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Catalytic Oxidation

VI. Oxidation of Labeled Olefins over Silver

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The oxidation of ethylene and propylene labeled with deuterium in various positions and the cooxidation of unlabeled olefins with the corresponding ^{14}C-labeled epoxides have been studied over a silver catalyst. The latter measurements showed that, in both systems at 200 to 220°C, a portion of the CO_2 was produced by destruction of the product epoxide, but that the oxygen exchange between olefin and epoxide was nil. Oxidation of either *cis*- or *trans*-ethylene-d_2 yielded a mixture of the *cis*- and *trans*-d_2 epoxides which was about 92% equilibrated. Relative rate measurements showed that substitution of deuterium for hydrogen in ethylene increased the yield of epoxide substantially. Such kinetic isotope effects were even more pronounced with propylene for which the oxidation of CD_3CHCH_2 and CD_3CDCD_2 gave a 10 to 14% selectivity to the corresponding epoxides compared with 2 to 5% for CH_3CHCH_2, CH_3CDCH_2, and CH_3CHCD_2. The kinetic isotope effects can be qualitatively explained in terms of a normal primary effect in the further oxidation of an intermediate which is common to both epoxide formation and total oxidation. The significance of these findings to previous suggestions regarding surface intermediates and the mechanism of these oxidations is discussed.

INTRODUCTION

The heterogeneous oxidation of ethylene to ethylene oxide is an unusually specific reaction. Silver is the only good catalyst for the direct conversion, and, even with silver, the epoxide yield is quite small for all olefins other than ethylene. It has been suggested (*1*) that the uniqueness of silver is associated with its ability to adsorb oxygen as the superoxide. Recent evidence in support of this view includes the detection of adsorbed O_2^- by EPR (*2*), the observation of infrared bands attributable to adsorbed species containing peroxide linkages (*3*), and the discovery that when the oxidizing agent is nitrous oxide (which forms predominantly oxygen atoms on adsorption) the epoxide yield is dramatically lower (*4*). Even so, kinetic models based on surface species containing only one oxygen are still being proposed (*5*) and O_2^- has been detected on many catalysts which do not produce ethylene oxide.

Data relevant to the vexing question of atomic versus peroxidic oxygen can be obtained through use of deuterium-labeled ethylenes in experiments defining stereochemistry. Thus, epoxidation in solutions of peracids is well known to proceed with retention of configuration (*6*), whereas mechanisms with radical intermediates do not (*7*). Similarly addition of O(^{3}P) oxygen atoms to olefins in the gas phase is predominantly nonspecific due to formation

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of a triplet biradical intermediate (*8a, b*); however, Cvetanovic (*8b*) has suggested that the corresponding reaction employing $O(^1D)$ oxygen atoms might also be specific. Our results using *cis*- and *trans*-ethylene-d_2 to establish stereospecificity, briefly mentioned elsewhere (*9*), have been superseded by those of others (*10, 23*). All these data showed extensive rotation about the C–C bond before ring closure, but with some retention of configuration. Here we give details of our stereochemical findings and of the kinetic isotope effects which accompany them.

The reason for the very low epoxide yields from propylene as compared to ethylene has not been widely studied. It has been suggested that propylene oxide is unstable under synthesis conditions but this is apparently not so (*11*). Tracer experiments by Margolis and Roginskii (*12*) have established that in *ethylene* oxidation the fully oxidized products CO_2 and H_2O can be formed both directly from the olefin and by further oxidation of the ethylene oxide. In the present work the cooxidation of mixtures of the ^{14}C-labeled epoxides with the corresponding olefins has been studied and the relative stability of the epoxides under reaction conditions has been estimated. Here we also describe experiments with various deuterium-labeled propylenes which serve to establish the dominant role of the hydrogens of the methyl group in facilitating further oxidation.

EXPERIMENTAL

An unsupported silver sponge was used in all experiments with labeled compounds in order to avoid complicating interactions with a support. It was prepared by the reduction of silver nitrate with hydrazine hydrochloride according to the method of Kulifay (*13*). Following prolonged washing with deionized water, drying at 100°C, and heating overnight in air at 300°C, the surface area was 0.13 $m^2\ g^{-1}$ as determined by the BET method using krypton as adsorbate. Although the catalysts were not analyzed for Cl, the moderate selectivities (~50%) found for the fresh catalyst suggest that the value is low. Most experiments were made with a 4.41-g sample which was reduced in flowing hydrogen at 300°C and purged with helium at 300°C prior to each reaction.

As prepared, the catalyst showed the 40 to 50% selectivity (for ethylene oxide formation) typical of relatively pure silvers (*14*). However, following an experiment in which monodeuterioethylene had been oxidized over one sample of the sponge, it was found that the rate had declined by a factor of nearly 5 and the selectivity had increased to over 70%. This accidental promotion was probably due to impurities in the olefin, possibly the halide-containing compounds from which it had been prepared. The catalyst in this resultant form will be referred to as promoted Ag sponge.

The single-pass flow reactor used for most of the catalytic experiments and general procedures have been described previously (*15, 16*). In brief, a mixture of olefin (5–100 Torr) and oxygen (20–100 Torr) was made up to atmospheric pressure with helium and was made to flow through a 2-cm^3 bed of catalyst contained in a Pyrex reactor. Labeled compounds were introduced from a syringe driven at constant rate by a syringe pump. Products and unreacted olefin present in the effluent stream during the final one-third of the addition period were collected in a trap cooled to −196°C. They were separated by gas chromatography and analyzed. Radioactive compounds were counted in the apparatus described by Hightower *et al.* (*17*); the epoxides were burned to CO_2 and counted as such. Mass spectral measurements were obtained with a 6-in. Nuclide instrument, and infrared spectra, with a Beckman IR-12 spectrometer.

The actual amount of product epoxide available from the experiments was quite small [0.2 to 1.0 cm^3 (STP)]; this necessitated the use of a small-volume gas cell (7 cm^3) with a path length of 5 cm for the ir measurements. Confirmatory experiments were made with the various d_2-ethylenes using a recirculating flow system with product removal (*18*); this yielded 10–20 cm^3 (STP) of the epoxide. Spectra of various pressures of this material in a standard gas cell were recorded using a Perkin–Elmer 621 spectrometer.

The deuterated propylenes were the same and had the same purity as specified elsewhere (*16*). All the deuterated ethylenes were obtained from Merck, Sharp and Dohme of Canada. Infrared spectra and mass spectral analysis showed they contained less than 2% of other than the specified labeled compound, except for C_2D_4 which contained 5% C_2HD_3. An authentic sample of *trans*-d_2-ethylene oxide, prepared from *trans*-d_2-ethylene by the bromohydrin method, was obtained from the same source. Infrared spectra indicated that its actual composition was 85% *trans* and 15% *cis*. [^{14}C]Ethylene oxide (250 mCi) was obtained from Baird Atomic, Inc., and was diluted to 250 ml (STP) with Matheson CP-grade ethylene oxide. The [2-^{14}C]propylene oxide was obtained from Mallincrodt-Nuclear and was similarly diluted.

RESULTS

Catalytic Results

The effects of temperature and reactant pressures on the rates of ethylene and propylene oxidation over the silver sponge catalyst were studied in order to ascertain appropriate conditions for the proposed tracer experiments, and to show that the characteristics of the catalyst were similar to those of the supported materials usually employed. These investigations were made at low conversions (<15%) so that the differential reactor model could be used and, as expected for a reaction which is *not* diffusion controlled, the measured reaction rates were unaffected by halving the total flow rate through the catalyst bed from 45 to 22 cm^3 (STP) min^{-1}. Figure 1 shows the variation in the reaction rates with temperature for both epoxide formation and total oxidation. The selectivity toward epoxide formation was much lower for propylene (2–3%) than for ethylene (near 50%), but even so sufficient propylene oxide was produced for its positive identification by mass spectrometry. Apparent activation energies calculated from the slopes of the lines in Fig. 1 are shown in Table 1.

TABLE 1

Characteristics of Ag Sponge for Olefin Oxidation

Olefin	Product	Activation energy[a]	Selectivity[b]	Relative activity[c]
C_2H_4	$CO_2 + H_2O$	14.5 ± 0.7	47	165 ± 3°C
	C_2H_4O	11.2 ± 0.5		
C_3H_6	$CO_2 + H_2O$	18.1 ± 0.6	4	195 ± 3°C
	C_3H_6O	21.1 ± 1.5		

[a] Expressed as kilocalories per mole ±SD.

[b] Mole percentage of olefin converted to epoxide.

[c] Temperature required to achieve rate of 10 μM (olefin) min^{-1} to all products with an olefin pressure of 20 Torr and an oxygen pressure of 65 Torr.

The dependences of reaction rate on

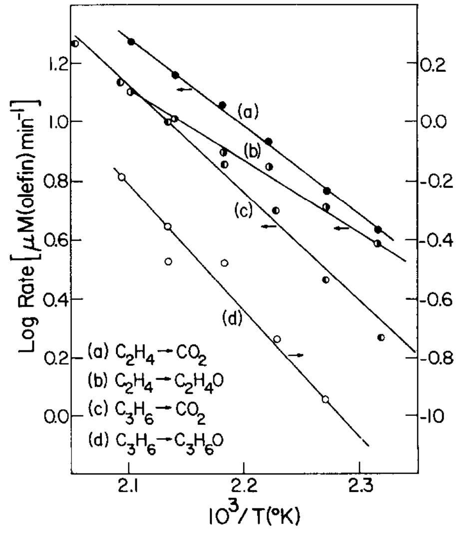


FIG. 1. Effect of temperature on rate of oxidation over silver with olefin pressure at 20 Torr and oxygen pressure at 65 Torr.

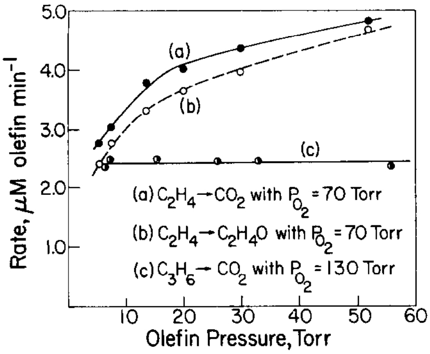


FIG. 2. Effect of olefin pressure on rate of olefin oxidation over silver at 158°C.

olefin and oxygen pressures are displayed in Figs. 2 and 3. For ethylene, partial and complete oxidation had the same kinetic dependence, both reactants tending to be first order at low pressures and zero order at high pressures. For complete oxidation of propylene, the reaction order in oxygen was greater than observed with ethylene whereas the reaction order in olefin was smaller and assumed negative values under some conditions. As with ethylene, epoxide formation from propylene (not shown) responded to external variables in the same way as did complete oxidation, thus indicating that in both instances the selectivity was substantially independent of reaction conditions. As shown in the last column of Table 1, the catalyst was considerably more active for ethylene oxidation than for propylene oxidation.

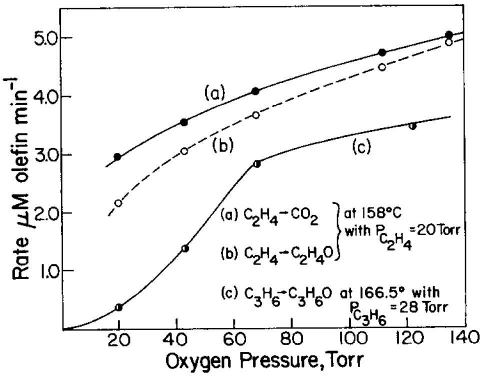


FIG. 3. Effect of oxygen pressure on rate of oxidation over silver.

Kinetic Isotope Effects in Ethylene Oxidation

Comparative measurements of the respective oxidation rates of C_2H_4 and C_2D_4 over the Ag sponge were made using a bracketing procedure in which the normal flow of unlabeled olefin was intermittently replaced for a short while by an equal flow of the labeled material. Olefin pressures that could be conveniently employed fell in the range of 5 to 15 Torr, in which regime the reaction order in olefin was about 0.4 (for the oxygen pressure of 65 Torr used). Relative rates of oxidation of C_2H_4 and C_2D_4 at low conversions under several conditions are summarized in Table 2. A small normal kinetic isotope effect was found for total oxidation ($r_D/r_H = 0.7 \pm 0.1$) and a large *inverse* isotope effect ($r_D/r_H = 1.75 \pm 0.1$) was found for epoxide formation. Consequently, the selectivity was considerably higher for C_2D_4.

The final lines of Table 2 detail competitive experiments using 1:1 mixtures of C_2H_4 and C_2D_4. Both the unreacted olefin and the product ethylene oxides were examined by mass spectrometry using a low ionizing voltage. Intermolecular mixing was negligible ($<2\%$) in both while the intensity ratio for peaks due to d_4- and d_0-ethylene oxides was 1.39. These data could not be directly translated into molar percentages since it was not known whether the ionization efficiencies were the same. According to George and Habgood (*20*) the ratio of the ionization efficiencies for d_6- and d_0-cyclopropanes (which is isoelectronic with ethylene oxide) is 0.91. Applying this factor to our results would indicate an apparent kinetic isotope effect of 1.53 in fair agreement with the results obtained by direct rate comparison.

Kinetic Isotope Effects in Propylene Oxidation

A similar bracketing procedure was used to obtain relative oxidation rates for the partial and complete oxidation

TABLE 2

Relative Oxidation Rates for C_2H_4 and C_2D_4[a]

Ethylene	Pressure (Torr)	Oxidation rate (μM min^{-1})		Selectivity (%)	Isotope effect[b] (rate ratio)	
		To CO_2	To epoxide		To CO_2	To epoxide
C_2H_4	6.2	1.50	1.45	49		
C_2D_4	5.4	0.93	2.50	73	0.64	1.75
C_2H_4	5.9	1.43	1.41	50		
C_2H_4	11.5	1.79	1.75	49		
C_2D_4	12.0	1.20	2.91	71	0.66	1.71
C_2D_4	12.0	1.19	3.11	72		
C_2H_4	12.3	1.80	1.76	49		
C_2H_4	8.8	1.74	1.65	49		
C_2D_4	7.6	1.12	2.86	72	0.64	1.79
C_2H_4	7.6	1.78	1.57	47		
C_2H_4	7.6	1.61	1.43	47		
C_2H_4/C_2D_4	8.7	1.13	1.73	61	0.6	1.5
C_2H_4/C_2D_4	8.5	1.30	1.63	56		
C_2H_4	7.0	1.69	1.49	47		
C_2H_4[c]	6.0	3.44	2.95	46	0.79	2.0
C_2D_4	7.1	2.73	5.55	67		

[a] At 145°C with an oxygen pressure of 65 Torr except as noted.

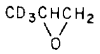
[b] Oxidation rate for C_2D_4 relative to C_2H_4.

[c] At 165°C.

of CH_3CHCH_2, CD_3CHCH_2, CH_3CHCD_2, CH_3CDCH_2, and CD_3CDCD_2 over silver. An oxygen pressure of 120 to 150 Torr was employed in conjunction with a low olefin pressure in order to ensure that the reaction order in olefin was zero rather than inverse. Results are given in Table 3. Within the overall experimental error all the propylenes were oxidized to CO_2 and H_2O at the same rate. Labeling in the 1 or 2 position was without effect on epoxide formation. However there was a very large *apparent inverse* kinetic isotope effect ($r_D/r_H = 2.5$ to 5) for propylene oxide formation from propylenes labeled with deuterium in the methyl group. This had the effect of increasing the selectivity to epoxide formation from 2.5–4% with the unlabeled material to 8–14% with C_3D_6 and CD_3CHCH_2. The significance of this finding in relation to the mechanism of oxidation will be considered in a later section.

Stereochemistry of Epoxide Formation

When CD_3CHCH_2 was oxidized the selectivity was sufficient (see Table 3) to enable collection of a sample of the epoxide which was large enough for infrared analysis. As expected it was exclusively



$CD_3\underset{\backslash O /}{CHCH_2}$

with no deuterium being detectable in positions other than the methyl group. No hydrogen–deuterium transfer was found to have taken place in the unreacted CD_3CHCH_2.

A number of experiments were carried out in which the three d_2-ethylenes were oxidized separately over the accidentally

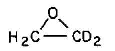
TABLE 3

Relative Oxidation Rates for Deuterium-Labeled Propylenes

Propylene	Pressure (Torr)	Oxidation rate (μM min^{-1})		Selectivity (%)	Isotope effect[a] (rate ratio)	
		To CO_2	To epoxide		To CO_2	To epoxide
At 166°C with oxygen pressure of 128 Torr						
C_3D_6	4.8	4.2	0.38	8.3	0.8	2.6
C_3H_6	4.9	5.3	0.14	2.7		
C_3H_6/C_3D_6	4.9	5.0	0.23	4.4		
CH_3CHCD_2	4.9	4.8	0.11	2.3	1.0	0.9
C_3H_6	4.9	4.7	0.13	2.6		
CD_3CHCH_2	4.9	4.0	0.43	9.8	0.85	3.5
CH_3CDCH_2	4.9	4.1	0.13	3.0	0.7	1.0
At 206°C with oxygen pressure of 145 Torr						
C_3H_6	5.5	6.5	$\approx$0.23	2.9		
CD_3CHCH_2	8.7	6.6	1.0	13.7	1.1	4.6
CD_3CHCH_2	4.2	7.4	1.1	13.0	1.2	3.0
C_3H_6	10.3	6.4	0.27	4.1		
C_3D_6	8.8	5.7	1.1	16.1	0.9	3.9
C_3H_6	10.0	6.7	0.28	4.0		
At 222°C with oxygen pressure of 140 Torr						
C_3H_6	5.7	9.1	0.33	3.5		
CD_3CHCH_2	7.2	10.0	1.6	14.0	1.1	5.0

[a] Rate of oxidation relative to average of values for C_3H_6.

promoted as well as the standard silver sponge in both the single-pass flow system and the recirculating flow apparatus. A typical set of infrared spectra of the product epoxides is compared with that of an authentic sample of the *trans*-d_2 isomer in Fig. 4. The spectrum of the epoxide from the gem-$C_2H_2D_2$ contained only the bands expected for this compound and not those characteristic of the other dideuterioethylene oxides. It therefore represents



alone. On the other hand, the spectra of the product epoxides obtained from oxidation of *cis*- and *trans*-1,2-dideuterioethylene, while similar, were not identical (with respect to relative band intensities) and the significance features of the spectrum of the gem species were missing. The former showed that substantial but not complete *cis–trans* equilibration accompanied oxidation, but without intra- or intermolecular hydrogen–deuterium transfer.

The amounts of *cis* and *trans* isomers present in the mixtures were calculated from the relative intensities of the two bands with B-type contour centered near 845 and 754 cm^{-1}, respectively. According to Cant and Armstead (*19*) these stem from the *cis* and *trans* isomers with relative extinction coefficients of *cis*/*trans* = 3.40. The composition and the extent of loss of configuration estimated in this way from experiments carried out in the two types of reactors are shown in Table 4. Our two results are essentially the same, but differ somewhat from those reported by Richey (*10*) given in the final lines.

It was important to establish that the observed loss of configuration was not due

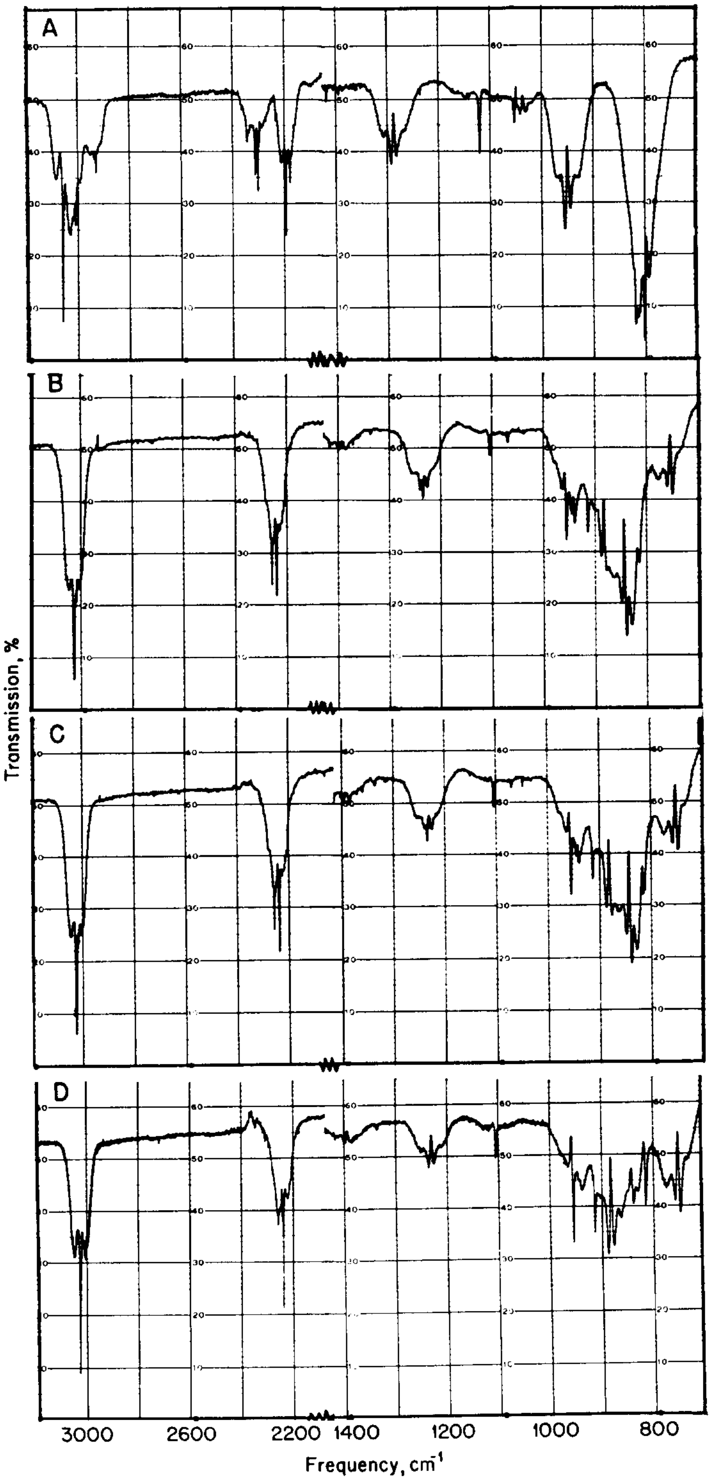


FIG. 4. Infrared spectra of dideuterioethylene oxides prepared from (A) gem-$C_2H_2D_2$ over Ag; (B) *cis*-$C_2H_2D_2$ over Ag; (C) *trans*-$C_2H_2D_2$ over Ag; (D) *trans*-$C_2H_2D_2$ via bromohydrin.

to (a) isomerization of ethylene prior to reaction or (b) isomerization of epoxide subsequent to formation. Infrared measurements (final column Table 4) showed that *cis–trans* interconversion in the unreacted olefin was always small but never zero. The second point was examined by passing some of the *trans*-d_2 epoxide over the catalyst both while oxidizing C_2H_4 and in a separate experiment with oxygen. The infrared spectra of the d_2 epoxides from these experiments did *not* differ significantly from those of the starting material.

Cooxidation of Olefins with Labeled Olefin Oxides

One question which arose from the data of Table 4 was whether the small amount of isomerization apparent in unreacted dideuterioethylenes might be due to slight back reaction of the near-equilibrated epoxides to the olefins in the manner of the ^{14}C-labeled olefin/epoxide exchange reaction reported by Manara and Parravano (*27*). This question could be answered by oxidizing [^{14}C]ethylene oxide together with unlabeled ethylene and examining the unreacted fraction of the latter for radioactivity. Measurement of the radioactivity in the product CO_2 from this same experiment and from the corresponding one from propylene also provided a measure of the extent to which CO_2 was produced by secondary reaction of product epoxide. The results of these experiments together with those from corresponding controls are summarized in Table 5. In both instances the recovered olefins were essentially nonradioactive, establishing that back reaction under these reaction conditions was negligible. Also, in both instances the overall rate of formation of the total oxidation products (CO_2 and H_2O) from olefin and oxide together did not differ greatly from that when the olefin was oxidized alone.

The amount of CO_2 which was formed from the ^{14}C-labeled epoxide was 31% in the case of C_2H_4 and 5 and 12% for the two experiments with C_3H_6. It will be noted that in each experiment the pressure of added epoxide was several times greater than its rate of formation from olefin in the control experiments (this was necessary for experimental reasons). The percentage of CO_2 from further oxidation of propylene

TABLE 4

Stereospecificity of Oxidation of *cis* and *trans* Dideuterioethylenes

System	Ethylene oxidized	Epoxide composition		Equilibrium in epoxides (%)	Isomerization in olefin
		cis (%)	*trans* (%)		
This work[a] (flow system)	*cis*-$C_2H_2D_2$	53.4	46.6	93.2	≈2.5
	trans-$C_2H_2D_2$	45.8	54.2	91.6	≈3.5
This work[b] (recirculating)	*cis*-$C_2H_2D_2$	53.8	46.2	92.4	≈3
	trans-$C_2H_2D_2$	45.9	54.1	91.8	≈7
Richey (*10*)[c] (recirculating)	*cis*-$C_2H_2D_2$	70 ± 5	30 ± 5	60	Unknown
	trans-$C_2H_2D_2$	32 ± 5	68 ± 5	64	Unknown

[a] At 187°C with olefin pressure of 11 Torr, oxygen pressure of 60 Torr, and total flow rate of 22 cm^3 (STP) min^{-1}, giving olefin conversion of about 50% and oxygen conversion of about 18%.

[b] At 168°C with initial olefin pressure at 44 Torr and oxygen pressure of 110 Torr, giving <3% conversion/pass. Reaction stopped at 60% conversion.

[c] Temperature and pressures not known.

TABLE 5

Cooxidation of Olefins with ^{14}C-Labeled Epoxides

Olefin	Inlet pressure (Torr)			Outlet pressure (Torr)		Specific activity[a]			CO_2 from added epoxide (%)
	Oxygen	Olefin	Epoxide	CO_2	Epoxide[b]	CO_2	Olefin	Epoxide	
C_2H_4	64	15.3	nil	1.74	2.4	—	—	—	—
(199°C)	64	12.8	6.6	2.16	8.4	50	0.1	122[c]	31
C_3H_6	111	20	nil	21.4	0.33	—	—	—	—
(215°C)	110	20	2.4	21.5	2.7	89	0.7	1560[d]	5
C_3H_6	110	20	6.2	23.3	6.8	220	0.4	1565[d]	12
(215°C)	108	20	nil	23.3	0.41	—	—	—	—

[a] In counts per minute per Torr (normalized for relative carbon content).

[b] Includes both added ^{14}C-labeled epoxide and product epoxide.

[c] The starting [1,2-^{14}C]ethylene oxide had a specific activity of 160 cpm Torr^{-1}.

[d] The starting [2-^{14}C] propylene oxide had a specific activity of 1820 cpm Torr^{-1}.

oxide was approximately linear with the pressure of epoxide added. Back extrapolating to the pressure of epoxide actually produced during the control experiments one could argue that only 2% of the CO_2 was formed via the epoxide. Applying the same reasoning to ethylene, one could conclude that, in the control experiments with this olefin, about 10% of total oxidation took place in this way. Thus, the reason for the low selectivity of silver for propylene oxide formation, as compared with ethylene oxide, does *not* lie in the instability of *gas-phase* propylene oxide under reaction conditions.

DISCUSSION

The silver catalyst used in the present work had characteristics similar to those of conventional supported preparations. The pressure dependencies shown in Figs. 1–3 mirror those given in the comprehensive studies of Klugherz and Harriott (*21*) on ethylene oxidation and Vaabel *et al.* (*22*) on propylene oxidation. Moreover, the activation energies and selectivities found in the present work fell within the range known for supported silver catalysts (*1*, *14*, *22*). Thus, we do not think our results with deuterium-labeled olefins are peculiar to the particular silver sponge employed. Indeed, they are in fair agreement with those of Larrabee and Kuczkowski (*23*) who found that from 54 to 57.5% of the epoxide formed from *cis*- or *trans*-1,2-dideuterioethylene had the same configuration as the starting material, as compared with our 53 to 54%. These results are, however, significantly different from those reported by Richey (*10*) who reported that up to 70% of the product epoxide had the same configuration as the starting olefin. If Richey's measurements are correct, it may be possible to deduce further mechanistic details from studies directed toward understanding this discrepancy. Larrabee and Kuczkowski have made a start in this direction. They have reported that the extent of retention of configuration is not temperature dependent over the range of 180 to 280°C, but responds weakly to space velocity. Their published data, however, do not afford strong support for the latter contention.

Larrabee and Kuzckowski (*23*) have suggested several ways in which the retention of configuration could occur and, on the basis of their experiments, have eliminated several of these. Among the latter was the possibility that the retention of configuration is caused by a hindered rotation. It was argued that if a small barrier to rotation existed, the extent of the retention should be temperature dependent and this was not observed over the 100°C range of their experiments. Nevertheless, in our view this remains the most plausible explanation and we advance the following arguments. (i) All the data clearly show a small preference to form the epoxide having the same isomeric structure as the initial olefin. (ii) A similar phenomenon has been observed and discussed for the epoxidation of the butenes with ground-state oxygen atoms O(3*p*); Scheer and Klein (*24*) and Cvetanovic (*8a, b*) advanced somewhat different suggestions as to the origin of the barrier, either of which could be applicable to the present system; in addition, the presence of the surface could further hinder the rotation. (iii) If the barrier to rotation were small (<1 kcal/mole), the percentage change with temperature near equilibrium would be on the order of the experimental error; (iv) Finally, it is possible that the lifetime in the transition state limits the extent of rotation, i.e., controls the retention of configuration. Whatever the cause, the important fact is that rotation does occur in the transition state to the point of nearly complete equilibration.

Force and Bell (*25*) quoted our results in support of a mechanism in which it was suggested that two complexes, $Ag\text{-}O\text{-}CH_2\text{-}CH_2^{\cdot}$ and $Ag\text{-}O\text{-}\dot{C}H\text{-}CH_3$, function as intermediates in the formation of ethylene oxide and $CO_2 + H_2O$, respectively. It is difficult to understand, however, why species living long enough to produce ir bands at 200°C would not be completely equilibrated. Their scheme is nevertheless compatible with our findings on isotope effects as outlined below.

The isotope effects reported herein have an important bearing on the mechanism. In fact, the ratio of the formation rates (C_3D_6O to C_3H_6O) of between 3 and 5 was much greater than has been calculated (*26*) for the possible range of true inverse isotope effects. These findings may be explained by the following basic scheme where *X* represents either H or D.

(1)

The adsorbed forms of olefin and oxygen are assumed to react together with a rate constant k_1 to produce an intermediate which is either decomposed to the epoxide (with rate constant k_2) or is oxidized further with rate constant k_3. The slow step in the latter is envisaged to be either a rearrangement or a decomposition involving the breakage of a C–H versus a C–D bond. No isotope effect would be expected for the other steps since they do not involve making or breaking such bonds. Thus, the primary isotope effect (k_{3H}/k_{3D}) operates to produce an inverse isotope effect for the formation of the epoxide. This may be demonstrated by the following steady-state treatment in which the steps for the reverse reactions, defined by k_{-1} and k_{-2}, are neglected for the sake of simplicity although their inclusion would not materially change the picture. This may be justified as follows. No isomerization was found in the unreacted olefin, but rotation must occur in the "intermediate." Moreover, our experiments with added [^{14}C]propene oxide produced no radioactivity in the propene and little in the CO_2; yet the exchange experiments of Manara and Parravano (*27*) suggested that this reverse pathway exists. Application of the steady-state treatment yields:

Concentration of intermediate

$$= \frac{k_1[C_3X_6(\text{ads})][O_2(\text{ads})]}{k_2 + k_{3(\text{H or D})}}. \quad (2)$$

The selectivity of C_3H_6O formation from C_3H_6 will be given by $k_2/(k_2 + k_{3H})$. The experimental value (0.025) thus requires that $k_{3H} \gg k_2$. Likewise $k_{3D} \gg k_2$. Assuming that there are no isotope effects on adsorption and the concentration of intermediate is small, it follows that

$$\frac{\text{rate of } CO_2 \text{ from } C_3H_6}{\text{rate of } CO_2 \text{ from } C_3D_6} = \frac{k_{3H}}{(k_2 + k_{3H})} \cdot \frac{(k_2 + k_{3D})}{k_{3D}}. \quad (3)$$

Applying the inequalities noted above, it follows that the ratio of the rates of formation of CO_2 should be near unity, whereas the ratio of the rates for production of the ethylene oxides will be given by:

$$\frac{\text{rate of } C_3D_6O \text{ from } C_3D_6}{\text{rate of } C_3H_6O \text{ from } C_3H_6} = \frac{k_2 + k_{3H}}{k_2 + k_{3D}} \approx \frac{k_{3H}}{k_{3D}}. \quad (4)$$

The results given in Table 3 are in accord with this treatment provided that the ratio k_{3H}/k_{3D} is approximately 4, a value quite close to the expected ratio for the rates of breaking of C–H versus C–D bonds at the temperature of our experiments (*26*). Moreover, our observations of similar oxidation rates to both classes of products for CD_3CDCD_2 and CD_3CHCH_2, on one hand, and for CH_3CHCH_2, CH_3CDCH_2, and CH_3CHCD_2, on the other, demonstrate that further oxidation of the intermediate takes place by reaction at the *methyl* group rather than at the vinyl or olefinic positions.

A similar treatment of the data for the ethylenes of Table 2 is less quantitative because k_2 is no longer negligible compared with k_{3H}. Adopting the approximate experimental finding that $k_2/(k_2 + k_{3H}) \approx 0.5$, the same procedure yields $k_2 \approx k_{3H}$ and $k_2 \approx 2.5k_{3D}$. So,

$$\frac{\text{rate of } CO_2 \text{ from } C_2H_4}{\text{rate of } CO_2 \text{ from } C_2D_4} \approx \frac{1}{2}\left(1 + \frac{k_2}{k_{3D}}\right) \approx 1.7, \quad (5)$$

and

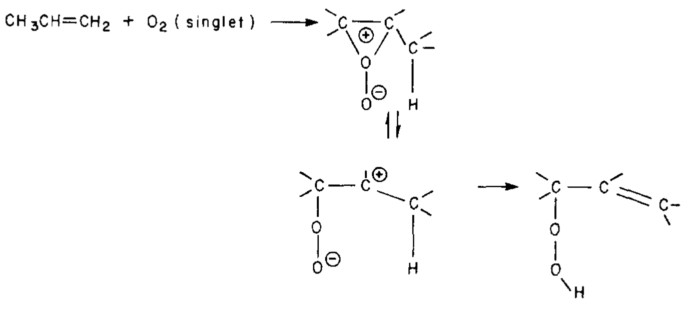
$$\frac{\text{rate of } C_2D_4O \text{ from } C_2D_4}{\text{rate of } C_2H_4O \text{ from } C_2H_4} \approx \frac{2k_{3H}}{k_{3H} + k_{3D}} \approx 1.4. \quad (6)$$

Comparison of these results with those of Table 2 shows approximate agreement.

The results presented herein are not inconsistent with the basic picture presented by others (*3*, *28*, *29*), but they do suggest that some modifications may be required. With ethylene the intermediate of Eq. (1) may be the dioxygen species CH_2–CH_2–O–O- (or $C_2H_4O_2^-$) so long as nearly free rotation is permitted about the C–C bond in the transition state. On the other hand, it is seen that the selectivity for ethylene oxide production is controlled by the rate at which the intermediate is destroyed through the breaking of a C–H or C–D bond rather than by the necessity to remove the remaining half of the oxygen left as the dioxygen species breaks to form ethylene oxide. Possibly, the latter factor becomes limiting at very high selectivities, e.g., 75 to 87%.

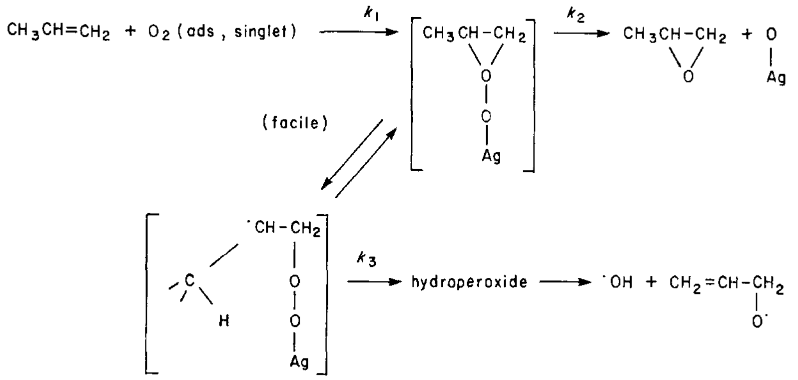
Minor modifications of the picture advanced by Kilty *et al.* (*3*), Sachtler (*28*), and Kilty and Sachtler (*29*) may be made by drawing on a model which has been developed for the mode of attack of *singlet molecular* oxygen on olefins in solution (*30*). Calculations by Beran *et al.* (*31*) indicate that such an oxygen species could function in these reactions on the silver surface although they regard it as less likely than attack by O_2^-. They state, however, that the exact extent of the charge transferred to the adsorbed dioxygen is uncertain. Moreover, their calculations do not explicitly include surface contributions. Thus, we believe that the following ideas are not inconsistent with known facts.

The dominant reaction between singlet molecular oxygen and methyl-substituted olefins is hydroperoxide formation with double bond shift (*30*, *32*), the favored mechanism being the following.



(7)

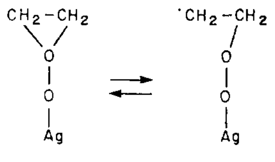
Applying the same ideas to the surface reaction, Eq. (1) may be rewritten as



(8)

In agreement with others (*3*, *28*, *29*), reaction between singlet adsorbed molecular oxygen and olefin will produce a perepoxide intermediate which may decompose directly into epoxide. On the other hand it may be supposed to be in facile equilibrium with the open-chain form which yields the hydroperoxide (as it does in solutions) by intramolecular hydrogen transfer (and hence be subject to the required isotope effect). There is little doubt that, once formed, the hydroperoxide would decompose rapidly at reaction temperature since silver is a good catalyst for such decompositions (*1*, *33*, *34*).

With ethylene, isomerization of the perepoxide to the open-chain form,



(9)

could not directly yield a hydroperoxide since an adjacent methyl group is not present. However, it is possible that the right-hand member of Eq. (9) undergoes an intramolecular isomerization to form the species suggested by Force and Bell (*25*), i.e., $Ag{-}O{-}\dot{C}HCH_3$. It is this species which they suggest as the intermediate leading to CO_2 formation. The right-hand member of Eq. (9) should be exceedingly reactive; consequently, many alternative pathways to total oxidation can be imagined. The oxygen atoms freed from the dioxygen species on epoxide formation are not returned to the gas phase; as pointed out by Sachtler (*28*), they must be consumed in the total oxidation process.

Equation (9) affords a possible explanation for the partial equilibration during the oxidation of *cis*- and *trans*-dideuterioethylene. Presumably, rotation could occur during the relatively short periods of time that the complex spends as the right-hand member. The observed retention of configuration would be found if only sometimes the left-hand member decomposes to ethylene oxide without undergoing this equilibration. These structures are of course identical with those proposed on the basis of infrared evidence at temperatures below 95°C (*3*). It is recognized that they cannot be detected in infrared measurements made at the usual reaction temperatures of above 200°C. However, this does not rule out their existence in the extremely small concentrations expected for reaction intermediates.

In conclusion, we feel that while the model presented herein is somewhat speculative, it does explain rather well our basic findings in respect to isotope effects and stereochemistry and has the virtue of offering a very reasonable explanation for the much lower selectivity of epoxidation for propene as compared to ethylene when using silver catalysts.

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