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# The Mechanism of Ethylene Epoxidation

R. A. VAN SANTEN AND C. P. M. DE GROOT

*Koninklijke/Shell Laboratorium Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam, The Netherlands*

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The mechanism of the epoxidation of ethylene with oxygen over silver catalysts has been examined. This study was prompted by the notion that if one wishes to increase the selectivity of epoxide formation one should know the phase of adsorbed oxygen that reacts to give epoxide. Experiments were undertaken (a) to determine whether adsorbed atomic oxygen is incorporated into ethylene to give epoxide, and (b) to establish the relative rates of reaction of molecular oxygen impinging from the gas phase and of preadsorbed atomic oxygen. Experiments were performed in a high-vacuum recirculation system designed to allow volumetric absorption studies as well as kinetic studies using a mass spectrometer to be made. The catalyst consisted of silver powder precovered with chemisorbed $^{16}O$ such that it gave epoxide upon reaction with ethylene. It was contacted with ethylene/$^{18}O_2$ gas mixtures of different ratios. It is shown that under conditions where oxygen isotope equilibration in the gas phase is slow, ethylene initially reacts more rapidly with preadsorbed oxygen atoms than with molecular oxygen adsorbed in the precursor state ($p_{O_2} < 20$ Torr; 1 Torr = 133.3 N m$^{-2}$) if $O_{ads}/Ag_s \sim 1$. If in the begining only subsurface oxygen atoms are present, this subsurface oxygen and gas-phase oxygen are incorporated into ethylene at about equal rates. It is concluded that ethylene reacts with atomic oxygen to give epoxide either directly, or indirectly, after recombination of the oxygen atoms. © 1986 Academic Press, Inc.

## INTRODUCTION

There is much interest in the question as to how the silver-catalyzed epoxidation of ethylene with oxygen can be steered to give a maximum selectivity toward the epoxide. According to a classical prediction (*1, 2*) the maximum selectivity is 6/7. This figure is based on the hypothesis that only molecularly adsorbed $O_2$ yields epoxide by reaction with ethylene and that only one oxygen atom of the oxygen molecule takes part in this reaction. Kilty and Sachtler (*2*) reported experimental data in favor of this hypothesis.

On the other hand, *in situ* infrared work has been interpreted in terms of a mechanism involving atomically adsorbed oxygen (*3*). Some time ago we reported on our studies (*4*) of the stoichiometric reaction of deuterated ethylene with oxygen adsorbed on silver powder. From these studies we concluded that adsorbed atomic oxygen can indeed react to give epoxide, provided that subsurface oxygen is present. Whereas the single-crystal studies of Grant and Lambert (*5*) seem to confirm our conclusion, Campbell (*6*) provided data on the steady-state oxygen coverage of single-crystal faces of silver, from which he concluded that there is no relation between concentration of atomic oxygen and epoxidation rate. This raises the question of how the rate of reaction of potentially short-lived adsorbed nondissociated oxygen with ethylene compares with the rate of reaction of adsorbed dissociated oxygen with ethylene. The work reported here aims to resolve this question.

To this end, silver powder, precovered with chemisorbed $^{16}O_2$ such that it gives epoxide upon reaction with ethylene, was contacted with an ethylene/$^{18}O_2$ mixture in the gas phase. Using a mass spectrometer the formation of ethylene oxide (EO) was followed as a function of time. In this way it

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could be established whether it is the gas-phase or the preadsorbed oxygen that reacts more rapidly.

## METHODS

The experiments were carried out in an all-metal/Pyrex high-vacuum recirculation system (Fig. 1) designed to permit volumetric adsorption studies as well as kinetic studies. Absolute pressure measurements were performed with the aid of a Barotron-220B pressure transducer (0–80 Torr). The gas mixtures were analyzed by means of a Balzer QMG-111 B mass spectrometer equipped with an SEM detector, enabling the overall pressure drop of the gas mixture as a result of sampling to be minimized. Using gas mixtures, the 90% response time of the mass spectrometer signal and the recirculation system upon a sudden change in the relative gas concentrations was found to be shorter than 80 s at a total pressure of 20 Torr and a recirculation volume of 263 ml.

Spectroscopically pure Ag powder (25.6 g; Johnson–Matthey Chemicals) was preconditioned (7), in order to stabilize the surface area, by a more than ten-times-repeated cycle of oxidation ($O_2$, 1 bar, 525 K, 1 h) and reduction ($H_2$, 1 bar, 625 K, 1 h). Prior to any experiment, the catalyst was pretreated by oxidation ($O_2$, 1 bar, 525 K, 2 h), reduction ($H_2$, 1 bar, 575 K, 16 h), and a final reduction ($H_2$, 1 bar, 625 K, 1 h), followed by evacuation (625 K, 1 h). The specific surface area of the Ag powder determined by $O_2$ adsorption measurements at 475 K proved to be about 0.11 $m^2/g$ after stabilizing, an area which diminished by some 20% in the course of our experiments. An average value of 0.10 $m^2/g$ Ag is used throughout this work.

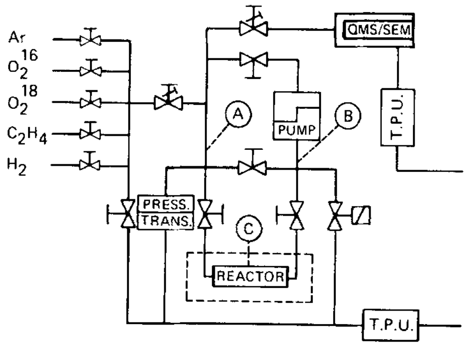

FIG. 1. Recirculation high-vacuum equipment. Scheme of the equipment used for the adsorption, desorption, and reaction studies. Volumes are as follows: Section A, including pressure transducer: 63 ml. Section B, including circulation pump: 113 ml. Section C, temperature-controlled reactor: 87 ml. QMS = quadrupole mass spectrometer. SEM = secondary electron multiplier. TPU = turbomolecular pumping unit.

The purity of the gases used was as follows: $^{16}O_2$, 99.995% (A45); $^{18}O_2$, 99.8% (isot. pur.); $C_2^=$, 99.95% (research grade); and argon, 99.9%. Argon was used as a calibration reference for determining the relative pressures of the other gases in the system.

A typical experiment was conducted in the following way. After pretreatment with 25.6 g Ag as mentioned above, oxygen ($^{16}O_2$ or $^{18}O_2$) was allowed to adsorb onto the Ag powder at 475 K for 30 min, after which the system was cooled to room temperature and evacuated. From the resulting pressure drop, the amount of adsorbed oxygen could be calculated. Then the reactants, i.e., $^{16}O_2$ or $^{18}O_2$, ethylene, and argon, were admitted (into Sections A + B; Fig. 1) and premixed; the resulting gas mixture was analyzed and then exposed to the evacuated sample (Section C). The initial pressures of ethylene and argon were 13.2 and 3.5 Torr, respectively. By means of a magnetically driven Pyrex plunger pump, the gas mixture was recirculated over the powder (WHSV $\approx$ 31 Nl $h^{-1}$ $kg^{-1}$), while the temperature was raised at a rate of 2.3 K/min. The gas was sampled continuously for on-line mass spectrometric analysis, the scanning rate being about 3 min per complete mass spectrum.

Mass spectrometric determination of ethylene, $^{16}O_2$, $^{18}O_2$, $E^{16}O$, $E^{18}O$, $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ was based on the scheme summarized in Table 1. Absolute sensitivities as well as relative fragmenta-

TABLE 1

Calibration and Mass Spectrometer Peak Signals Used

| Compound | $p(c)$ | $\mu$mol/$x$ g Ag |
|---|---|---|
| $^{16}O_2$ | $\Delta(32)$ | $* \frac{1}{S_{O_2}} * A$ |
| $^{18}O_2$ | $\Delta(36) - 0.0046 * \Delta(40)$ | |
| $C_2H_4$ | $0.5 * [\Delta(26)/0.687 + \Delta(27)/0.693]$ | $* \frac{1}{S_{C_2H_4}} * A$ |
| $E^{16}O$ | $0.797 * [\Delta(29) - 0.0235 * p(C_2H_4)]$ | $* \frac{1}{S_{EO}} * A$ |
| $E^{18}O$ | $0.797 * [\Delta(31) - 0.0010 * p(^{18}O_2)]$ | |
| $E^{16}O + E^{18}O$ | $\Delta(15) - 0.0095 * p(C_2H_4)$ | |
| $C^{16}O_2$ | $\Delta(44) - 0.443 * p(E^{16}O) - 0.08 * p(E^{18}O)$ | $* \frac{1}{S_{CO_2}} * A$ |
| $C^{16}O^{18}O$ | $\Delta(46) - 0.443 * p(E^{18}O) - 0.0015 * p(^{18}O_2)$ | |
| $C^{18}O_2$ | $\Delta(48) - 0.0015 * p(^{18}O_2)$ | |

*Note.* $p(c)$ = peak height of compound c. $\Delta(x')$ = peak height $m/e{:}x'$ − blank peak height $m/e{:}x'$. $S_c$ = sensitivity of compound $c$ compared to argon sensitivity. $A$ = ($\mu$mol argon/$x$ g Ag)/$\Delta(40)$. $x$ = g of Ag. Asterisks indicate multiplication.

tion patterns of compounds differing only in the type of oxygen isotope present are assumed to be the same.

## RESULTS

A silver powder with $Ag_s/O_{ads} \approx 1$ was prepared by exposing the hydrogen-reduced silver sample at 473 K for half an hour to oxygen gas. The final oxygen pressure was 2–20 Torr, depending on the pressure required in the subsequent experiment. Earlier (*4*) we reported that half of the chemisorbed oxygen atoms are adsorbed as surface atoms and the other half as subsurface atoms. The surface layer of oxygen atoms can be removed by evacuating the sample while heating it to a temperature above 575 K.

Table 2 reports for some experiments the amounts of oxygen adsorbed at 473 K. In three experiments, 1, 2 and 3, the samples were cooled to room temperature, evacuated, and exposed to ethylene at 13 Torr initial pressure and, respectively, to $^{18}O_2$ or $^{18}O_2$ at 2.6 Torr initial pressure of $^{18}O_2$ at 20.4 Torr initial pressure. In experiments 4 and 5 the samples were similarly treated, but after heating to 591 K. In experiment 4 the sample was exposed to ethylene and $^{18}O_2$ at 20.4 Torr initial pressure; in experi-

TABLE 2

Summary of $E^{16}O$ Formation and $^{16}O_2$ Incorporation

| Expt | $^{16}O_2$ preads ($\mu$mol/g Ag) | $^{18}O_2$ initial gas pressure (Torr) | Maximum $E^{16}O$ produced ($\mu$mol/g Ag) | $^{16}O_2$ incorporated[a] ($\mu$mol/g Ag) |
|---|---|---|---|---|
| 1 | 1.09 | — | 0.12 | 0.51 |
| 2 | 0.94 | 2.6 | 0.19 | 0.43 |
| 3 | 1.08 | 20.4 | 0.42 | 0.9 |
| 4 | 0.46 | 20.4 | 0.12 | 0.28 |
| 5 | 0.46 | — | — | 0.03 |

*Note.* Total number of silver surface atoms = 2 $\mu$atom/g Ag. 1 Torr ≡ 0.58 $\mu$mol/g Ag.

[a] Measured at temperature where $E^{16}O$ production is maximum.

ment 5 the sample was exposed to ethylene only.

Figure 2 shows the production of EO and $CO_2$ as a function of temperature. Initially 1.09 μmol $O_2$/g Ag is adsorbed; at the maximum EO signal the total $O_2$ consumption is 0.51 μmol/g Ag (Table 2). Surface oxygen is then completely removed and EO is found to disappear because of decomposition and/or polymerization. Exposing the sample after this experiment to $^{16}O_2$ at 20 Torr initial pressure resulted in a $CO_2$ production of 0.5 μmol/g Ag.

Figures 3a–c show the results obtained with 2.6 Torr initial $^{18}O_2$ pressure. Figure 3a gives the total EO and total $CO_2$ production and $^{18}O_2$ consumption as a function of temperature. Comparison of Fig. 3a with Fig. 2 shows a significantly larger maximum in EO production when gas-phase oxygen is present and again EO disappears from the gas phase when no reactive oxygen is left.

Figure 3b presents $E^{16}O$ and $E^{18}O$ production and $E^{18}O/E^{16}O$ ratios. The statistical ratio would be 1.6. Clearly, in the beginning $E^{16}O$ formation is faster than $E^{18}O$ formation, indicating that under the conditions of this experiment adsorbed $^{16}O$ reacts more rapidly with impinging ethylene than does gas-phase $^{18}O_2$-derived oxygen. Whereas in experiment 1, the amount of oxygen incorporated into EO at the maximum of its signal is 0.06 μmol/g Ag, in experiment 2 the figures for $E^{16}O$ are 0.095 μmol/g Ag and that for $E^{18}O$, 0.08 μmol/g Ag. In the latter experiment the total amount of $^{16}O_2$ reacted is 0.43 μmol/g Ag.

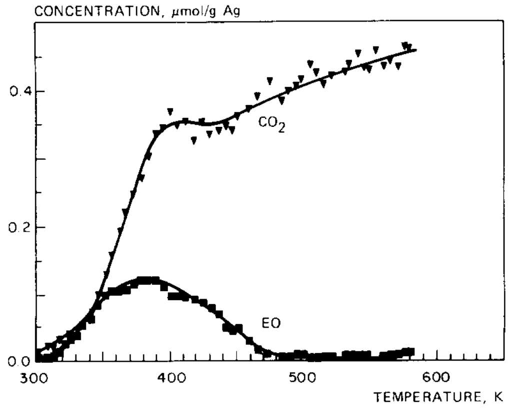

FIG. 2. Experiment 1. Production of EO and $CO_2$ as a function of temperature. Initial ethylene pressure: 13 Torr.

Figure 3c shows $CO_2$ production. The oxygen in $CO_2$ is found to scramble rapidly.

Figures 4a–d contain the results of similar experiments, but this time performed with 20.4 Torr $^{18}O_2$ in the gas phase. Figure 4a shows the $^{18}O_2$ consumption, and the total EO and total $CO_2$ production as a function of temperature.

Figure 4b shows $E^{16}O$ and $E^{18}O$ production as a function of temperature. Again, in the beginning $^{16}O$ adsorbed on the surface is found to react more rapidly with ethylene than gas-phase oxygen. The maximum amount of $E^{16}O$ formed is 0.42 μmol/g Ag, to be compared with 0.19 μmol/g Ag found in the previous experiment. The total amount of $^{16}O_2$ reacted in experiment 3 is 0.9 μmol/g Ag. This is nearly all of the $^{16}O_2$ adsorbed initially (1.08 μmol/g).

Figure 4c shows the formation of different $CO_2$ species with rapidly scrambled oxygen atoms.

Figure 4d shows the ethylene signal and $O_2$ consumption. It is seen that ethylene is released when the gas-phase oxygen has been consumed, pointing to adsorption of ethylene in the presence of adsorbed oxygen or to decomposition of the epoxide.

Figures 5a–d show the results of experiments performed with silver containing only subsurface oxide. As mentioned in Table 2, in the absence of gas-phase oxygen no epoxide is formed upon exposure of such a silver sample to ethylene, confirming earlier results (*4*); upon exposure to ethylene 0.03 mol $CO_2$/g Ag is formed. As demonstrated in Fig. 5, the results are completely different if gas-phase oxygen is present. Figure 5a shows total EO and total $CO_2$ production and gas-phase $^{18}O_2$ consumption.

Figure 5b shows $E^{16}O$ and $E^{18}O$ production. More $E^{16}O$ than $E^{18}O$ ($E^{16}O/E^{18}O$ = 0.0087) is formed than is expected from the

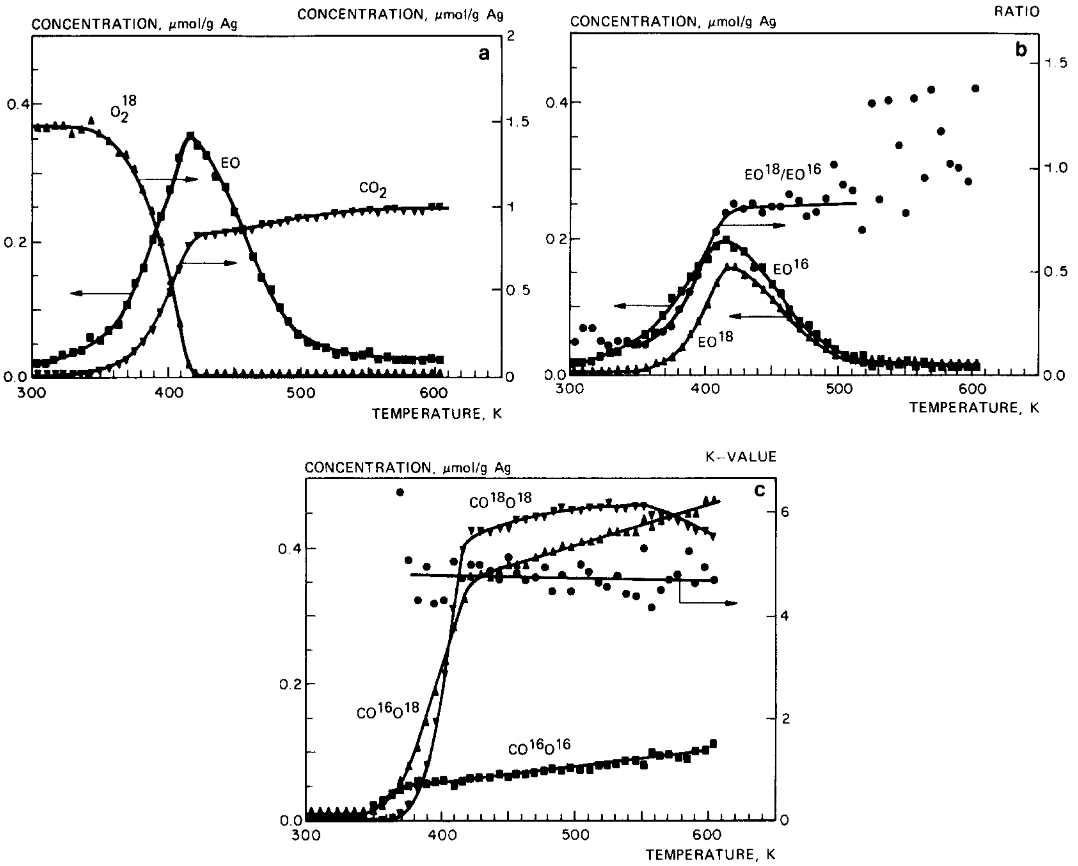

FIG. 3. Experiment 2. Initial gas-phase $^{18}O_2$ pressure: 2.6 Torr; initial ethylene pressure: 13 Torr. (a) Total EO and total $CO_2$ production and $^{18}O_2$ consumption as a function of temperature. (b) $E^{16}O$ and $E^{18}O$ production as a function of temperature. (c) $C^{18}O^{18}O$, $C^{16}O^{18}O$, and $C^{16}O^{16}O$ production as a function of temperature.

overall $^{16}O_2/^{18}O_2$ ratio (0.039). It is of interest to note that the responses of $E^{16}O$ and $E^{18}O$ run parallel, whereas in the earlier experiment first $E^{16}O$ is formed and later, $E^{18}O$. This observation confirms the absence of surface $^{16}O$. The similarity in maximum and width of the curves indicates a rapid exchange between subsurface oxygen and surface-adsorbed oxygen compared with the rate of oxidation. A maximum amount of 0.12 μmol $E^{16}O$/g Ag is formed; 0.28 μmol $^{16}O_2$ is found to react with ethylene.

Figure 5c shows $CO_2$ production and Fig. 5d, consumption and release of ethylene, as a function of temperature.

Table 3 gives the turnover numbers (TONs) and the selectivity calculated from the data obtained in experiment 3. Table 4 contains the TONs and selectivity figures for a constant-temperature experiment. A

TABLE 3

Turnover Numbers Calculated for Experiment 3

| Temp (K) | Time[a] (s) | μmol/g Ag formed | | Selectivity, S (%) | TON[b] (*$10^4$) | |
|---|---|---|---|---|---|---|
| | | ΔEO | $\Delta CO_2$ | | EO | $CO_2$ |
| 362 | 360 | 0.065 | 0.070 | 65 | 0.9 | 1.0 |
| 382 | 360 | 0.130 | 0.240 | 52 | 1.8 | 3.3 |
| 403 | 360 | 0.240 | 0.630 | 43 | 3.3 | 8.8 |

[a] Period during which product formation is calculated at the tabulated average temperatures.

[b] Turnover number in units of $10^{15}$ molecules produced. $cm^{-2}.s^{-1}$.

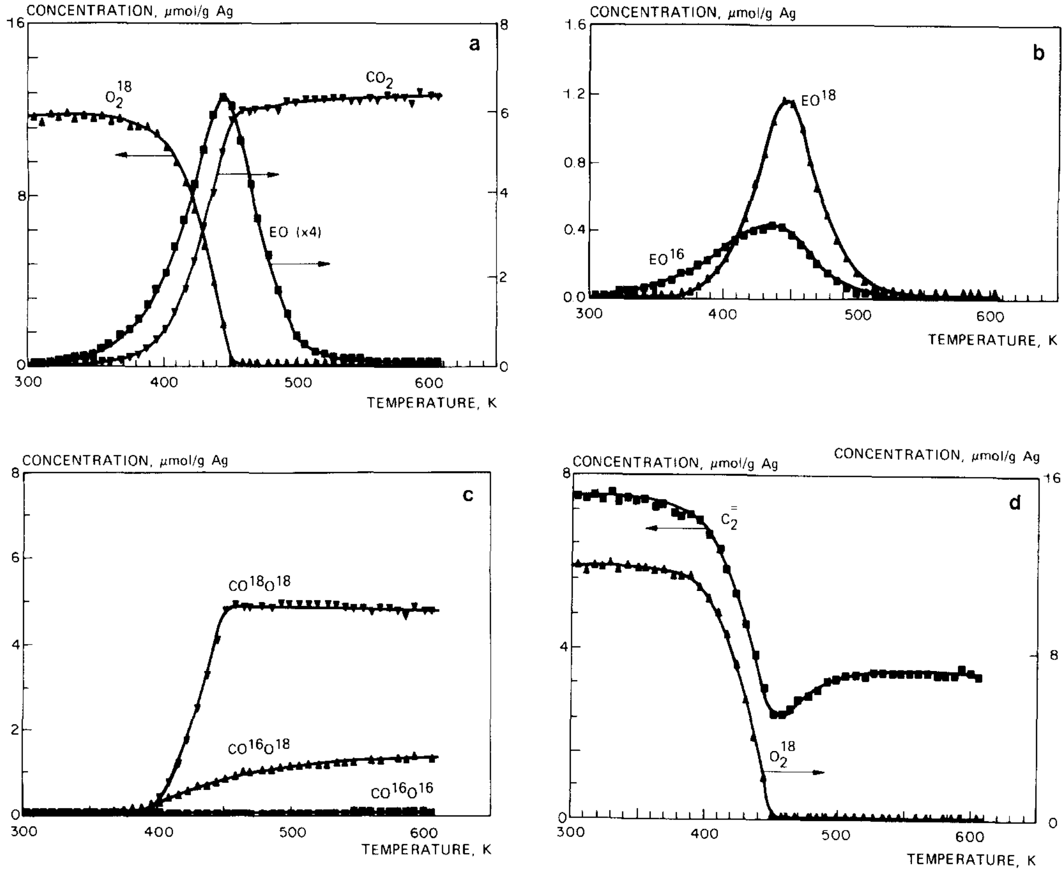

FIG. 4. Experiment 3. Initial gas-phase $^{18}O_2$ pressure: 20.4 Torr; initial ethylene pressure: 13 Torr; $^{16}O_2$ preadsorbed: 1.08 μmol/g Ag. (a) Total EO and total $CO_2$ production and $^{18}O_2$ consumption as a function of temperature. (b) $E^{16}O$ and $E^{18}O$ production as a function of temperature. (c) $C^{18}O^{18}O$, $C^{16}O^{18}O$, and $C^{16}O^{16}O$ production as a function of temperature. (d) Ethylene consumption and release, and $^{18}O_2$ consumption as a function of temperature.

strong decline in activity is observed, because of product inhibition. So the data in Table 3 should be interpreted with care. The TONs have not been measured under strictly isothermal conditions, but are values averaged over a small temperature region. The data relating to the lowest temperature are least affected by product inhibition. If one assumes an activation energy of 105 kJ/mol, as measured by Campbell and Paffett (*6a*), the TONs calculated at $T = 362$ K extrapolate to a value of 0.8 at $T = 490$ K. This is to be compared with a value of 1, measured by Campbell (*6c*) for the (111) face at this temperature and comparable gas-phase compositions.

TABLE 4

Turnover Numbers Measured in Stationary Experiment[a]

| Temp (K) | Run time (s) | μmol/g Ag formed | | Selectivity, *S* (%) | TON[b] (*10⁴) | |
|---|---|---|---|---|---|---|
| | | ΔEO | $ΔCO_2$ | | EO | $CO_2$ |
| 348 | 5,400 | 0.212 | 0.143 | 75 | 0.20 | 0.13 |
| 348 | 60,900 | 0.026 | 0.309 | 14 | 0.002 | 0.025 |

[a] Conditions: 13 Torr ethylene, 20 Torr $O_2$.
[b] Turnover number in units of $10^{15}$ molecules produced. $cm^{-2}.s^{-1}$.

## DISCUSSION

The aim of experiments 1–3 was to compare the rates at which adsorbed oxygen

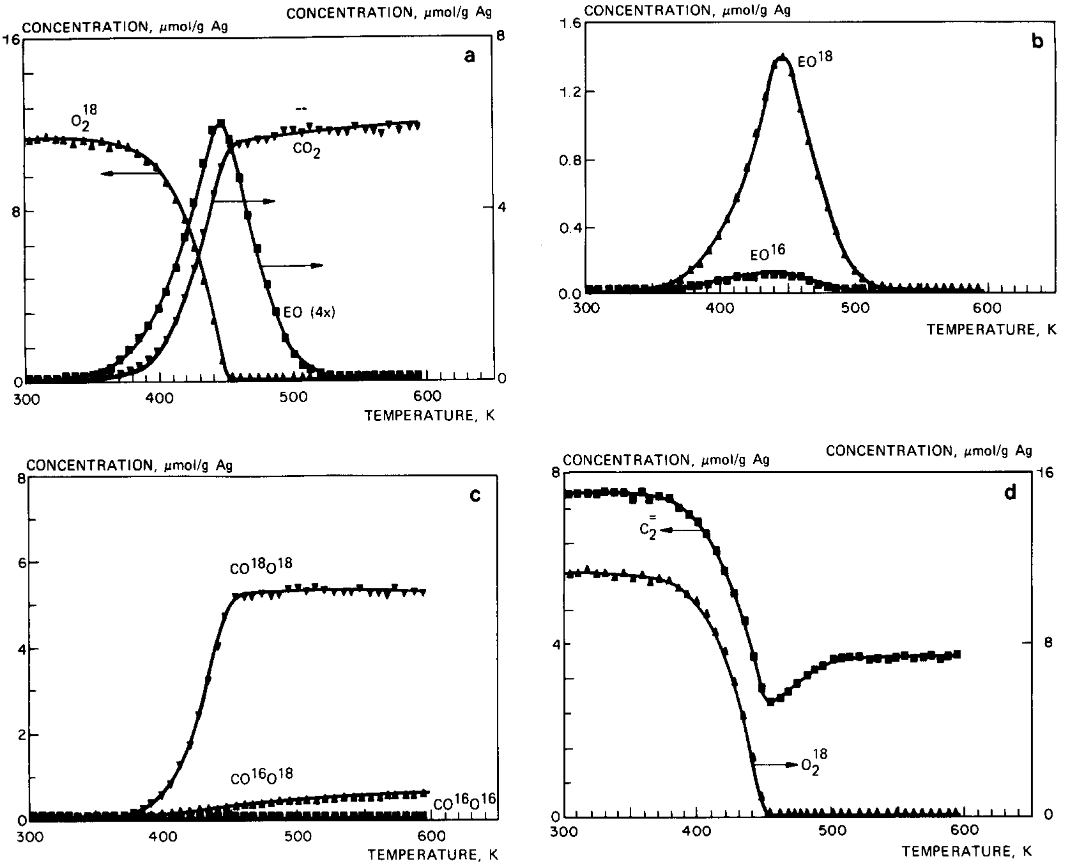

FIG. 5. Experiment 4. Initial gas-phase $^{18}O_2$ pressure: 20.4 Torr; initial ethylene pressure: 13 Torr; $^{16}O_2$ preadsorbed: 0.46 µmol/g Ag. (a) Total EO and total $CO_2$ production and $^{18}O_2$ consumption as a function of temperature. (b) $E^{16}O$ and $E^{18}O$ production as a function of temperature. (c) $C^{18}O^{18}O$, $C^{16}O^{18}O$, and $C^{16}O^{16}O$ production as a function of temperature. (d) Ethylene consumption and release, and $^{18}O_2$ consumption as a function of temperature.

and gas-phase oxygen are incorporated into ethylene. The temperatures were chosen such that gas-phase $^{18}O_2/^{16}O_2$ exchange was slow because of a limited rate of oxygen desorption (*8*). Experiment 4 indicates that there is a rapid exchange between surface-adsorbed and subsurface-absorbed oxygen. The oxygen gas-phase pressure in the experiments was such that it allows a comparison with the experiments of Campbell (*6*). We observe clearly that initially only preadsorbed oxygen reacts. Once surface vacancies have been created, gas-phase $^{18}O_2$ becomes adsorbed and from this point onward preadsorbed $^{16}O$ and adsorbed $^{18}O$ react at comparable rates, if allowance is made for the increasing concentration of $^{18}O$ and depletion of $^{16}O$. The results for $CO_2$ production also point to rapid $^{16}O/^{18}O$ exchange in the adsorbed state.

The TONs calculated for EO and $CO_2$ formation extrapolate well to the values found at higher temperatures. A point of interest is the increasing absolute amount of subsurface oxygen incorporated into EO with increasing gas-phase $^{18}O_2$ pressure (Table 2). At the maximum, 25% of the subsurface oxygen is recovered in EO. This proves unambiguously that oxygen atoms from dissociated oxygen molecules can be incorporated into ethylene to give epoxide.

As discussed earlier (*4*), the maximum amounts of preadsorbed oxygen (20% in experiment 3, of which at least 11% stemmed from subsurface oxygen) incorporated into ethylene to give the epoxide indicate that epoxide is predominantly formed from adsorbed atomic oxygen, since under our conditions the $O_2^-$ concentrations observed are much lower (*9*). However, the possibility of recombination of oxygen atoms before reaction with ethylene cannot be ruled out.

Our results confirm our earlier postulate that at least two kinds of oxygen exist on the reactive silver surface. Previously, we reported (*4*) that in the absence of subsurface oxygen, oxygen adsorbed on the Ag surface will give only $CO_2$ and $H_2O$ upon reaction with ethylene. In the presence of subsurface oxygen the nature of the adsorbed oxygen changes and epoxide formation can occur as well.

The data of Czanderna (*10*) indicate that the heat of adsorption of oxygen is significantly lower in the presence of subsurface oxygen than in its absence. The reported heat of adsorption of oxygen on silver powder (*10*) in the range of surface coverages $\theta = 0.17$ to $0.33$ is initially 176 kJ/mol, decreasing to 76 kJ/mol, and remaining constant over the range $\theta = 0.33$ to $\theta = 0.9$. It is of interest to compare the initial value to the values of 171 kJ/mol (*6d*) reported for the (111) face of silver and 186 kJ/mol for the (110) face of silver (*6c*) at a surface coverage $\theta < 0.5$. Czanderna interprets the decrease at higher coverage in terms of oxide island formation (*10*).

EO formation is much less exothermic than total combustion (at 600 K the $\Delta G$ values are $-54.5$ and $-1370$ kJ/mol $C_2^{2-}$, respectively). Assuming that epoxide is formed by reaction of gas phase ethylene with adsorbed oxygen, one derives an upper limit for the free energy of adsorption of the oxygen species that gives epoxide, viz., 110 kJ/mol.

Campbell and co-workers (*6*) noted that the strongly adsorbed oxygen they observed did not give epoxide, which is not unexpected for thermodynamic reasons. Therefore it is not surprising that they find no correlation between selectivity and amount of strongly adsorbed oxygen. More weakly adsorbed oxygen will have a lower activation energy for epoxide formation and is present on the silver powders at high oxygen coverage. Czanderna (*10*) suggests that the main quantity is present in the form of atomic oxygen. The reason that this more weakly adsorbed oxygen has not been observed so far in ultrahigh-vacuum experiments is probably related either to the conditions under which oxygen is adsorbed onto the surface and the way in which the surface is treated afterward or to the absence of steps and edges. Indeed, Campbell and Paffett (*6a*) report a slightly lower heat of adsorption for oxygen adsorbed with a coverage $\theta_0 = 0.67$ at the Ag(110) face.

A tentative explanation for the changes in heat of adsorption could be that at low oxygen coverage, the adsorbed oxygen atoms are bridge- or multicoordinated to silver surface atoms and that at higher coverage, in the presence of subsurface oxygen, they also adsorb on top of the silver atoms, where they will be monocoordinated. The possibility of different coordinations of oxygen with silver can be derived from the lattice of AgO (*11*). Weakly monocoordinated oxygen would lead to epoxide formation, and strongly bonded multicoordinated oxygen to total combustion. Using this postulate, the effect of chlorine can be explained in a fashion very similar to that originally proposed by Kilty and Sachtler (*2*). If we assume that chlorine suppresses the formation of multicoordinated oxygen atoms, then the only oxygen atoms left are monocoordinated and weakly adsorbed on top of the Ag atoms. This is an alternative to the explanation of Force and Bell (*3*) for the chlorine effect for mechanisms that assume epoxide to be formed via atomic oxygen.

It is of interest that in the homogeneous phase two epoxidation routes are possible. One proceeds via the hydroperoxide (*12*); here the dioxygen-containing hydroperoxide transfers one oxygen atom to the alkene, while the other becomes deactivated and is left in water or alcohol. The other route proceeds via a compound containing one oxygen atom and giving the epoxide upon reaction with alkene. Examples of such compounds are $TlO^+$ ($L_x$) (*13*) and $MnO^{3+}$ ($L_x$) (*14, 15*), where $L_x$ denotes ligands. Upon oxygen transfer the cation becomes reduced by a two-electron transfer. The mechanism is similar to that of the Wacker reaction, except that hydrogen transfer becomes suppressed. Dimerization (*15, 16*) of the oxomanganese(V) complex suppresses epoxide formation.

Recently, Van der Eijk (*17*) demonstrated the feasibility of electrochemical epoxidation by regeneration of silver ions in the solution. On the basis of the order in $Ag^{2+}$ and the pH dependence he postulated the presence of an $(AgO^+) \cdot (\text{pyridine})_x$ complex as the epoxidizing agent. The reactions postulated are

$$2Ag(Py)_2^+ + 4\ Py \xrightarrow[\text{anode}]{} 2Ag(Py)_4^{2+} + 2e$$

$$2Ag(Py)_4^{2+} + H_2O \rightleftharpoons Ag(Py)_2^+ + Ag(Py)_2O^+ + 4Py + 2H^+$$

$$Ag(Py)_2O^+ + \text{alkene} \longrightarrow Ag(Py)_2^+ + \text{epoxide}.$$

Interestingly, at a surface stoichiometry of $Ag/O \sim 1$, at which we find epoxide formation from the oxidized silver surface, the formal charge of the silver ions would be 2+. Bulk AgO contains two different silver sites, one formally $Ag^+$ and the other $Ag^{3+}$ (*11*). Hence, it is not unreasonable to expect that at the surface also such $Ag^{3+}$ ions exist.

UPS and XPS studies by Au and coworkers (*18*) of oxygen adsorbed at the Ag (110) surface show a significant change in the chemical shift of adsorbed oxygen with increasing oxygen coverage. Adsorbed oxygen appears to acquire a lower charge with increasing coverage.

The work of Canning and Madix (*19*) indicates the electropositive character of adsorbed oxygen at low coverage in the reaction with acetylene. Earlier it was shown (*20, 21*) by means of isotopes that the nonselective combustion reaction with ethylene also proceeds via an electropositive reaction of oxygen with the CH bond.

Epoxidation, however, occurs by electrophilic attack of the electron-rich $\pi$ bond by oxygen, which we have shown to occur only at high oxygen coverage.

Hence spectroscopic as well as chemical data indicate the presence of oxygen species with different charges.

## CONCLUSIONS

We have presented experimental proof that oxygen preadsorbed on a silver surface with an $O_{ads}/Ag_s$ ratio ~1 reacts more rapidly with ethylene than gas-phase oxygen up to pressures of 20 Torr. At conditions where gas-phase $^{16}O_2/^{18}O_2$ isotope equilibration is slow one finds that after an initial period both isotopes are incorporated into epoxide at comparable rates. This indicates that in both cases the same oxygen adsorption state is responsible for epoxidation.

From experiments with oxygen preadsorbed with $O_{ads}/Ag_s < 0.5$ and pretreated such that the oxygen atoms reside below the surface, it is concluded that subsurface oxygen atoms become incorporated in the epoxide upon exchange with adsorbed oxygen surface atoms. Thus oxygen atoms that have been dissociated during adsorption of oxygen are incorporated into the epoxide. From this it can be concluded that ethylene reacts with atomic oxygen to give epoxide either directly, or indirectly, after recombination of the oxygen atoms. The latter reaction is, however, unlikely under our conditions.

According to our model, there is in principle no reason why the epoxidation selectivity should be limited to 6/7.

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