of such bands from the spectra of adsorbed ethylene oxide cannot be given.

The two bands at 1740 and 2270 cm^{-1} observed under reaction conditions (see Fig. 3A) cannot be associated directly with the adsorption of either reactants or products. These bands appear as soon as the reaction starts and increase in intensity over the course of the reaction. An increase in the concentration of carbon dioxide in the gas phase maintaining all other species concentrations the same causes the intensities of these two bands to increase. In both instances the increases in intensity are accompanied by a decrease in the rates of epoxidation and combustion.

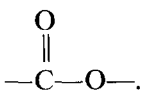
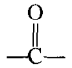
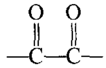
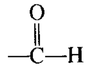
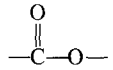
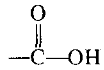
The band at 1740 cm^{-1} can readily be assigned to the vibration of a C=O bond by comparison with numerous compounds containing such bonds (*39*). As shown in Table 6 it appears that this bond is part of a structure such as  $-\overset{O}{\overset{\|}{C}}-O-$.

TABLE 6
Frequencies of C=O Vibrations in Different Structures

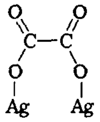
Structure	$\nu_{C=O}(cm^{-1})$
 $-\overset{O}{\overset{\|}{C}}-$	1715
 $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$	1720
 $-\overset{O}{\overset{\|}{C}}-H$	1725
 $-\overset{O}{\overset{\|}{C}}-O-$	1735
 $-\overset{O}{\overset{\|}{C}}-OH$	1760

By contrast, the band observed at 2270 cm^{-1} cannot be assigned as easily. Table 7 lists three structures comprised of silver, carbon, and oxygen atoms and three gaseous molecules comprised of carbon and oxygen atoms for which infrared bands have been observed in the vicinity of 2000 cm^{-1}. It is evident from Table 7 that C-O vibrational frequencies associated with the structures containing silver are considerably lower than 2270 cm^{-1}. It is also evident that molecules containing only carbon and oxygen do possess vibrational frequencies which are very close to 2270 cm^{-1}. In view of this and the observation that the band at 2270 cm^{-1} is best ascribed sity together with the pair of bands centered at 2350 cm^{-1}, which is associated with adsorbed carbon dioxide, we propose that the band at 2270 cm^{-1} is best ascribed

TABLE 7
A Comparison of C-O Vibrational Frequencies in Various Carbon Oxide and Silver Carbon Oxide Structures

Structure	$\nu(cm^{-1})$	Ref.
C_3O_2	2258	(*38*)
CO	2143	(*38*)
CO_2	2349	(*38*)
$Ag_3C_3O_2$	2000	(*39*)
Ag_2C_2O	2060	(*40*)
Ag-CO	2180	(*41*)

to a form of adsorbed carbon dioxide produced via reaction rather than gas phase adsorption. A candidate for this surface species might be structure **II** shown earlier. Formation of this structure could occur through the decomposition of an oxalate type structure such as **IX.**

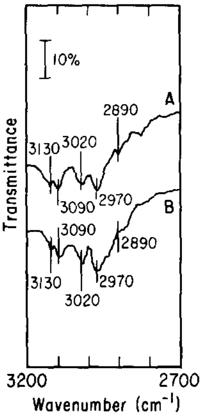


IX

Thus it seems reasonable to assign both the band at 1740 cm^{-1} and the one at 2270 cm^{-1} to intermediates in the complete combustion of ethylene to carbon dioxide and water.

In the course of this work no bands were observed which could be related to presence of adsorbed water or hydroxyl groups. These species if they were present would have contributed bands in the region of 3600 to 3800 cm^{-1} (*42*). The failure to observe bands for water or its precursors does not necessarily signify their total absence but may instead be due to the relative opaqueness of the silica support in the region noted.

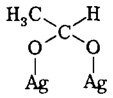
Finally, we note that the spectra presented here provide some evidence that the adsorption of one species can influence the adsorption of another. For example, a comparison of Figs. 4 and 5 shows that the presence of even very small amounts of ethylene oxide alters the spectrum for adsorbed ethylene. Although the partial pressures of ethylene and oxygen associated with the spectra in Figs. 4 and 5 are essentially the same, the bands in Fig. 5 are less intense than those in Fig. 4. Furthermore, the positions of similar bands in the two figures are not identical and Fig. 5 shows the presence of some additional bands beyond those seen in Fig. 4. The influence of ethylene oxide is probably due to its ability to tie up the free silver sites needed for ethylene adsorption. By contrast, the adsorption of carbon dioxide does not appear to have any influence on the adsorption of ethylene. This conclusion is based upon an examination of C–H stretching portion of spectra C and D which is shown in Fig. 10. There it is seen that a 50% increase in the partial pressure of carbon dioxide for fixed partial pressures of all other components does not influence the position or intensity of the bands due to C–H stretching vibrations.



Spectrum	A	B
Run	R-2	R-3
Time (hr)	9	14
P_{O_2} (atm)	0.270	0.270
$P_{C_2H_4}$ (atm)	0.110	0.110
P_{CO_2} (atm)	0.060	0.096
P_{H_2O} (atm)	0.060	0.062
$P_{C_2H_4O}$ (atm)	0.031	0.027
$r_{C_2H_4O}$ $\left(\frac{\mu mole}{min\ g\ Ag}\right)$	69	22
r_{CO_2} $\left(\frac{\mu mole}{min\ g\ Ag}\right)$	115	57
$S_{C_2H_4O}$ (%)	55	44

FIG. 10. Comparison of the CH stretching portions of the spectra for reaction runs with and without added carbon dioxide: $T = 220°C$.

A further indication of the influence of one adsorbed species on another is suggested by the position of the band in the 800 cm^{-1} portion of the spectrum. In Fig. 2B a band first appears at 870 cm^{-1} and then shifts to 820 cm^{-1} as the reaction proceeds. Likewise, in Fig. 8, spectrum C exhibits a band at 840 cm^{-1} but when the partial pressure of carbon dioxide is increased the band shifts to 820 cm^{-1}. Since ethylene oxide and carbon dioxide, each coadsorbed with oxygen, produce bands at 860 and 810 cm^{-1} respectively, the band observed in Figs. 2B and 8 is quite possibly due to a form of surface bonding common to both ethylene oxide and carbon dioxide. Candidate surface structures are **V** and **X.** Structure **X,** which is shown below, could easily be formed by reaction of structure **VII** with an adsorbed oxygen atom.



X

Since structure **V** does not require an isomerization of the adsorbate, its formation should proceed more easily than the formation of structure **X**. This might explain why the band in the 800 cm^{-1} region shifts downscale as the partial pressure of carbon dioxide increases.

CONCLUSION

Through the use of infrared spectroscopy the present study has shown that the surface of a silver catalyst is covered by a variety of species when the catalyst is used to promote the oxidation of ethylene. Comparison of the spectra obtained under reaction conditions with those observed when individual reactants or products are adsorbed allowed the reaction run spectra to be interpreted. By this method it was determined that ethylene adsorbs only in the presence of oxygen to form an olefinic structure similar to that noted for complexes of ethylene with individual silver ions. Ethylene oxide adsorbs to form two major structures, a ring-open alkoxide structure in which the oxygen of ethylene oxide bonds directly to the silver surface and a ring-closed structure in which bonding occurs through a peroxide linkage formed between an adsorbed oxygen atom and the oxygen atom of ethylene oxide. The first of these structures occurs both in the presence and absence of oxygen while the second structure occurs only in the presence of oxygen. In addition to the two structures just described, a third structure is observed. It is interpreted as an isomer of the first, formed through the transfer of a hydrogen atom to the terminal methylene group. This structure is also formed both in the presence and absence of oxygen. The adsorption of acetaldehyde gives spectra which are nearly identical to those produced by adsorbed ethylene oxide which suggests that acetaldehyde isomerizes upon adsorption to form a structure which can also be produced by the adsorption of ethylene oxide. Finally, it was noted that carbon dioxide adsorbs in two forms. In the first the axis of the carbon dioxide molecule is parallel to the catalyst surface and the bonding to the surface is weak enough to allow rotation of the adsorbate. In the second form the carbon dioxide interacts with adsorbed oxygen atoms to form monodentate and bidentate carbonates.

While most of the features found in the spectra recorded under reaction conditions can be ascribed to species formed by the adsorbed reactants and products, two bands were observed which could not be assigned this way. The first is a carbonyl band which is most likely due to carbonyl groups present in the partially oxidized intermediates which precede the formation of carbon dioxide and water. The second band occurs at a frequency only slightly downscale from that for carbon dioxide. This band is ascribed to a carbon dioxide molecule adsorbed through one of its oxygen atoms. This structure is believed to be formed via oxidation of ethylene since it is not observed when carbon dioxide is adsorbed by itself.

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