

Ethylene Oxidation over Silver Catalysts: A Study of Mechanism Using Nitrous Oxide and Isotopically Labeled Oxygen

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The mechanism of ethylene epoxidation over a silver sponge catalyst under steady-state conditions has been probed by comparison of nitrous oxide and oxygen as oxidants. Under noncompetitive conditions the reaction with oxygen is about five times as fast and more than twice as selective. When both are present oxygen inhibits participation by nitrous oxide and the ratio of rates is much larger. Reaction has been carried out with a mixture of $^{18}\text{O}_2$ and N_2^{16}O . The aim was to see if ^{18}O was preferentially incorporated into ethylene and ^{16}O into carbon dioxide, as would be expected if diatomic adsorbed oxygen is the source of the epoxide. The data indicate that this does not occur and hence that ethylene oxide and carbon dioxide are both derived from oxygen atoms. However, it is very difficult to exclude artifacts since the minimal involvement of nitrous oxide makes the isotope analyses difficult. No isotopic mixing occurred between $^{18}\text{O}_2$ and N_2^{16}O ; neither is it observable when ethylene is oxidized by $^{16}\text{O}_2/^{18}\text{O}_2$ mixtures. It is detectable when ethylene is absent but the rate is lower than that of ethylene oxidation under similar conditions. Studies have been made using the same silver catalyst promoted by inclusion of dichloroethane in the feed. This raises selectivity to 80% when oxygen is used but the rate is much lower. The chlorine-moderated catalysts have no measurable activity for ethylene oxidation by nitrous oxide. This difference in behavior between the two oxidants can be correlated with their dissociation rates in the absence of ethylene. Surface chlorine sufficient to depress isotope mixing between $^{16}\text{O}_2$ and $^{18}\text{O}_2$ by a factor of 7 relative to unpromoted silver renders dissociation of nitrous oxide undetectable. Dissociation of nitrous oxide is also inhibited by adsorbed oxygen even when surface chlorine is present. It is concluded that the rate of ethylene oxidation is related to the rates of dissociation of the respective oxidants. Ethylene oxidation can be faster than oxidant dissociation in the absence of ethylene because reaction with ethylene prevents buildup of inhibiting surface oxygen atoms. © 1990

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INTRODUCTION

Silver is unique as the only catalyst for the formation of ethylene oxide by direct combination of ethylene and oxygen. In commercial operation using chlorine, moderated silver selectivities to the epoxide approaching 80% can be achieved. Two views have existed concerning the nature of the adsorbed oxygen species involved in the reaction. One suggests that the crucial step is cleavage of an undissociated oxygen species by reaction with ethylene to yield the epoxide and deposition of a lone oxygen atom. Byproducts carbon dioxide and water are supposed to arise from the latter,

derived either in this way or by direct dissociation of other oxygen molecules. Evidence for this model to 1981 was reviewed by Sachtler *et al.* (1) and has been supported by some subsequent single-crystal studies (2, 3). The second model holds that both epoxide and byproducts arise from the same monatomic oxygen species. Recent transient isotope studies (4), reviewed by van Santen and Kuipers (5) support this view. They show that if silver, predosed to retain ^{16}O in atomic form, is heated in a mixture of ethylene and $^{18}\text{O}_2$, then significant amounts of ethylene oxide containing ^{16}O are evolved. Thus conversion of oxygen atoms to epoxide is possible. The result does not preclude combination of atoms and the immediate reaction of the diatomic

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species so produced with ethylene, but the authors argue that this is unlikely.

One finding which has been used as evidence against the second model is the observation that N_2O , for which the oxygen species deposited must be atomic initially, exhibits a much lower selectivity for epoxide production than does O_2 . The original study of Herzog (6) gave selectivities of 2–8% but values ranging from zero (7) to 79% (8) have since been reported. This divergence led us to make a comprehensive comparison of reactions using the two oxidants over several silver catalysts. It was shown (9) that the reaction rate with N_2O was typically one-tenth to one-third that with O_2 . For unmoderated catalysts the selectivities were 10 to 20% with N_2O and 35 to 55% with O_2 . It is difficult to use these findings as evidence in favor of either monatomic or diatomic oxygen as the epoxidizing agent. To support the former, one must explain why the selectivities differ so significantly when N_2O should produce the required oxygen species. On the other hand, if diatomic oxygen is involved, then rapid combination of oxygen atoms is required to explain the formation of ethylene oxide from N_2O .

Potentially, the two models can be distinguished through competitive experiments in which the oxygen atoms of N_2O and O_2 are isotopically different. For example, if $^{18}O_2$ and $N_2^{16}O$ are used then the monatomic model would predict that the $^{16}O/^{18}O$ ratio should be equal to all products and in proportion to the relative reaction rates of the two oxidants. On the other hand, if diatomic oxygen is required for epoxidation, then preferential incorporation of ^{18}O into ethylene oxide should be observed. One aim of this study was to work out the experimental conditions required for a definitive isotope experiment of the above type. The result of an attempt at it is reported. Earlier, Yokohama and Miyahara (7) carried out reactions using $^{18}O_2/N_2^{16}O$ mixtures but their work gives no information on the composition of the epoxide product.

EXPERIMENTAL

All catalytic measurements were carried out over samples of a high-purity silver sponge catalyst (BET area = $0.4 \text{ m}^2/\text{g}$) using a conventional single-pass flow system with analysis by multicolumn gas chromatography. Catalyst preparation, reduction procedures, and reactor operation were as described previously (9, 10). Most measurements were made with the catalyst operating in the steady-state situation reached after some hours on stream. Rate information is reported here as the conversion rate defined as

$$\text{conversion rate}/\mu\text{mol C}_2\text{H}_4 \text{ g Ag}^{-1} \text{ min}^{-1} \\ = FX/W$$

where F is the input molar flow rate of ethylene, X its conversion, and W the weight of silver catalyst. Conversion rates were calculated from product analyses, knowing the overall reaction stoichiometry and the total flow rate. Most measurements were made under differential conditions (conversions $\leq 15\%$). However this was not always practical for all reactants during interchange or combination of oxidants, particularly when the effect of added dichloroethane (DCE) was being followed. Situations in which high conversions would cause the conversion rate, defined as above, to differ substantially from the true differential rate are noted in the text.

Oxygen-18 was obtained from Cambridge Isotope Laboratories, Cambridge, Massachusetts, in a 150-cm^3 cylinder. Mass spectral analysis showed approximately 2% $^{16}O^{18}O$ but no detectable $^{16}O_2$. The other gases used were as described previously (9). Mass spectral analyses were carried out using a Vacuum Generators SX 200 quadrupole instrument. Isotope analysis of ethylene oxide was carried out by infrared spectroscopy with the sample as a gas in a 10-cm cell using a Perkin-Elmer Model 580 dispersive instrument fitted with a Model 3600 data station. The instrument was operated in the mode providing lowest noise.

This required a scan of 32 min over the range 1000 to 700 cm^{-1} with a spectral slitwidth of 3.7 cm^{-1} and provided a peak-to-peak noise level of ± 0.0008 absorbance unit with negligible drift between successive spectra. Comparison measurements were made with a Mattson Cygnus 100 Fourier transform instrument fitted with a TGS detector. While this provided the entire spectrum from 4000 to 400 cm^{-1} the signal-to-noise was not quite as good as the dispersive instrument over the limited wavenumber range of interest when acquisition was carried out for the same time.

Product samples for isotope analysis were obtained as follows. The catalyst sample was reduced in the standard way at 270°C in hydrogen (9). The catalyst and the entire collection train (comprising a CaSO_4 trap for water removal and two U-tube traps) were then flushed with ultrahigh-purity helium for an extended period. Reaction was commenced directly with the reactant mixtures of interest to avoid any possible carryover of oxygen from earlier experiments. After 10 min the first U-tube trap was cooled with liquid nitrogen and condensable products collected. The contents of the second U-tube trap at the end of this collection period provided the sample of noncondensable material (helium, oxygen, and nitrogen, if present). The relative amounts of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ in the latter were determined by mass spectrometry without further separation. The condensable materials in the first U-tube were separated into ethylene oxide and carbon dioxide plus nitrous oxide fractions by trap-to-trap distillation on a vacuum line. Known pressures (8–10 Torr) of each were then admitted into a 10-cm gas cell for infrared analysis as described above.

RESULTS

An isotope tracing experiment using $\text{C}_2\text{H}_4/^{18}\text{O}_2/\text{N}_2^{16}\text{O}$ mixtures can succeed only under conditions such that both oxidants participate in reaction, ideally in roughly equal amounts. Under noncompetitive con-

ditions with unmoderated catalysts, rates using N_2O are one-tenth to one-third that with O_2 under equivalent conditions (9). The situation is different under competitive conditions. When progressively larger partial pressures of O_2 were incorporated into $\text{C}_2\text{H}_4/\text{N}_2\text{O}$ mixtures of fixed composition, the results shown in Fig. 1 were obtained. The added O_2 clearly enhanced the rates of conversion both to ethylene oxide (curve a) and to the total oxidation products (CO_2 plus H_2O) (curve b). However, this increase in rate was accompanied by a decline in N_2 production (curve c) and hence the participation of N_2O in ethylene oxidation. The dominance by oxygen was so effective that its conversion was near complete at low O_2 pressures (>98% up to 33 Torr) and was still 33% for 145 Torr of added O_2 . By contrast the conversion of N_2O dropped from 12.4% without O_2 to 0.5% when 145 Torr of O_2 was included. Correspondingly, the selectivity to ethylene oxide increased from 22% with N_2O alone to 44% when O_2 became the dominant oxidant.

The effect of adding N_2O to a reacting $\text{C}_2\text{H}_4/\text{O}_2$ mixture was much less dramatic as shown in Fig. 2. Formation rates for both ethylene oxide and total oxidation products were not increased by the inclusion of 150 Torr of N_2O . If anything there is a slight decline. For N_2O pressures above 30 Torr some N_2 formation can be observed (curve c). However, it is very small, bearing in mind that the scale range for N_2 in Fig. 2 is one-tenth that for C_2H_4 and that the $\text{N}_2\text{O}/\text{C}_2\text{H}_4$ reaction stoichiometry is approximately 4. The selectivity to ethylene oxide remained constant at approximately 40% irrespective of N_2O pressure as expected for a reaction dominated by oxygen.

Table 1 summarizes these findings for the two reactions under noncompetitive and competitive conditions when the pressure of the added oxidant in the latter experiments equals the fixed pressure of the same oxidant in the other experiments. The extreme inhibition of N_2O reactivity by O_2 is obvious. With both oxidants present

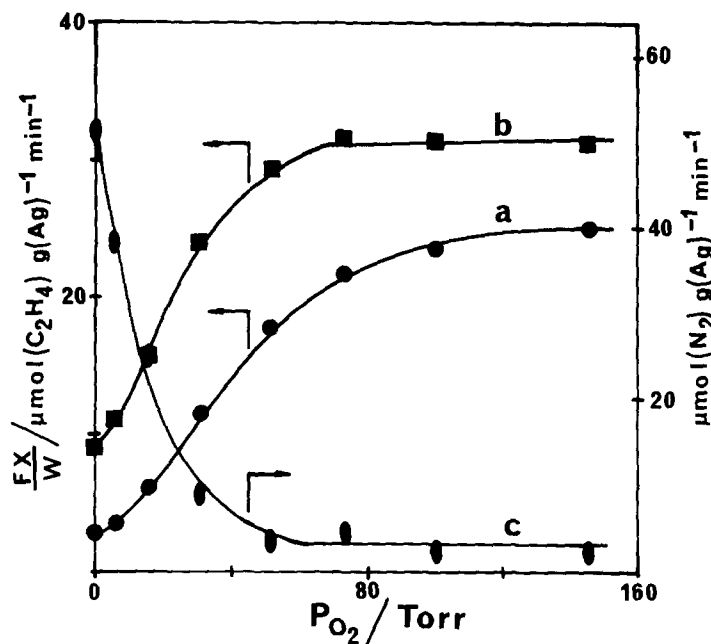


FIG. 1. Effect of adding oxygen to the reaction between ethylene (26 Torr) and nitrous oxide (167 Torr) at 234°C, other conditions as per Table 1. (a) Conversion of ethylene to ethylene oxide; (b) conversion of ethylene to carbon dioxide and water; (c) formation of nitrogen from nitrous oxide.

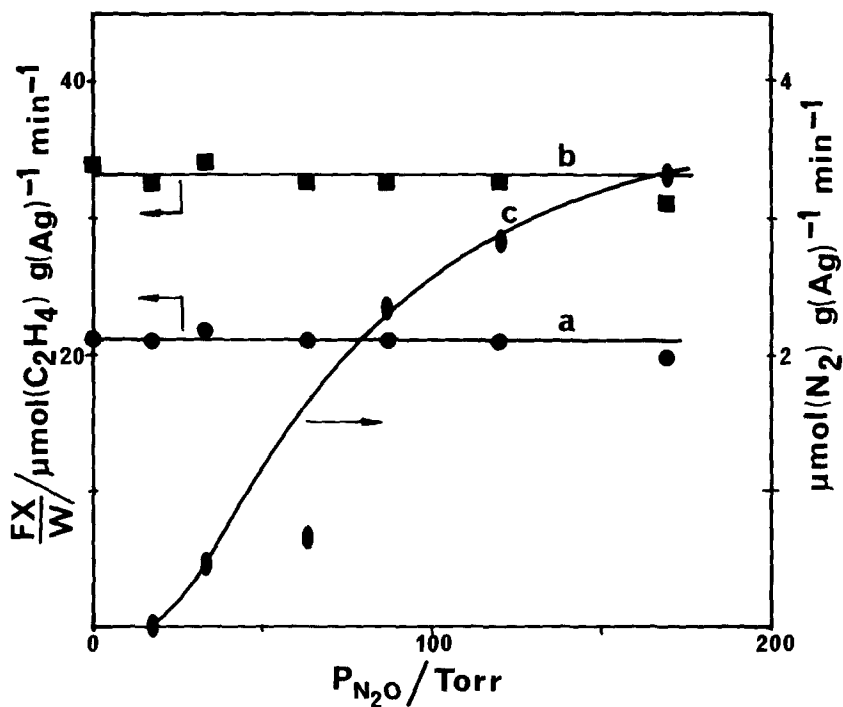


FIG. 2. Effect of adding nitrous oxide to the reaction between ethylene (26 Torr) and oxygen (63 Torr) at 234°C, other conditions as per Table 1. (a) Conversion of ethylene to ethylene oxide; (b) conversion of ethylene to carbon dioxide and water; (c) formation of nitrogen from nitrous oxide.

TABLE 1

Comparison of C_2H_4/O_2 and C_2H_4/N_2O Reactions with the Reaction of $C_2H_4/O_2/N_2O$ Mixtures over 1.04-g Silver Sponge^a

	$C_2H_4 + O_2$ alone	$C_2H_4 + N_2O$ alone	$C_2H_4 + O_2 + N_2O$
Selectivity (%)	39	23	39
Ethylene conversion (%)	84	19	74
O_2 conversion (%)	69	—	70
N_2O conversion (%)	—	13	0.85
Conversion rate ($\mu\text{mol } C_2H_4 \text{ g Ag}^{-1} \text{ min}^{-1}$)			
C_2H_4	55	12	51
O_2	102 ^b	—	101 ^b
N_2O	—	52	3.3

^a From data of Figs. 1 and 2 for reaction at 234°C with pressures as follows: C_2H_4 , 26 Torr; O_2 , 63 Torr; N_2O , 167 Torr.

^b Calculated from product analysis.

(column 3) N_2O contributes only $\sim 0.75\%$ of the oxygen atoms provided by O_2 . This finding makes isotope tracing using $C_2H_4/^{18}O_2/N_2^{16}O$ mixtures extremely difficult since one is faced with the need for accurate analysis of $C_2H_4^{16}O$ in $C_2H_4^{18}O$ at the level of 1% or less. Only limited optimization of operating conditions to increase the N_2O/O_2 rate ratio is possible. There is little point in considering much lower oxygen pressures since this would increase its already high conversion and exacerbate the problem of different rate ratios for N_2O versus O_2 along the catalyst bed. Higher N_2O pressures do help but the limit then is the presence of small amounts of impurity oxygen in the nitrous oxide (about 0.1% in our supplies).

Based on these considerations the optimum conditions for the use of $C_2H_4/^{18}O_2/N_2^{16}O$ mixtures for our experimental arrangements are as shown in Table 2. The experiment was carried out under such conditions, approaching the problem of accurate analysis of small amounts of $C_2H_4^{16}O$ in $C_2H_4^{18}O$ in the following way. First, a reaction using $C_2H_4/^{18}O_2$ alone was carried out and the condensable products were collected at -196°C . The ethylene oxide present, entirely ^{18}O except for impurity ^{16}O in the $^{18}O_2$ used, was separated out by trap-

to-trap distillation. Its infrared spectrum, as a gas in the region 940 to 780 cm^{-1} , is shown in Fig. 3a. The dominant structure, centered at the dip in absorbance at 853 cm^{-1} , is due to the ν_5 symmetric vibration with a type B contour (11). The small sharp peak at 807 cm^{-1} has been assigned to the ν_{15} vibration (11). A mixture comprising $C_2H_4^{18}O$ to which 5% $C_2H_4^{16}O$ was deliberately added produced spectrum b in Fig. 3. Apart from a few small shoulders near 879, 871, and 820 cm^{-1} it appears to differ little from that of $C_2H_4^{18}O$ alone. However, subtraction of a from b after normalization and multiplication by 10 gave c, which is readily recognizable as that of $C_2H_4^{16}O$ when recorded alone as d in Fig. 3. There is some discrepancy near 850 cm^{-1} , probably due to different pressure broadening effects on lineshape since total pressures for a and b were different. The spectrum of $C_2H_4^{16}O$ is similar to that of $C_2H_4^{18}O$ except that ν_5 and ν_{15} are displaced upward to 877 and 820 cm^{-1} respectively (11). The above test shows that determination of $C_2H_4^{16}O$ in $C_2H_4^{18}O$ is readily possible at the 5% level and should be feasible at lower concentrations.

Following the above trials, reaction was carried out using a $C_2H_4/^{18}O_2/N_2^{16}O$ mixture under the conditions of Table 2. The infrared spectrum of the ethylene oxide

TABLE 2

Conditions Used for Oxidation of Ethylene over Silver Sponge using $^{18}O_2/N_2^{16}O$ Mixtures

Catalyst	1.04-g Ag sponge
Temperature	233°C
Pressure	
C_2H_4	24 Torr
$^{18}O_2$	63 Torr
$N_2^{16}O$	111 Torr
Total flow rate	$30 \text{ cm}^3 \text{ STP min}^{-1}$
Conversion	
C_2H_4	92
$^{18}O_2$	48%
N_2O	$\approx 1\%$
Selectivity	$\approx 41\%$

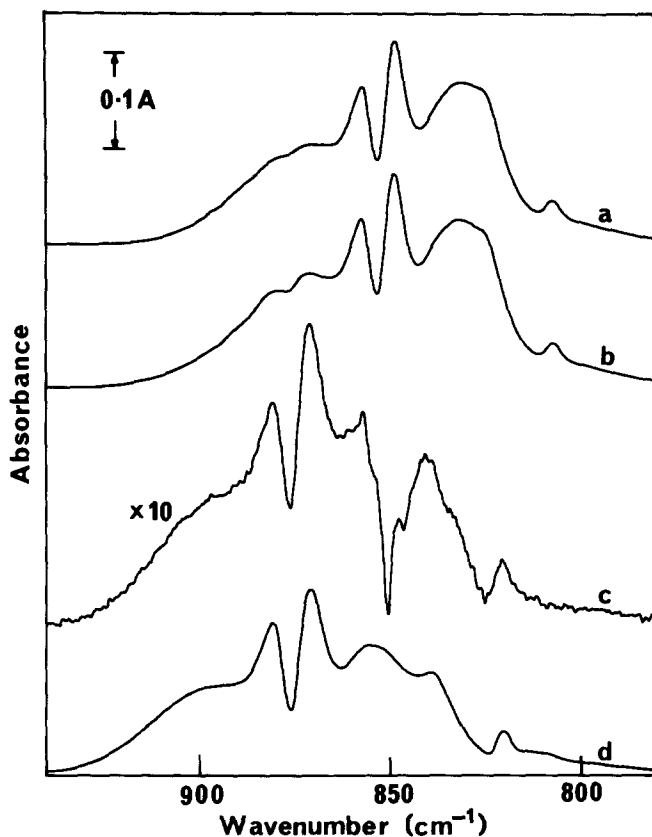


FIG. 3. Infrared spectra of gaseous ethylene oxides. (a) $C_2H_4^{18}O$; (b) 5% $C_2H_4^{16}O$ + 95% $C_2H_4^{18}O$; (c) difference spectrum comprising b less a (in taking the difference, spectrum a was first multiplied by 1.053 to compensate for the difference in pressure between the two samples); (d) $C_2H_4^{16}O$.

product after separation is shown in Fig. 4a. Subtraction of the normalized $C_2H_4^{18}O$ spectrum (i.e., Fig. 3a) and multiplication by 50 gave b in Fig. 4. Despite the increased noise level the spectrum of $C_2H_4^{16}O$ is readily recognizable by comparison with the pure sample (spectrum c). The two horns of the B-type contour of ν_5 at 882 and 871 cm^{-1} , together with the peak of ν_{15} at 820 cm^{-1} , can be used for quantitation of $C_2H_4^{16}O$. This is done by ratioing absorbances at these wavenumbers against those of the corresponding features for $C_2H_4^{18}O$ and comparing these ratios with those obtained for the synthetic mixture of known composition (Figs. 3c and b).

The results of these determinations are shown in Table 3 in comparison with the

predictions of four schemes. Scheme i assumes that nitrous oxide and oxygen exhibit the same selectivity when both are present. Scheme ii corresponds to the situation in which nitrous oxide and oxygen retain the selectivities they exhibit when tested separately under the same conditions (i.e., 20 and 41%, respectively). The third (iii) assumes that reaction of $N_2^{16}O$ proceeds by decomposition through to $^{16}O_2$ which reacts identically to $^{18}O_2$. The basis of scheme iv is that nitrous oxide and oxygen give rise to separate pools of different type and only the pool from oxygen gives rise to ethylene oxide. In regard to the two mechanisms discussed in the Introduction it may be noted that scheme i corresponds to the one with atomic oxygen, whereas the

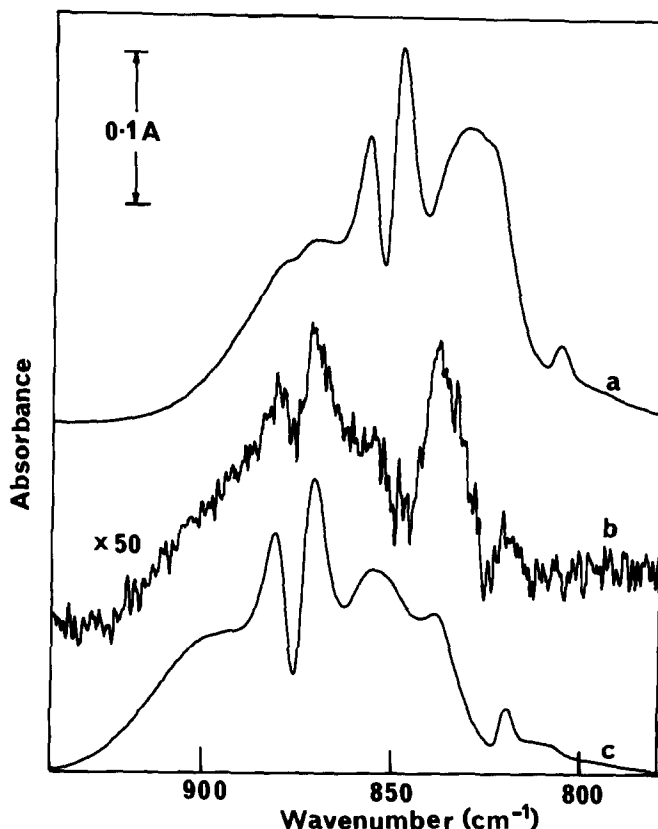


FIG. 4. Infrared spectra of gaseous ethylene oxides. (a) Product ethylene oxide from reaction using mixture of $^{18}\text{O}_2$ and N_2^{16}O (see text); (b) difference spectrum comprising spectrum a less spectrum of $\text{C}_2\text{H}_4^{18}\text{O}$ (Fig. 3a) (in taking the difference, spectrum 3a was first multiplied by 1.158 to compensate for the difference in pressure between the two samples); (c) $\text{C}_2\text{H}_4^{16}\text{O}$.

diatomic model is represented by either scheme ii or iv depending on whether interconvertibility between the two surface oxygen species is possible or not. The analytical results at the three wavenumbers are consistent. The average value falls fairly close to that expected for Scheme i, the single pool situation, after allowance for reaction of $^{16}\text{O}_2$ present as an impurity in the nitrous oxide used. Note that it is unnecessary to allow for the ^{16}O content of the $^{18}\text{O}_2$ used since the $\text{C}_2\text{H}_4^{18}\text{O}$ spectrum used for subtraction corresponds to a sample made from the same $^{18}\text{O}_2$ in the absence of N_2O . Other possible corrections were considered. Kinetic isotope effects leading to different reactivities for the oxygen isotopes

are unlikely to exceed one or two parts in one hundred (12). Checks by repeated transfers between vacuum line and infrared cell showed no evidence of cross-contamination between samples. Thus, we tentatively conclude from the data of Table 3 that nitrous oxide and oxygen form a single oxygen pool.

The above result would also be expected if oxygen scrambling between oxygen and nitrous oxide gas took place faster than reaction. This possibility was excluded by determination of the $^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2$ ratio in the product stream from the above experiment and in separate experiments in which an equimolar mixture of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ was used as oxidant. These results are given in

TABLE 3

Comparison of Predicted and Measured $C_2H_4^{16}O$ Content of Ethylene Oxide Formed during Oxidation of Ethylene by $N_2^{16}O/^{18}O_2$ Mixtures under Conditions Listed in Table 2

	% $C_2H_4^{16}O$ in ethylene oxide
Predicted	
i Identical selectivity for N_2O and O_2	1.0
ii Retention of individual selectivities	0.4
iii $N_2^{16}O \rightarrow ^{16}O_2$ then reaction	0.5
iv Pool from N_2O does not give epoxide	0.0
Measured	
882 cm^{-1}	1.3
871 cm^{-1}	1.1
820 cm^{-1}	1.5
Average	1.3
Correction for $^{16}O_2$ in N_2O	<0.3
Net amount	1.0

Table 4. Within the limits of experimental error, the $^{16}O^{18}O/^{18}O_2$ ratio is the same in feed and product for each experiment. One must conclude that recombination of any oxygen atoms formed on the surface is much slower than the overall rate of ethylene oxidation (at least by a factor of 20 under our conditions). This is in accord with our earlier finding (9) that the rate of conversion of nitrous oxide to nitrogen is much faster when ethylene is present than when it is not.

The isotopic composition of the carbon dioxides formed during epoxidation using $^{16}O_2/^{18}O_2$ mixtures at 233°C was also determined by mass spectrometry. As one might expect the distribution was indistinguishable from equilibrium. The values were $C^{16}O_2 = 30.4\%$, $C^{16}O^{18}O = 48.6\%$, and $C^{18}O_2 = 21.0\%$ by analysis compared to $C^{16}O_2 = 29.9\%$, $C^{16}O^{18}O = 49.6\%$, and $C^{18}O_2 = 20.5\%$ for equilibrium assuming an equilibrium constant of 4 for the production of $C^{16}O^{18}O$ from $C^{16}O_2$ and $C^{18}O_2$.

Silver catalysts used industrially for ethylene oxide synthesis are operated with a few parts per million of an organochlorine compound in the feed. This produces higher selectivity at the expense of some loss in activity. The possibility of carrying out isotope experiments similar to the above with a chlorine-moderated catalyst was examined. Our earlier work (9) suggested that this would be difficult since at temperatures to 240°C the inclusion of dichloroethane seemed to reduce the rate of the $C_2H_4 + N_2O$ reaction much more than that of the $C_2H_4 + O_2$ reaction. Table 5 shows the results of further tests extending to higher temperatures. In tests under conditions similar to those for Table 1 the inclusion of 6.7 ppm of dichloroethane (DCE) in the feed reduced the conversion rate for the $C_2H_4 + N_2O$ reaction at 239°C to below the limit of detectability in 2 h (rows 1 and 2). This exposure to dichloroethane is suffi-

TABLE 4

Formation of $^{16}O^{18}O$ by Exchange during Ethylene Oxidation using $^{16}O_2 + ^{18}O_2$ and $N_2^{16}O/^{18}O_2$ Mixtures^a

Reaction temperature (°C)	Oxidant	% Oxygen conversion ^b	$^{16}O^{18}O$ as a % of $^{18}O_2$ ^c	
			In feed	In product
157	$^{16}O_2 + ^{18}O_2$	2.2	2.2 ± 0.2	2.1 ± 0.2
233	$^{16}O_2 + ^{18}O_2$	51	2.0 ± 0.2	1.8 ± 0.2
233	$N_2^{16}O + ^{18}O_2$	48	1.8 ± 0.2	2.0 ± 0.2

^a Conditions similar to those in Figs. 1 and 2.

^b % of feed oxygen ($^{16}O_2 + ^{18}O_2$ or $^{18}O_2$ alone) incorporated into all oxidation products.

^c Calculated from relative intensities of peaks with $m/e = 34$ and $m/e = 36$.

TABLE 5

Effect of Dichloroethane (DCE) on Ethylene Oxidation over 2.16-g Silver Sponge using Nitrous Oxide and Oxygen

Feed ^a	Oxidant	Temperature (°C)	Time on stream (h)	Conversion rate ^b	Selectivity (%)
43 Torr C ₂ H ₄ , 183 Torr N ₂ O (or 90 Torr O ₂) + 6.7 ppm DCE	N ₂ O	239	0.05	4.7	16
	N ₂ O	239	2	<0.05	—
	N ₂ O	260	4	<0.05	—
	O ₂	260	4.3	3.7	81
167 Torr C ₂ H ₄ , 53 Torr N ₂ O (or 55 Torr O ₂) + 1.8 ppm DCE	N ₂ O	239	0.05	3.0	32
	N ₂ O	239	2	1.6	51
	N ₂ O	239	6	<0.05	—
	N ₂ O	260	6.5	<0.05	—
	O ₂	260	6.8	1.4	68
	O ₂	260	30	1.9	80
	O ₂	306	32.6	17.1	71
	N ₂ O	306	35.6	<0.05	—

^a Balance helium.

^b In $\mu\text{mol C}_2\text{H}_4 \text{ g Ag}^{-1} \text{ min}^{-1}$.

cient to give a chlorine coverage (atoms per surface Ag atom) of 0.2 assuming total chlorine deposition. The reaction rate remained unmeasurable on raising the temperature to 260°C (row 3) but substitution of N₂O by O₂ gave reaction with the high selectivity (81%) characteristic of chlorine-moderated silver (row 4). The rate ratio using O₂ versus N₂O must be greater than 30, compared to 5 when chlorine is absent (Table 1). A second series was carried out under conditions of ethylene excess (as used industrially). Inclusion of 1.8 ppm dichloroethane extinguished the rate with N₂O in 6 h at 239°C (rows 5 to 7 of Table 5). No reaction was observed at 260°C (row 8) or 306°C (row 12), even though ethylene oxide synthesis occurred with high selectivity (rows 9 to 11) using oxygen under similar conditions. The conclusion from the two tests is that chlorine-containing moderators cause complete inhibition of ethylene oxidation by N₂O. Experiments using N₂¹⁶O/¹⁸O₂ mixtures under such conditions cannot provide useful data since no N₂¹⁶O will react.

The above results suggest that chlorine

adsorption prevents N₂O decomposition. This supposition was confirmed by measurements of the rate of N₂ and O₂ formation from N₂O under steady-state conditions in the absence of ethylene. Results are shown in Table 6 for the decomposition of approximately 50 Torr of N₂O at 306°C. A conversion of 6.3% was obtained for hydrogen-reduced silver (row 1) but no decomposition occurred after predosing the same catalyst with dichloroethane to a chlorine coverage equivalent to that which extinguished the C₂H₄/N₂O reaction. The effect of oxygen, fed continuously or predosed on N₂O decomposition, was also examined. Inclusion of O₂ at a partial pressure one-sixth that of N₂O lowered the decomposition rate by 60% (row 3). Predosing the catalyst with oxygen also lowered the rate but by a much smaller amount (row 4). These results indicate that inhibition of N₂O decomposition by adsorbed oxygen is the likely cause of the reduced participation of N₂O in ethylene oxidation when oxygen is also present (Table 1 and Fig. 1).

The effect of surface chlorine on the rate

TABLE 6

Effect of Dichloroethane (DCE) and Oxygen on the Rate of Decomposition of N₂O over 2.16-g Silver Sponge at 306°C

Feed ^a	Catalyst treatment	% N ₂ O converted	Formation rate (μmol g Ag ⁻¹ min ⁻¹)	
			N ₂	O ₂
54 Torr N ₂ O	H ₂ reduction	6.3	3.1	1.35
50 Torr N ₂ O + 1.9 ppm DCE	H ₂ reduction, then DCE exposure ^b	<0.1	<0.05	<0.05
55 Torr N ₂ O + 9 Torr O ₂	H ₂ reduction	2.5	1.2	^d
50 Torr N ₂ O	H ₂ reduction, then O ₂ exposure ^c	5.5	2.6	1.2

^a Balance helium with total flow rate of 33 cm³ STP min⁻¹.

^b 3.7 h at 239°C to 1.9 ppm DCE in helium at total flow rate of 42 cm³ STP min⁻¹.

^c 44 min to 40 Torr O₂ in helium at 306°C followed by flushing with helium alone.

^d Not measurable due to large amount of O₂ added.

of isotope exchange in ¹⁶O₂/¹⁸O₂ mixtures was investigated similarly. Results are shown in Table 7. Inclusion of 3.3 ppm dichloroethane in the feed lowers the mixing rate by a factor of 6 or 7 compared to the unmoderated sample. The rate of oxygen consumption during ethylene oxidation over a similarly moderated catalyst at 306°C (second last row Table 5) is about 13 μmol O₂ g Ag⁻¹ min⁻¹, i.e., substantially greater than the mixing rate.

DISCUSSION

The present results using N₂¹⁶O/¹⁸O₂ mixtures, while suggestive as to the active surface oxygen species for ethylene oxide for-

mation, ideally require verification over a wider range of conditions. This will not be easy given the predominant involvement of oxygen in the reaction. Two approaches may be considered. Nitrous oxide of higher purity (say <100 ppm oxygen) would enable the use of higher nitrous oxide/oxygen pressure ratios. This would increase formation of ethylene oxide from the former oxidant and improve the precision with which the oxygen isotope ratio in this product could be determined. Analysis of the ¹⁶O/¹⁸O ratio in carbon dioxide, not attempted here, might then be possible also. Alternatively, reverse labeling (i.e., N₂¹⁸O/¹⁶O₂) could be tried. This is the preferred arrangement for mass spectral analysis since the determination of small amounts of a heavier label in a dominant unlabeled product is less prone to interference. (Mass spectral measurements were impractical in the present work since parent ions from the minor C₂H₄¹⁶O component were overwhelmed by fragment ions from C₂H₄¹⁸O). However, the cost of ¹⁸O-labeled nitrous oxide would make measurements with it under steady-state conditions very expensive.

The current isotope data (Table 3), assuming their correctness, show that nitrous

TABLE 7

Effect of Dichloroethane (DCE) on Isotope Exchange in ¹⁶O₂/¹⁸O₂ Mixtures Passed over 0.5-g Silver Sponge at 311°C

Feed composition	Sample	% Composition			Exchange rate (μmol ¹⁶ O/ ¹⁸ O g Ag ⁻¹ min ⁻¹)
		¹⁶ O ₂	¹⁶ O/ ¹⁸ O	¹⁸ O ₂	
144 torr O ₂ ^a	product (feed)	49.4 (50.7)	3.9 (1.3)	46.6 (48.0)	15.2
144 torr O ₂ ^a + 3.3 ppm DCE	product (feed)	51.3 (52.8)	1.8 (1.4)	46.9 (45.8)	2.3

^a Balance helium to total flow rate of 34.1 cm³ STP min⁻¹.

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