formance, and short equilibrium time. The apparatus was tested at 200 and 1 mm. Hg pressure, giving entirely satisfactory results at both pressures.

ACKNOWLEDGMENT

The guidance of Dr. Juan R. Suárez during the early stages of the investigation is gratefully acknowledged. Thanks are also given to Mr. C. Araujo, Mr. J. Benitez, and Mr. J. L. Pardo for their help in the experimental work.

NOTATION

P^0 = vapor pressure, mm. Hg
T = temperature, °C.

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Kinetics of Ethylene Oxidation on a Supported Silver Catalyst

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Since Lefort's original description of the process in a patent issued in 1931 (*1*), the oxidation of ethylene to ethylene oxide on a silver catalyst, with concurrent formation of carbon dioxide and water as by-products, has been extensively studied. Although much fundamental work has been done, uncertainties remain concerning the effects of reactant concentrations and the nature of the species adsorbed on the catalyst. Contradictions are apparent when the results of adsorption studies on silver are compared with conclusions based on models of the reaction kinetics. Furthermore, the mode of action of moderators and promoters is still not well understood. The purpose of this work was to obtain accurate kinetic data over a wide range of reactant concentrations and to provide some insight into the mechanism of the reaction.

SUMMARY OF PREVIOUS WORK

Several reviews of catalytic oxidation have been published recently (2 to 5), and an extensive review is given in the thesis by Klugherz (*6*). Only certain studies on adsorption and kinetics are reviewed here.

Adsorption

The chemical composition of the catalyst must first be considered. At 220°C. the equilibrium pressure of oxygen in a silver oxide-silver system is 2.7 atm. (*7, 8*), and the oxide phase cannot exist at the conditions usually used for ethylene oxidation studies. Most adsorption studies have been concerned therefore with the interaction of various gases with silver. Only recently has it been recognized that even though silver oxide does not exist as a separate phase at reaction conditions, its properties as an adsorbent should be investigated.

Oxygen adsorption on silver has been studied most extensively. Both kinetic and equilibrium measurements have been made, and oxygen is known to be fairly strongly chemisorbed in at least two different forms. However, the nature of these species is still in doubt. Some investigators, such as Smeltzer et al. (*9*), Ostrovskii and Temkin (*10, 11*), and Czanderna (*12*), believe that atomic and molecular oxygen species exist on the surface. Others, such as Sandler and co-workers (*13, 14*), believe that both adsorbed species are oxygen atoms which differ only in their binding energy. Based on measurements of oxygen

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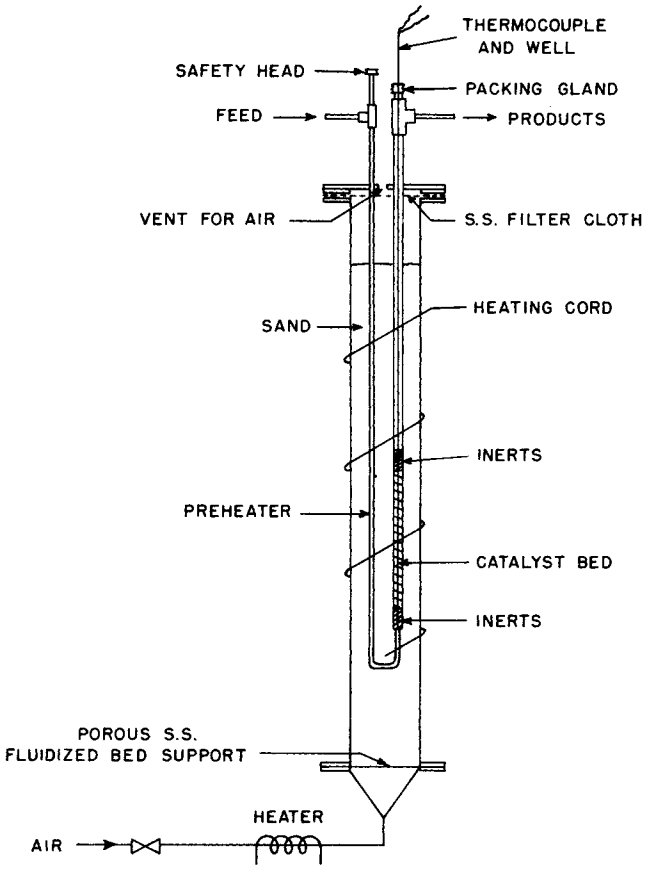


Fig. 1. Reactor and fluidized sand bath.

adsorption equilibria (*15*) and heats of chemisorption (*10, 11, 15, 16*), it is concluded that either surface heterogeneity or repulsive interactions of adsorbed species is significant.

Most investigators, including Twigg (*17, 18*) and Trapnell (*19, 20*), as well as others (*21* to *24*), agree that ethylene is not adsorbed on metallic silver. However, it has been reported by Trapnell (*19, 20*), Margolis (*25*), and Gerei et al. (*21, 22*) that ethylene is adsorbed on an oxygen-covered silver surface at temperatures low enough so that reaction does not occur. Allen and Sciafe (*26*) found the same to be true when bulk silver oxide was the adsorbent. Although not strictly an adsorption study, the results of a study by Belousov and Rubanik (*27*) are particularly relevant to this discussion. Based on experiments utilizing a "competing reaction" technique, these workers concluded that the reaction must involve an adsorbed ethylene species as well as adsorbed oxygen.

Ethylene oxide, carbon dioxide, and water are all adsorbed on silver oxide (*28* to *32*). Significantly, of the three reaction products, only ethylene oxide is extensively adsorbed on metallic silver as well (*17, 18, 33*). Water is slightly adsorbed (*29*), while carbon dioxide is not chemisorbed at all on the reduced metal surface (*30, 31*).

Kinetics and Mechanism

Initial work on the kinetics of ethylene oxidation was done by Twigg (*17, 18*). Orzechowski and MacCormack (*34*), Nault et al. (*35*), Buntin (*36*), and Temkin and coworkers (*37* to *39*) have also contributed significantly to knowledge of the reaction kinetics. One significant conclusion of most kinetic studies is that ethylene is strongly adsorbed on the catalyst, quite in contrast to results reported for adsorption on silver. This conclusion is based on the observation that the apparent order of the reaction with respect to ethylene decreases and approaches zero as the ethylene pressure is raised. With regard to the dependence on oxygen, various reaction orders have been reported. It is frequently concluded from the kinetics that oxygen is only weakly adsorbed, but even the question of atomic or molecular oxygen adsorption has so far gone unanswered. In addition, workers are not entirely in agreement as to whether adsorption or surface reaction is the rate-controlling step.

Finally, some interesting work has been done using alloys of silver as catalysts for ethylene oxidation. Thus, based on an investigation of the palladium-silver system, Moss and Thomas (*40*) concluded that ethylene oxide is produced by interaction of ethylene with the more weakly adsorbed of two oxygen species, which, they felt, is atomic. Flank and Beachell (*23*) studied gold-silver alloys and concluded that ethylene reacts with oxygen atoms to form ethylene oxide, while carbon dioxide results from a molecular oxygen species.

EXPERIMENTAL APPARATUS AND MATERIALS

The Reactor

The differential reactor was fabricated from a 28-in. length of ½-in. stainless steel tubing (0.430-in. I.D.). Temperature control was provided by immersing the reactor in an electrically heated fluidized bed of sand. A short length of ¼-in. stainless steel tubing was used to preheat the entering gases to reaction temperature. Figure 1 is a sketch of the reactor and sand bath. The catalyst bed was 7 in. long and contained 10.0 g. of active catalyst, diluted with an equal weight of inert alumina catalyst support. An iron-constantan thermocouple was used to measure the axial temperature profile within the reactor. The 1/16-in. O.D. sheathed probe was inserted into a ⅛-in. O.D. thermowell concentric with the reactor.

Gas Flow System

The feed to the reactor contained ethylene, oxygen, and helium. Helium rather than nitrogen was used as the inert diluent to get high thermal conductivity and high diffusion coefficients and to simplify the analysis. The reactants were supplied from standard gas cylinders. After pressure reduction with two-stage regulators, the three gases were passed through short beds of activated charcoal. Flow rates were controlled with precision needle valves and metered with capillary flowmeters. The gases were mixed and the feed stream entered the preheater and catalyst bed. Manometers were provided so that pressure in the reactor and pressure drop across the bed could be measured. The product stream leaving the reactor flowed through a needle valve used to control the back pressure in the reactor and then through the sample loop of a gas-sampling valve before being vented.

Analysis

Using the gas-sampling valve, a 0.5-cc. slug of product gas at atmospheric pressure and room temperature was injected into a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity detector. A ⅛-in., 6-ft. long stainless steel column packed with 100-120 mesh Porapak Q was used for the analysis (*41*). The helium carrier gas flow rate was maintained at 40.0 cc./min. (STP), and the column oven was operated isothermally at 80°C. The chromatograph was calibrated directly in moles versus peak area for each component except water.

Catalyst Preparation and Description

The silver catalyst was prepared by impregnation of 20-28 mesh particles of a low surface area α-alumina, using a procedure similar to that of Buntin (*36*). The Alcoa T-71 alumina used has a surface area of approximately 0.5 sq. m./g. and a pore volume of 0.15 to 0.20 cc./g. The alumina was washed and dried, and then impregnated with an aqueous solution of lactic acid and silver oxide at 93°C. for 1 hr. The solution contained 60 g. of 85% lactic acid and 30 g. of silver oxide in 60 cc. of distilled water. After impregnation the excess liquid was removed and the particles were cooled. The catalyst was

then heated in a furnace for 16 hr. at 360° to 380°C. to decompose the silver lactate to metallic silver. After removal from the furnace the catalyst was cooled in nitrogen and weighed. Based on its weight gain, the catalyst contained 8.1% silver. The alumina, which had originally been white, was now a grayish-brown. By breaking open some of the particles it was determined that the support was apparently uniformly impregnated. No further treatment was given to the catalyst before its use in the reactor. The same batch of catalyst was used throughout this study.

Transmission electron micrographs of the catalyst showed the silver to be present as nearly spherical particles, about 2,000 Å. in diameter, on the surface of the alumina. This result can be compared with that presented by Vasilevich et al. (*42*), who reported silver particle sizes ranging from 200 to several thousand Å. with primary crystals of about 300 Å.

PROCEDURE

For most runs the sand bath temperature was adjusted to give an average reactor temperature of 220°C. Gas samples were taken approximately 30 to 40 min. after setting the desired flow rates and reactor pressure. The mole fractions of ethylene oxide and carbon dioxide in the product stream were obtained from the chromatogram with the aid of the calibration curves. The concentration of water was assumed to be equal to the measured concentration of carbon dioxide. Average reaction rates were then calculated, based on the assumption of a differential reactor. It was assumed also that all the carbon dioxide was formed directly from ethylene, and none was produced by the further oxidation of ethylene oxide. The calculated reaction rates are assumed to correspond to the average partial pressures of reactants and products in the reactor. Mass transfer, both external and within the catalyst particles, was estimated to be sufficiently rapid that the reaction rate is not affected (*6*). Temperature gradients were also small enough to be neglected.

In agreement with previous work, variations in catalyst activity were observed in this study, and could not be eliminated. The varying activity of silver catalysts used in the oxidation of ethylene is a problem which has plagued many investigators. These slow increases and decreases in activity are considered to be an effect apart from that of the attainment of steady state with respect to the catalyst surface. Orzechowski and MacCormack (*34*) were the first to discuss the phenomenon in detail, but the subject has been brought up frequently since then (*35, 36, 38, 43*)

RELATIVE RATES

It was recognized that, without allowing for catalyst activity variations in planning and carrying out the experiments, a study of the kinetics of ethylene oxidation would be futile. For this reason all reaction rates in this work are compared with rates measured at a set of defined "standard conditions." The conditions selected for the standard run were

Reactor pressure	= 1.32 atm.
Average reactor temperature	= 220°C.
Total feed flow rate	= 390 cc./min. (STP)
Average partial pressure of ethylene	= 0.263 atm.
Average partial pressure of oxygen	= 0.263 atm.
Average partial pressure of helium	= 0.789 atm.

A pair of runs at standard conditions bracketed each "kinetic run." Sinfelt (*44*) used a similar procedure to allow for catalyst activity variations in studies of ethylene hydrogenation and ethane hydrogenolysis. It must be assumed that changes in the catalyst which result in variations in activity affect only the magnitudes of the reaction rates and not the form of the dependence of rate upon the various process parameters (*45*).

Throughout the course of the kinetics experiments, the rate of ethylene oxidation to ethylene oxide at the standard conditions was usually about

$$6 \text{ to } 7 \times 10^{-6} \frac{\text{g.-moles ethylene reacted}}{\text{min., g. catalyst}}.$$

The corresponding range of values for oxidation to carbon dioxide was

$$4 \text{ to } 6 \times 10^{-6} \frac{\text{g.-moles ethylene reacted}}{\text{min., g. catalyst}}.$$

Conversions for the standard runs were primarily between 2.5 and 3.5%, depending on the activity of the catalyst. The selectivity (moles ethylene converted to ethylene oxide per mole of ethylene reacted) ranged from about 51 to 65%.

The kinetics results are expressed as relative rates of ethylene oxidation to ethylene oxide and carbon dioxide. Relative rate is defined as the ratio of the reaction rate for a kinetic run to an average of the corrected rates of standard runs made immediately before and immediately after the kinetic run.

The corrections were applied to the standard runs to compensate for differences in product concentrations. They were determined simply by measuring the rates of ethylene oxide and carbon dioxide formation at several different conversions (that is, various feed flow rates), with other conditions identical to those used in the standard runs. The effects of each of the three products on the reaction rates could not be evaluated separately using this procedure. Therefore throughout this work the concentrations of products are lumped together as one parameter P_P, defined as the sum of the average product partial pressures:

$$P_P = P_{C_2H_4O} + P_{CO_2} + P_{H_2O} \tag{1}$$

A value of P_P equal to 0.01 atm. was chosen as the base to which the product concentrations of all standard runs are corrected. This value is close to an average of all those obtained for standard runs during the course of the experiments.

The relative rate R can then be thought of as follows. It can be assumed that

$$r = \alpha f(P_E, P_O, P_P, T_R) \tag{2}$$

Then the ratio of rates for kinetic runs and standard runs is

$$R = \frac{\alpha f(P_E, P_O, P_P, T_R)}{\alpha f(P_E = 0.263, P_O = 0.263, P_P = 0.01, T_R = 220°\text{C.})} \tag{3}$$

or, simply

$$R = \beta f(P_E, P_O, P_P, T_R) \tag{4}$$

where β is a constant, independent of activity variations.

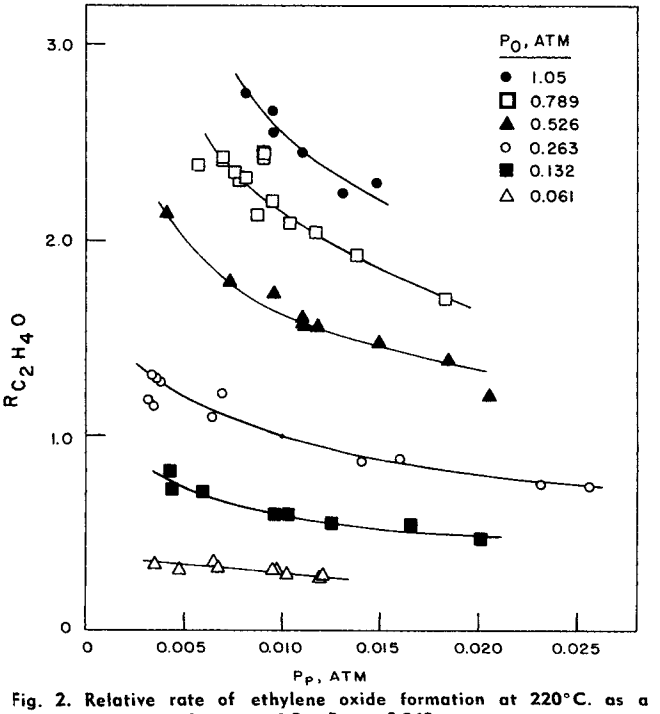


Fig. 2. Relative rate of ethylene oxide formation at 220°C. as a function of P_P. P_E = 0.263 atm.

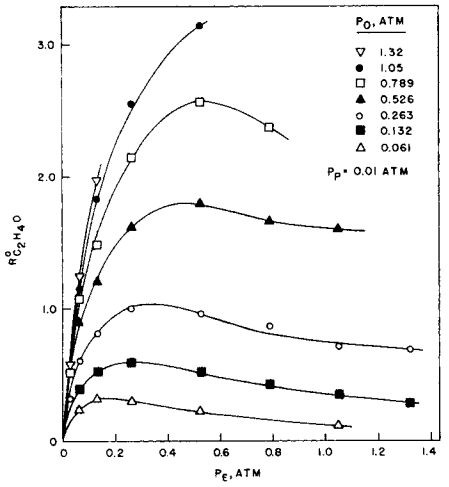


Fig. 3. Effect of ethylene pressure on the relative rate of ethylene oxide formation at 220°C.

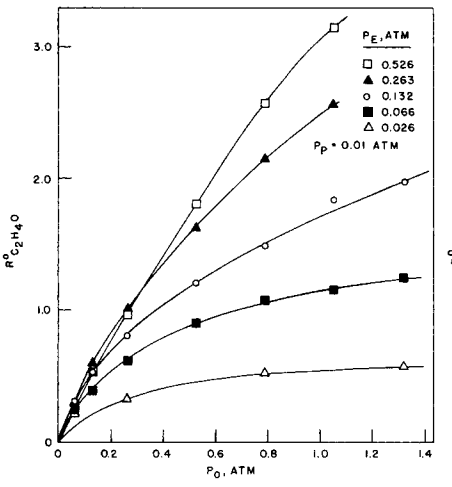


Fig. 4. Effect of oxygen pressure on the relative rate of ethylene oxide formation at 220°C. (low ethylene pressures).

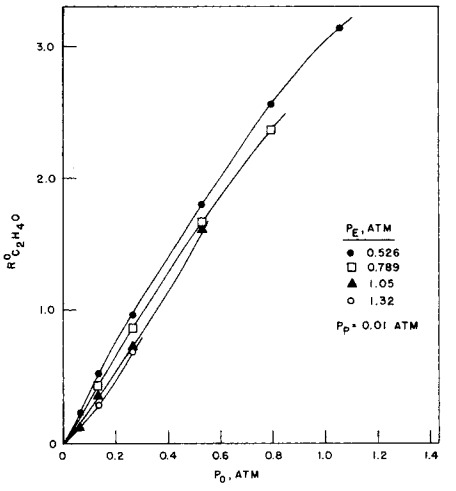


Fig. 5. Effect of oxygen pressure on the relative rate of ethylene oxide formation at 220°C. (high ethylene pressures).

SCOPE OF EXPERIMENTAL WORK

The major variables of interest in this study of the kinetics of ethylene oxidation on silver are the partial pressures of ethylene, oxygen, and the three reaction products, as characterized by P_P. The term partial pressure as used here refers to the average partial pressure within the reactor. Thirty-nine different combinations of ethylene and oxygen partial pressures were studied, each at several different flow rates (that is, several values of P_P). The only runs accepted were those in which the partial pressures were within 3% of their desired values. Only the nominal values of these pressures were used throughout this work. Ethylene partial pressures from 0.026 to 1.32 atm. were investigated. Oxygen pressures ranged from 0.061 to 1.32 atm.

The average temperature in the reactor was 220°C. for nearly all the experiments. The only exceptions were a few runs at 240°C. The average temperature within the catalyst bed was usually within 0.5°C. of 220°C. in all runs for which this was the desired temperature. The observed reaction rates were not corrected for these minor differences.

Although mentioned several times, it is worth repeating that each kinetic run was bracketed by runs at standard conditions. Relative rates of ethylene oxidation to ethylene oxide and carbon dioxide were computed. The dependence of the relative rates upon the reactant and product partial pressures (P_E, P_O, and P_P) and temperature will be discussed in the next section. First, the kinetics results will be described and compared with previous work. This will be followed by a discussion of possible reaction mechanisms and development of the associated rate expressions.

PRESENTATION OF RESULTS

The kinetic data at 220°C. can be presented graphically by plotting the relative rates as a function of P_P for each set of ethylene and oxygen pressures. As an example, the data for the relative rate to ethylene oxide for various oxygen pressures at an ethylene pressure of 0.263 atm. are shown in Figure 2. Smooth curves have been drawn through each set of data points corresponding to a particular combination of ethylene and oxygen pressures. The data for other ethylene pressures are similar; the only significant differences are in the slopes of the curves. Similar results are obtained, too, for the relative rates to carbon dioxide. [Due to lack of space, the data for carbon dioxide formation will not be discussed here in detail. Additional data are available elsewhere (*6*). When appropriate, any differences in the observed kinetics of the two reactions will be noted.]

It is apparent from Figure 2 that the effects of the reaction products must be taken into account when determining the dependence of relative rates upon ethylene and oxygen pressures. Rather than attempt to extrapolate or correct results back to zero conversion, it was decided that all relative rates would be compared at a single value of P_P equal to 0.01 atm. Thus, as seen from Equation (4), with P_P and T_R constant at 0.01 atm. and 220°C., respectively, the relative rates depend only on the average partial pressures of oxygen and ethylene.

The values of the relative rates at $P_P = 0.01$ atm., designated as $R^0_{C_2H_4O}$ and $R^0_{CO_2}$, are obtained from curves such as those in Figure 2. The effects of P_E and P_O on these rates can then be determined. Figure 3 shows the effect of ethylene pressure on the relative rate of ethylene oxidation to ethylene oxide. Smooth curves have been drawn through the data for each oxygen pressure. Similarly, the effect of oxygen pressure at various ethylene pressures is shown in Figures 4 and 5. (For clarity the data for the high and low ethylene pressures are separated.) In addition, Figure 6 shows the dependence of the relative rate to carbon dioxide on ethylene pressure.

Dependence of Rate on Ethylene Pressure

The most prominent feature in Figures 3 and 6 is that the relative rate passes through a maximum with increasing ethylene pressure at constant oxygen pressure. The maximum shifts to higher ethylene pressures as the oxygen pressure increases. Ethylene pressures corresponding to the rate maxima are higher for oxidation to ethylene oxide than to carbon dioxide. Furthermore, the rate to carbon dioxide falls off much more sharply with increasing pressure after the maximum has been reached than does the rate to ethylene oxide.

The results obtained here at low ethylene pressures are in general agreement with results published earlier (*34* to *36*). However, the appearance of maxima in the relative rates as the ethylene pressure is increased has not been reported before for the oxidation of ethylene on silver. In the work of Orzechowski and MacCormack (*34*), Nault et al. (*35*), and Buntin (*36*), for example, the ethylene pressures investigated were all less than 0.15 atm. Thus the absence of maxima in previous studies is understandable, since maxima were observed in the present study only at ethylene pressures greater than 0.2 atm.

Similar observations of rate maxima have been published recently by Gerberich et al. (*46*) for the oxidation of ethylene on palladium. A relationship of this type be-

tween reaction rate and reactant pressure is typically associated with a dual-site Langmuir-Hinshelwood mechanism for bimolecular reactions. In this mechanism reaction occurs between two adsorbed species competing for sites on the surface of the catalyst. Also, such a mechanism accounts for the influence of one reactant on the apparent order for the other. In fact, Nault et al. (35) found that both their data, originally reported by Bolme (47), and Orzechowski and MacCormack's data (34) could be fitted to a rate expression developed on the basis of reaction between competitively adsorbed ethylene and oxygen molecules.

Dependence of Rate on Oxygen Pressure

As seen from Figures 4 and 5, the relative rates increase with increasing oxygen pressure. At the lowest ethylene pressures, the rates increase only slightly as the oxygen pressure is increased. At moderate ethylene pressures the reactions are nearly first order in oxygen. Most significantly, at the two highest ethylene pressures the reactions are greater than first order in oxygen. The deviation from a straight line in Figure 5 is admittedly slight, but reproducible. Several runs are used to get each value of $R^0_{C_2H_4O}$ and an examination of the original data shows that upon doubling the oxygen pressure $R_{C_2H_4O}$ increased by a factor of about 2.4 to 2.5, depending on the value of P_P. Similar results were observed for R_{CO_2}.

In previous studies of ethylene oxidation on silver only orders in oxygen less than unity have been observed. However, orders in oxygen greater than 1 have been observed by Moro-oka and Ozaki (48) for propylene oxidation to carbon dioxide on metallic catalysts, including silver. In addition, for the silver catalyst they found that the order in propylene was positive at low propylene concentrations and negative at high concentrations. This is indicative of a maximum in rate with respect to olefin, similar to that observed for ethylene oxidation in the present study.

Effect of Reaction Products on the Rate

As Figure 2 shows, the products have a strong effect on the reaction rate even though the sum of the partial pressures is only 0.005 to 0.02 atm. The products adsorb on the catalyst and compete for reaction sites, and the interaction should therefore be less noticeable at high reactant pressures. While this is not true for the data in Figure 2 it is true for changes in ethylene pressure. For example, when P_P is decreased twofold from 0.014 to 0.007 atm. at $P_O = 0.132$ atm., $R_{C_2H_4O}$ is increased by a factor of 1.50 for $P_E = 0.066$ atm. but only by a factor of 1.08 for $P_E = 0.789$ atm. The relationship between oxygen pressure and P_P is less apparent, probably because oxygen is less strongly adsorbed on the active sites than are the reaction products.

A number of published studies have included work on the inhibiting effect of reaction products. In most investigations all three reaction products are found to have some influence on both ethylene oxide and carbon dioxide formation rates. The results obtained in this study on the effect of reaction products on the kinetics can most easily be compared with those of Gorokhovatskii et al. (49). They found that increasing the flow rate of a stream containing about 3% ethylene and 97% oxygen by a factor of 3.7 caused the rate of ethylene oxidation at 220°C. to increase by a factor of 1.8. This corresponded to a decrease in P_P from nearly 0.019 atm. to about 0.008 atm. in their recirculating reactor. The results obtained in the present study at $P_E = 0.026$ atm. compare quite favorably. Decreasing P_P from 0.014 to 0.007 atm. increases the reaction rates by a factor of 1.5 to 1.6. Considering that a slightly smaller change in P_P is involved here, agreement is excellent.

Effect of Temperature on the Kinetics

Activation energies, estimated on the basis of several experiments at 240°C. in addition to runs at the standard temperature of 220°C., fall within the range reported in the literature. Since the apparent activation energies will depend on reactant and product concentrations, a range of reported values is expected.

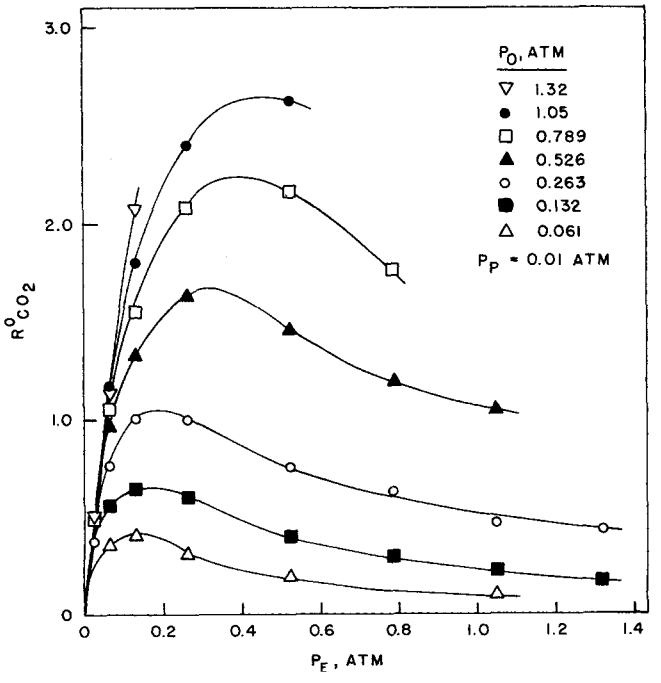


Fig. 6. Effect of ethylene pressure on the relative rate of carbon dioxide formation at 220°C.

REACTION MECHANISMS

The mechanisms of ethylene oxide and carbon dioxide formation are discussed in terms of Langmuir-Hinshelwood mechanisms. Even though adsorption studies indicate that the catalytic surface is energetically heterogeneous, the reaction actually may take place on only a small portion of the total surface, that is, on a limited number of active sites. If these sites have only a narrow range of surface energies the catalyst can be considered to have an ideal surface, and the reaction can be interpreted in terms of Langmuir-Hinshelwood mechanisms.

In postulating reaction mechanisms for the oxidation of ethylene to ethylene oxide and carbon dioxide a number of factors must be considered.

1. Relative rates at 220°C. and $P_P = 0.01$ atm. pass through maxima with increasing ethylene pressure. This implies a dual-site mechanism involving a strongly adsorbed ethylene species.
2. The dependence of rate on ethylene pressure is affected by the level of oxygen pressure. The reverse is also true. This suggests that ethylene and oxygen compete for adsorption sites on the surface.
3. The relationship between rate and oxygen pressure is very unusual. The behavior at low ethylene concentrations is characteristic of a strongly adsorbed oxygen species. At moderate ethylene pressures, though, the rates vary approximately linearly with P_O, which would suggest that oxygen is only weakly adsorbed. At high ethylene pressures a greater than first-order dependence on oxygen is found.
4. The reaction products inhibit both reactions. They

appear to do this by competing with the ethylene and oxygen for adsorption sites on the surface.

5. With respect to previous work, the results of adsorption studies must be given particular consideration. Oxygen is strongly adsorbed on a silver surface. Ethylene is only weakly adsorbed on silver, if at all. On the other hand, ethylene is strongly adsorbed on oxygen-covered silver. Furthermore, carbon dioxide and water are adsorbed only on an oxygen-covered surface, while ethylene oxide is adsorbed on both bare and oxygen-covered silver.

6. In one published study (27), a competing reaction technique was used to show that ethylene is definitely adsorbed on the catalyst during reaction.

7. As discussed by Nault et al. (35), the effects of oxygen and ethylene pressure indicate that the rate of adsorption of either reactant or the rate of desorption of product are not controlling steps. Thus the discussion to follow will concentrate on mechanisms in which surface reaction is the rate-controlling step.

8. It is assumed that there is only one rate-controlling step. Furthermore, the reaction is essentially irreversible, so the reverse reaction can be neglected in developing the rate equations. It is also assumed that ethylene oxide and carbon dioxide are formed in parallel reactions and there is no further oxidation of ethylene oxide to carbon dioxide.

Most reaction mechanisms can immediately be excluded from further consideration, based on the above discussion. One familiar mechanism whose rate equation does satisfy most of the requirements is a dual-site Langmuir-Hinshelwood mechanism, in which reaction occurs between adsorbed ethylene and an adsorbed oxygen species on competitive sites to form either ethylene oxide or carbon dioxide. However, such a mechanism cannot explain a reaction order in oxygen greater than unity. Besides this, it disregards the fact that ethylene is not adsorbed on silver, although it is obviously adsorbed on the catalyst during the reaction.

In spite of these shortcomings, however, it is worthwhile to examine further the kinetic data in terms of such a reaction mechanism. The rate expression for a mechanism involving a molecular oxygen species can be written as

$$r = \frac{kP_EP_O}{(1 + K_EP_E + K_OP_O + K_PP_P)^2} \qquad (5)$$

If this is the correct mechanism, plots of $(P_EP_O/r)^{1/2}$ versus P_E at constant P_O and constant P_P or $(P_EP_O/r)^{1/2}$ versus P_O at constant P_E and P_P should be linear. This can be done for the data obtained in this study using the relative rates at $P_P = 0.01$ atm. The parameter $(P_EP_O/R^0_{C_2H_4O})^{1/2}$ is shown as a function of the partial pressures of ethylene and oxygen in Figures 7 and 8.

The plots in Figure 7 are essentially linear, as they should be. This indicates that the relationship between reaction rate and ethylene pressure shown in Equation (5) is probably correct. However, based on the variation in slope in Figure 7 and the unusual curves in Figure 8 it is obvious that the mechanism does not predict the correct dependence on oxygen pressure. The equation for a reaction involving an atomic oxygen species results only in a poorer correlation. A better model is needed.

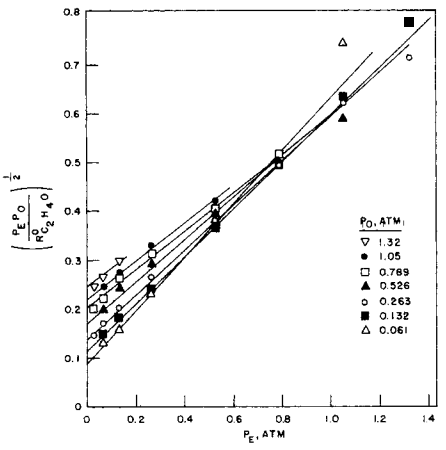


Fig. 7. Test of Equation (5) for rate of ethylene oxide formation.

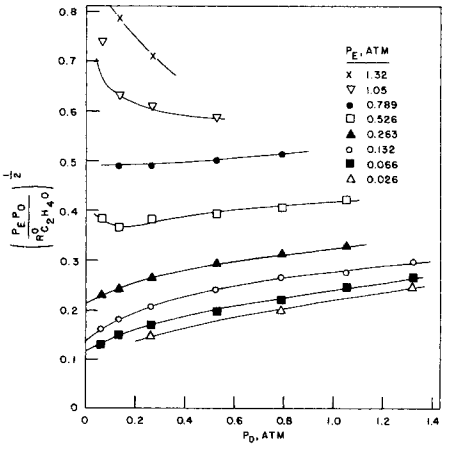


Fig. 8. Test of Equation (5) for rate of ethylene oxide formation.

PROPOSED MECHANISM FOR ETHYLENE OXIDATION

In order to account for the maxima in the rates as a function of ethylene pressure and the orders in oxygen greater than unity, it is proposed that reaction takes place between adsorbed ethylene and adsorbed oxygen on top of an oxygen-covered silver surface. Such a mechanism is consistent with the fact that ethylene is not adsorbed on silver but is adsorbed on silver covered with preadsorbed oxygen and on silver oxide. It is postulated that oxygen atoms are adsorbed on silver, forming the active sites. While silver oxide cannot exist as a separate phase at reaction conditions, it is felt that a surface of oxygen adsorbed on silver behaves much the same as a silver oxide surface. It is believed that reaction occurs between adsorbed ethylene and an adsorbed oxygen species, which compete for adsorption sites on the "silver oxide" surface. The maxima in the rate-ethylene pressure profiles can easily be explained on the basis of this competitive adsorption. Since oxygen is frequently found to be adsorbed on metal oxides, the suggestion of two layers of oxygen adsorption on silver is not unreasonable. Also, studies have often indicated that at least two adsorbed oxygen species, differing in binding energy, are present on silver. Perhaps these differences can be attributed to different layers of oxygen on the surface, as proposed here. It should be recalled, too, that Nault et al. (35) concluded that the catalyst is partially oxidized silver.

Kemball and Patterson (*50, 51*) have studied the oxidation of a number of olefins on metal films. They paid particular attention to the oxidation of ethylene and propylene on palladium and platinum catalysts. For propylene oxidation on platinum, for example, they observed a slightly negative order in propylene and an order in oxygen of about one-half. In the oxidation of ethylene on palladium, the reaction was zero order in oxygen and decreased from first order in ethylene at low pressures to zero order

at high pressures. They concluded (*51*) that, for olefin oxidation in general, "the rate-determining step involves an adsorbed olefin molecule, possibly on top of an oxygen-covered surface and a chemisorbed oxygen atom . . . ." However, it does not appear that they were thinking in terms of a mechanism whereby both olefin and oxygen were adsorbed and reacted on top of the oxygen-covered metal surface. It must be recognized that reaction of adsorbed ethylene solely with oxygen beneath it would not lead to a maximum in the dependence of reaction rate on ethylene pressure. Gerberich et al. (*46*) felt that the negative order in olefin at higher pressures could be attributed to a change to a situation in which oxygen adsorption is the rate-controlling step. However, this would not explain the dependence on oxygen pressure observed here.

It is nearly always true that the number of active sites on a catalyst surface is assumed to be constant. It is one of the factors incorporated into the rate constant. As part of the mechanism postulated here, however, it is imagined that the concentration of oxygen in the lower layer, that is, the number of active sites, is a function of the partial pressure of oxygen. Reaction orders in oxygen greater than unity can then arise because oxygen pressure affects both the number of active sites and the rate of ethylene oxidation on top of these sites.

Studies of oxygen adsorption on silver have shown that the surface is nearly completely covered at relatively low oxygen pressures. It is possible, though, that the number of active sites can still depend on the partial pressure of oxygen since the silver surface is heterogeneous. The sites for ethylene oxidation likely involve only a small portion of the available surface, having only a narrow range of adsorption energies.

The idea that the concentration of oxygen in the gas phase affects the number of active sites is in accord with Boreskov's recent suggestion that reactants may alter the behavior of a catalyst by changing its composition (*52*). Parravano (*53, 54*) has discussed this aspect of catalysis, too, referring to the effect as one of equilibration of the surface with the gas phase. While Boreskov's discussion was directed toward changes in the bulk composition of the solid catalyst, there is no reason why the idea could not be extended to include changes in the composition of the surface. When the composition of the catalyst reaches steady state rapidly compared with the rate of reaction, Boreskov concluded that "the reaction rate (as a function of reactant concentrations) depends not only on the number of collisions between the reacting systems present in the rate-limiting step, but also on the changes in rate constant arising from the effects of the reactants on the catalyst" (*52*). The rate constant is considered to be concentration dependent.

One other aspect of the proposed mechanism is that it provides an explanation for the strong inhibition of the reaction by the products. Carbon dioxide and water are adsorbed on silver oxide only and not on metallic silver. Therefore, except in the case of ethylene oxide, it is difficult to explain product inhibition in terms of a catalyst with a silver surface. However, if the catalyst surface is considered, instead, to be similar to silver oxide, product inhibition can be explained easily.

Reaction Scheme

The possible reaction mechanisms for ethylene oxidation can be represented by the following scheme. The first step, shown in Equation (6), is the formation of the active sites by dissociative adsorption of oxygen on the silver surface.

$$Ag + O_2 \rightleftharpoons 2S \qquad (6)$$

Ag represents the silver surface but its use does not imply that only one silver atom is involved per site. It is more likely that each adsorbed oxygen atom is associated with at least two silver atoms on the catalyst surface. Czanderna has proposed (*12*) that an oxygen adatom is bound to three silver atoms in a tetrahedral hole. The combination of oxygen adsorbed on silver can be represented by S, the active site.

Ethylene and oxygen are then adsorbed on these active sites. The oxygen which participates in the reaction might be either an atomic or a molecular species.

$$C_2H_4 + S \rightleftharpoons C_2H_4 \cdot S \qquad (7)$$

$$O_2 + S \rightleftharpoons O_2 \cdot S \qquad (8a)$$

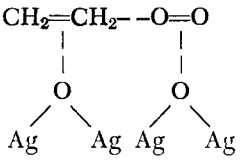
or

$$O_2 + 2S \rightleftharpoons 2O \cdot S \qquad (8b)$$

The rate-controlling step is the reaction between adsorbed ethylene and the adsorbed oxygen species. The latter is represented by $O_n \cdot S$, where $n = 1$ or 2, depending on whether the oxygen is an atomic or molecular species. The reaction is shown in Equation (9).

$$C_2H_4 \cdot S + O_n \cdot S \rightarrow \rightarrow C_2H_4O \qquad (9)$$

The formation of carbon dioxide and water is thought to proceed similarly. Several steps are probably involved after the rate-limiting step. In particular, it is possible that the underlying oxygen, as well as the competitively adsorbed oxygen, participates in the oxidation of ethylene to carbon dioxide. For reaction between ethylene and oxygen molecules, the transition state is visualized as being something like



Of course, the proposed mechanism does not require that the reacting species are adsorbed on the adsorbed oxygen that creates the active sites. It is likely that the Ag atoms (partially ionic due to the presence of adsorbed oxygen) play a significant role in the adsorption of ethylene and reacting oxygen. The bonding may be analogous to that which is involved in the formation of olefin-silver ion π-complexes.

Formulation of Rate Expressions

In developing the rate equations it is assumed that the surface reactions are the rate-controlling steps and that the oxygen atoms adsorbed on silver which form the active sites are in equilibrium with oxygen molecules in the gas phase. This dissociative adsorption is assumed to follow the Langmuir isotherm. Furthermore, this equilibrium is assumed to be unaffected by the adsorption, desorption, and reaction which take place on top of this oxygen-covered surface. Langmuir adsorption of reactants and products on the "silver oxide" surface is assumed, too. It is significant that if only the oxygen adsorbed on silver which is not covered by reactants or products is assumed to be in equilibrium with oxygen in the gas phase, the resulting equations are entirely unrealistic.

If θ_S is the fraction of the silver surface covered by atomic oxygen, forming the active sites, and θ_E, θ_O, and θ_P are the fractions of the silver surface covered by ethylene, oxygen, and products, respectively, adsorbed on active sites, then $(1 - \theta_S)$ is the fraction of bare silver surface. Also, $(\theta_S - \theta_E - \theta_O - \theta_P)$ is the fraction of the silver

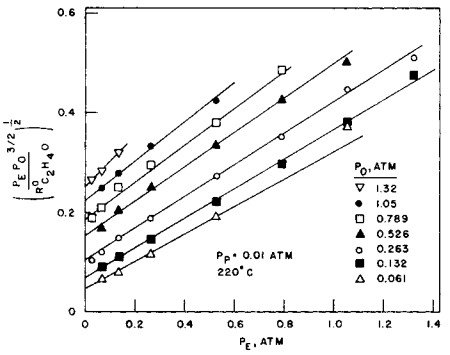


Fig. 9. Test of Equation (27) for rate of ethylene oxide formation.

surface covered by vacant active sites. For Equation (6)

$$\text{rate of oxygen adsorption} = k_S P_O (1 - \theta_S)^2 \quad (10)$$

$$\text{rate of oxygen desorption} = k_{-S}\theta_S^2 \quad (11)$$

At equilibrium the rates of adsorption and desorption are equal, and

$$\theta_S = \frac{\sqrt{K_S P_O}}{1 + \sqrt{K_S P_O}} \quad (12)$$

For Equation (7)

$$\text{rate of ethylene adsorption} = k_E P_E (\theta_S - \theta_E - \theta_O - \theta_P) \quad (13)$$

$$\text{rate of ethylene desorption} = k_{-E}\theta_E \quad (14)$$

At equilibrium

$$\theta_E = K_E P_E (\theta_S - \theta_E - \theta_O - \theta_P) \quad (15)$$

If reaction occurs between adsorbed ethylene and adsorbed oxygen molecules [Equation (8*a*)], then a similar equation can be written for oxygen

$$\theta_O = K_O P_O (\theta_S - \theta_E - \theta_O - \theta_P) \quad (16)$$

Likewise for adsorption of products on active sites

$$\theta_P = K_P P_P (\theta_S - \theta_E - \theta_O - \theta_P) \quad (17)$$

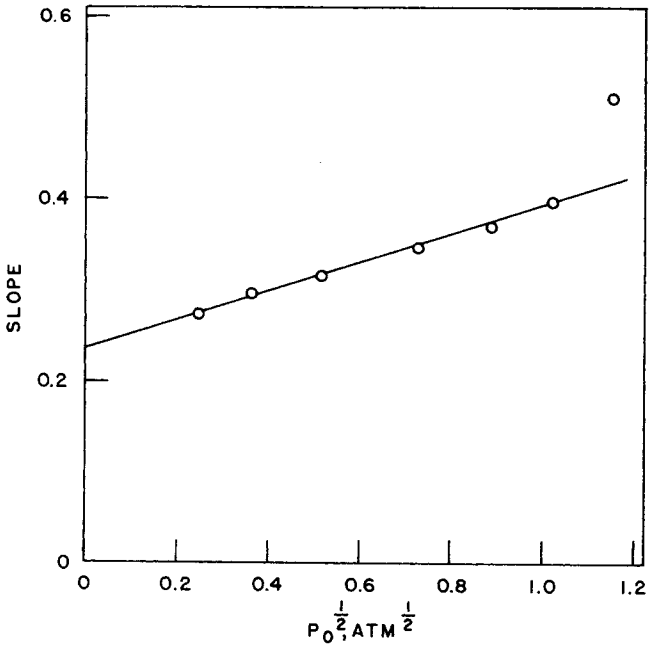


Fig. 10. Test of Equation (27) for rate of ethylene oxide formation.

Combining Equations (15), (16), and (17) and rearranging yield

$$\theta_E = \frac{K_E P_E}{(1 + K_E P_E + K_O P_O + K_P P_P)}\theta_S \quad (18)$$

$$\theta_O = \frac{K_O P_O}{(1 + K_E P_E + K_O P_O + K_P P_P)}\theta_S \quad (19)$$

Use of Equation (12) for θ_S results in

$$\theta_E = \frac{K_E P_E}{(1 + K_E P_E + K_O P_O + K_P P_P)}\left(\frac{\sqrt{K_S P_O}}{1 + \sqrt{K_S P_O}}\right) \quad (20)$$

$$\theta_O = \frac{K_O P_O}{(1 + K_E P_E + K_O P_O + K_P P_P)}\left(\frac{\sqrt{K_S P_O}}{1 + \sqrt{K_S P_O}}\right) \quad (21)$$

The rate of surface reaction between adsorbed ethylene and adsorbed oxygen molecules [Equation (9)] is expressed as

$$r = k_1 \theta_E \theta_O \quad (22)$$

Thus it follows that

$$r = \frac{k_1 K_E K_O P_E P_O}{(1 + K_E P_E + K_O P_O + K_P P_P)^2}\left(\frac{\sqrt{K_S P_O}}{1 + \sqrt{K_S P_O}}\right)^2 \quad (23)$$

or

$$r = \frac{k P_E P_O^2}{(1 + K_E P_E + K_O P_O + K_P P_P)^2 (1 + \sqrt{K_S P_O})^2} \quad (24)$$

The derivation of the rate equation for reaction between ethylene and adsorbed oxygen atoms on the active sites is similar. The expression for θ_O becomes

$$\theta_O = \sqrt{K_O P_O}\,(\theta_S - \theta_E - \theta_O - \theta_P) \quad (25)$$

and the final rate expression is

$$r = \frac{k_1 K_E K_O^{1/2} P_E P_O^{1/2}}{(1 + K_E P_E + \sqrt{K_O P_O} + K_P P_P)^2}\left(\frac{\sqrt{K_S P_O}}{1 + \sqrt{K_S P_O}}\right)^2 \quad (26)$$

or

$$r = \frac{k P_E P_O^{3/2}}{(1 + K_E P_E + \sqrt{K_O P_O} + K_P P_P)^2 (1 + \sqrt{K_S P_O})^2} \quad (27)$$

In Equations (23) and (26) the term $[\sqrt{K_S P_O}/(1 + \sqrt{K_S P_O})]^2$ represents the effect of the partial pressure of oxygen on the number of active sites. The remainder of each equation represents the effect of ethylene and oxygen pressures on the rate of reaction on top of these sites.

Equations (24) and (27) predict, qualitatively, the proper dependence of the rate on the partial pressures of reactants and products. As observed experimentally for the relative rates of ethylene oxide and carbon dioxide formation, these equations both predict that the rates first increase and then decrease with increasing ethylene pressures. Reaction orders in oxygen greater than unity would be expected at high ethylene pressures and low oxygen pressures, where $K_E P_E$ is significantly larger than $K_O P_O$ and $(1 + \sqrt{K_S P_O})$ is fairly insensitive to changes in P_O. Maxima in the rates with respect to oxygen pressure are also predicted. While this has not been observed, it is always possible that the studies simply were not extended to high enough pressures.

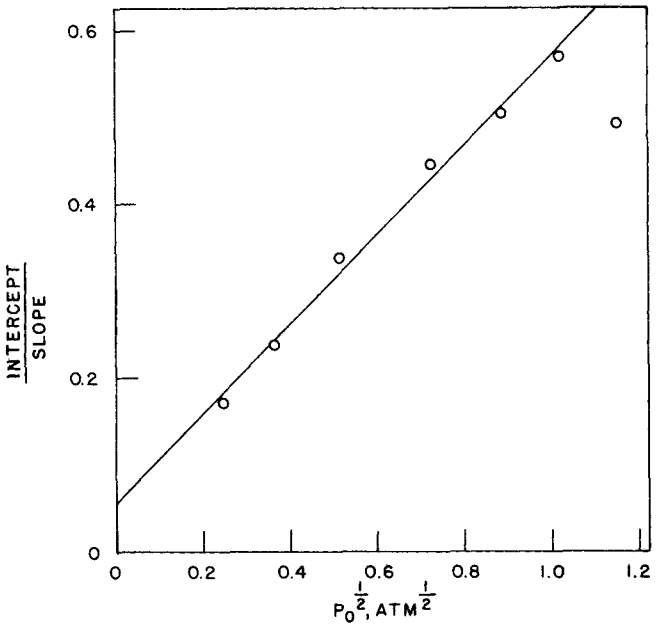


Fig. 11. Test of Equation (27) for rate of ethylene oxide formation.

Testing of Rate Equations

To check the agreement with the kinetic data, the derived rate expressions are linearized. For example, using relative rate in place of r, Equation (27) can be rewritten in the form

$$\left(\frac{P_E P_O^{3/2}}{R}\right)^{1/2} = \left(\frac{1}{\sqrt{k}} + \frac{K_E}{\sqrt{k}} P_E + \frac{\sqrt{K_O}}{\sqrt{k}} P_O^{1/2} + \frac{K_P}{\sqrt{k}} P_P\right)(1 + \sqrt{K_S P_O}) \quad (28)$$

Thus, from the data at $P_P = 0.01$ atm. and 220°C., a plot of $(P_E P_O^{3/2}/R^0_{C_2H_4O})^{1/2}$ versus P_E at constant values of P_O should be linear with positive slope and intercept if the mechanism associated with Equation (27) is correct. This plot is shown in Figure 9 and the lines are essentially straight.

According to Equation (28) the slope and intercept should both be functions of the oxygen pressure.

$$\text{Slope} = \frac{K_E}{\sqrt{k}}(1 + \sqrt{K_S P_O}) \quad (29)$$

$$\text{Intercept} = \left(\frac{1}{\sqrt{k}} + \frac{\sqrt{K_O}}{\sqrt{k}} P_O^{1/2} + \frac{K_P}{\sqrt{k}} P_P\right)(1 + \sqrt{K_S P_O}) \quad (30)$$

The ratio of the intercept to the slope can be calculated as a simplification.

$$\frac{\text{Intercept}}{\text{Slope}} = \frac{1}{K_E}(1 + \sqrt{K_O} P_O^{1/2} + K_P P_P) \quad (31)$$

A plot of the slope versus $P_O^{1/2}$ is shown in Figure 10. Similarly, the plot of the intercept/slope ratio against $P_O^{1/2}$ is shown in Figure 11. Except for one point corresponding to the data at the highest oxygen pressure, the resulting lines are straight, as predicted. Determination of the slopes and intercepts of Figures 10 and 11 provides estimates of the following parameters at P_P equal to 0.01 atm.: $(K_E/\sqrt{k})$, $(\sqrt{K_O}/\sqrt{k})$, $[(1 + 0.01K_P)/\sqrt{k}]$, and K_S.

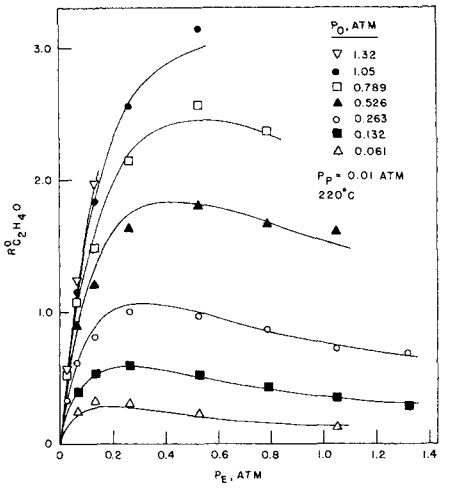


Fig. 12. Comparison of predicted relative rate of ethylene oxide formation based on Equation (32) with experimental data (lines are predicted rates).

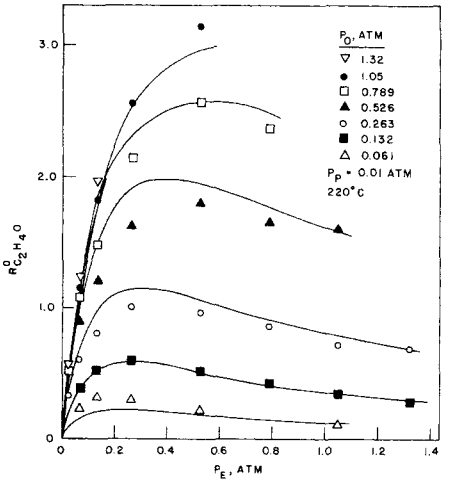


Fig. 13. Comparison of predicted relative rate of ethylene oxide formation based on Equation (33) with experimental data (lines are predicted rates).

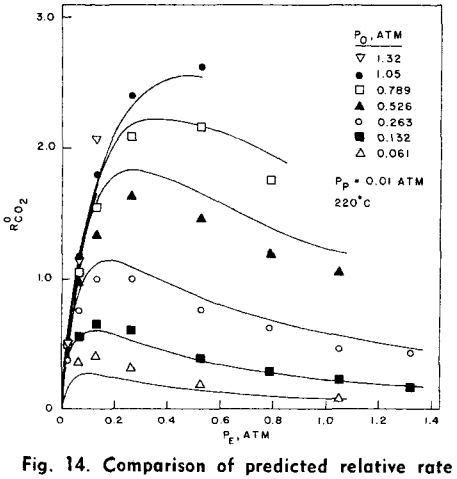


Fig. 14. Comparison of predicted relative rate of carbon dioxide formation based on Equation (34) with experimental data (lines are predicted rates).

The data for the dependence of the relative rate upon P_P should provide a second relationship between K_P and $\sqrt{k}$. Separate values for the parameters could then be calculated. However, information obtained from the effects of P_P on the rate is not considered sufficiently reliable for a number of reasons. Foremost among these is the fact that the adsorption equilibrium constants are all quite large. Small differences in the slopes and intercepts of plots used to analyze the data for the effect of products resulted in large changes in the calculated values for K_P. Accurate data at low reactant pressures would have to be used to determine the dependence of rate upon P_P. Furthermore, the fact that P_P is used, rather than the individual product partial pressures, is certain to introduce some error. Finally, the use of arithmetic averages for the product pressures when the reaction is so strongly inhibited by products introduces additional error.

The final rate equation, which applies only at 220°C. and $P_P = 0.01$ atm., is

$$R^0_{C_2H_4O} = \frac{P_E P_O^{3/2}}{(0.0130 + 0.236P_E + 0.121\sqrt{P_O})^2(1 + 0.661\sqrt{P_O})^2} \quad (32)$$

Predicted values for the relative rate of ethylene oxidation to ethylene oxide can be calculated for the various combinations of ethylene and oxygen pressures studied. Figure 12 compares the predicted curves for rate versus ethylene pressure with the data obtained in this study. The agreement is quite good. The average deviation between calculated and experimental rates is about 5.5%.

In similar fashion Equation (24) has been tested with the data for ethylene oxide. Again, nearly linear plots were obtained. Equation (33) was developed.

$$R^0_{C_2H_4O} = \frac{P_E P_O^2}{(0.0106 + 0.053P_E + 0.0199P_O)^2(1 + 6.32\sqrt{P_O})^2} \quad (33)$$

A comparison of the model with the data is shown in Figure 13. The average deviation is 10.4%, indicating a slightly poorer fit of the equation to the data.

The data for the kinetics of carbon dioxide formation have been tested, too. Here, it is found that only the mechanism involving molecular oxygen [Equation (24)] is acceptable. The comparison of the model with the data is shown in Figure 14. The equation on which the curves are based is

$$R^0_{CO_2} = \frac{P_E P_O^2}{(0.0080 + 0.103P_E + 0.0390P_O)^2(1 + 3.57\sqrt{P_O})^2} \quad (34)$$

The fit here is poorer than for the ethylene oxide data. The average deviation between calculated and experimental rates is 14.0%.

DISCUSSION

Based on the agreement between the data obtained in this study and the rate equations which have been developed, it appears that the proposed mechanisms for the oxidation of ethylene on a silver catalyst are reasonable. For ethylene oxide formation, analysis of the data suggests that the adsorbed oxygen could be either an atomic or molecular species, whereas for carbon dioxide formation only the mechanism involving a molecular oxygen species is consistent with the data.

One significant assumption that has been made in the development of the rate equations concerns the lower layer of oxygen adsorbed on silver. It has been postulated that oxygen molecules dissociate on the catalyst surface to form adsorbed oxygen atoms. The assumption has been made that a dynamic adsorption-desorption equilibrium exists between oxygen atoms on the surface and oxygen molecules in the gas phase. It is likely that this assumption is not valid, that is, that the desorption of oxygen is slow and the oxygen does not equilibrate between the surface and the gas phase. The adsorbed oxygen atoms in the lower layer might be removed by reaction after the rate-controlling step in the formation of carbon dioxide. There would then be an equilibrium between the rate of adsorption of oxygen and the rate of removal by reaction. The concentration of active sites would be dependent upon the rate of reaction itself.

SUMMARY AND CONCLUSIONS

The kinetics of ethylene oxidation on a supported silver catalyst have been investigated over a relatively wide range of ethylene and oxygen pressures, particularly at 220°C. The data are expressed in terms of relative reaction rates to allow for observed variations in catalytic activity. Ratios of rates relative to the rates at a defined set of reference conditions are calculated. Data corresponding to a constant sum of average product partial pressures are of primary interest. The rates of formation of ethylene oxide and carbon dioxide are found to pass through maxima with increasing ethylene pressure. The relative rates increase with increasing oxygen pressure. The dependence on oxygen pressure is unusual, however, in that the reaction order is greater than unity at high ethylene pressures and low oxygen pressures. Competition between reactants for active sites and inhibition of the reaction by products are also observed.

It is concluded that reaction takes place between adsorbed ethylene and an adsorbed oxygen species on active sites formed by the dissociative adsorption of a lower layer of oxygen on metallic silver. Ethylene and oxygen, as well as the reaction products, compete for adsorption sites on the catalyst surface, which is considered to be similar to silver oxide. The concentration of active sites depends on the oxygen partial pressure. Such a mechanism can explain the rate maxima with respect to ethylene pressure and the orders in oxygen greater than unity. In contrast to previous work, this mechanism takes into account known adsorption behavior. Furthermore, conclusions regarding adsorption on the catalyst as determined from the reaction kinetics are consistent with those established experimentally for adsorption on silver oxide.

Rate expressions have been postulated assuming that the adsorption of oxygen to form the active sites and the adsorption of ethylene and oxygen on these sites follow Langmuir isotherms. Adsorption-desorption equilibria are assumed for all species. It is found that the ethylene oxide kinetic data can be fitted with relatively little error to equations derived for reaction of adsorbed ethylene with either molecular or atomic oxygen adsorbed on the oxide surface. The carbon dioxide data can be reasonably fitted only to an equation developed for reaction of ethylene with molecular oxygen. In all cases, ethylene is more strongly adsorbed than oxygen on the "silver oxide" surface. The two reactions probably take place on different sites, involving different binding energies for oxygen adsorption.

It is felt that the mechanisms have not yet been uniquely established. It is believed, however, that use of a Langmuir-Hinshelwood type approach, in which adsorption-desorption equilibria are assumed, has been extremely useful qualitatively. It is likely that the lower layer of oxygen, formed by dissociative chemisorption of oxygen,

is desorbed only slowly from the surface and is not in equilibrium with oxygen in the gas phase. Oxygen adsorbed in this layer might be removable only by reaction.

Of particular significance, it is concluded that in the oxidation of ethylene on silver, the composition of the reactant mixture affects the composition of the catalyst surface and the number of active sites and thereby influences the catalyst's behavior. This conclusion has particular relevance to studies of olefin oxidation on metals. There are, as well, broad implications for the field of catalysis, in general.

NOTATION

k, k_1 = constants in rate equations
k_E, k_O, k_P, k_S = rate constants for adsorption
k_{-E}, k_{-O}, k_{-P}, k_{-S} = rate constants for desorption
K_E, K_O, K_P, K_S = adsorption equilibrium constants, atm.$^{-1}$
P_E = average partial pressure of ethylene, atm.
P_O = average partial pressure of oxygen, atm.
$P_{C_2H_4O}$ = average partial pressure of ethylene oxide, atm.
P_{CO_2} = average partial pressure of carbon dioxide, atm.
P_{H_2O} = average partial pressure of water, atm.
P_P = average product partial pressure = $(P_{C_2H_4O} + P_{CO_2} + P_{H_2O})$, atm.
r = rate of C_2H_4O or CO_2 formation
R, $R_{C_2H_4O}$ = relative rates, rate at any P_E, P_O, and P_P relative to rate at standard conditions corrected to $P_P = 0.01$ atm.
$R^0_{C_2H_4O}$, $R^0_{CO_2}$ = relative rates corresponding to $P_P = 0.01$ atm.
T_R = average temperature in reactor

Greek Letters

α = activity factor
β = constant
θ_E, θ_O, θ_P, θ_S = fractional surface coverages

Subscripts

E = ethylene
O = oxygen
P = products
S = active site oxygen

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