

## The Stereochemistry of Ethylene-1,2- $d_2$ Epoxidation over Silver Catalysts

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Received November 1, 1979; revised March 19, 1980

The stereochemistry of the catalytic epoxidation of *cis*-ethylene-1,2- $d_2$  to ethylene oxide over four unsupported and two supported silver catalysts as well as over  $Ag_2O$  and  $AgO$  was studied. Variations of the stereochemistry with reaction composition including addition of  $C_2H_4Cl_2$  to moderate the catalyst and the use of  $N_2O$  as the oxidant were also explored. Equilibration in the product ranged between 57 and 99%. A correlation in the equilibration with extent of oxidation of the surface was proposed. Several models were discussed which could rationalize the observed partial equilibration and the sensitivity of the randomization kinetics to certain reaction variables such as oxygen concentration or addition of  $C_2H_4Cl_2$  or  $N_2O$  but not others such as temperature and catalyst selectivity.

### INTRODUCTION

There have been three previous reports directed at the stereochemistry of the oxidation of ethylene-1,2- $d_2$  (ET) to ethylene oxide (ETO) over unsupported silver catalysts. The earliest study indicated 60–64% equilibration in the epoxide (1). In two later reports, Cant and Hall (2) obtained 91.6–93.2% equilibration, while Larrabee and Kuczkowski (3) reported 84–87% equilibration for a low-activity high-selectivity catalyst and 90–91% equilibration for a high-activity low-selectivity catalyst. These last authors also reported an absence of temperature dependence on the equilibration results and some preliminary experiments suggesting a weak dependence on catalyst mass and flow rate.

It appeared valuable to direct additional stereochemical experiments at understanding the differences between these studies in order to deduce further mechanistic details. Therefore, experiments were performed with two supported and four unsupported

silver catalysts using similar, controlled experimental techniques during the reaction runs and product analyses. These catalysts varied in their activity and selectivity characteristics so that any correlation with randomization might be observed. Experiments were conducted over about a 140° temperature range and for various contact times and flow rates. Pretreatments of the catalysts and the reaction mixture compositions were also varied. The latter variation included the addition of 1,2-dichloroethane to the reactant gas, since it is often used to improve the selectivity toward ETO (4). Several experiments were conducted in which nitrous oxide was employed as the source of oxygen. Nitrous oxide has been shown to produce predominantly monoatomic oxygen species on adsorption (5), and it was of interest to determine what correlation this might have with the randomization process. The stereochemistry of epoxidation was also studied during the reduction of silver oxides ( $Ag_2O$  and  $AgO$ ) with ethylene in the absence of any gaseous oxygen.

### EXPERIMENTAL

*Reagents.* Four unsupported silver cata-

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lysts were employed. Ag(1) and Ag(2) were the silver powders previously described in Ref. (3), while the Ag-sponge was similar in type to that reported in Ref. (2). Their selectivities/activities as well as surface area were redetermined as necessary in the new system employed here and some differences were noted from the previous reports. The Ag(3) catalyst was obtained by reducing  $\text{Ag}_2\text{O}$  with  $\text{C}_2\text{H}_4$  at  $180^\circ\text{C}$  for more than 3 hr. Two supported silver catalysts were 1.5% Ag/ $\alpha$ - $\text{Al}_2\text{O}_3$  which was prepared by Engelhard Industries and 5% Ag/ $\text{SiO}_2$  of the type used by Wu and Harriott (6).  $\text{Ag}_2\text{O}$  was prepared by precipitation from a silver nitrate solution with sodium hydroxide, followed by washing 20 times and drying at  $85$ – $88^\circ\text{C}$  for 2 days (7). AgO was obtained by the reaction of silver nitrate with potassium peroxydisulfate, followed by thorough washing and drying in air for 3 days (8).

Matheson CP-grade  $\text{C}_2\text{H}_4$  and  $\text{N}_2\text{O}$ , extrady  $\text{N}_2$ , and prepurified  $\text{O}_2$  were employed. *cis*- and *trans*-ET- $d_2$  were obtained from Merck Sharp and Dohme, and their isomeric purity was the same as specified before (3).

*Apparatus and procedure.* A single-pass flow reactor which could be evacuated was employed. The catalyst (0.15–10.0 g) was held in a 6-, 10.5-, or 12.5-mm-i.d. Pyrex tube reactor.

Pretreatment of the Ag catalysts normally consisted of reduction in flowing  $\text{H}_2$  at  $310^\circ\text{C}$  for several hours except for Ag(3) which was reduced with  $\text{C}_2\text{H}_4$ . Reaction runs were then conducted at a desired temperature ( $140$ – $300^\circ\text{C}$ ) for 1–3 hr until the catalyst stabilized. It was noticed that when a catalyst was exposed to room air its activity markedly decreased unless it was reduced again. This led to several experiments where room-temperature air was passed over the catalyst for 1–3 days before conducting an oxidation run. These runs of unreduced catalyst are labeled "air catalyst."

To study the effect of diffusion-controlled

conditions on the randomization, the flow rate of the gas mixture was varied over the range of 15 to  $90\text{ cm}^3\text{ min}^{-1}$ . For most studies the typical flow rate was  $60\text{ cm}^3\text{ min}^{-1}$ , where it was confirmed that the reaction was not diffusion controlled. The typical composition of the reactant gas was 3%  $\text{C}_2\text{H}_4$ , 10.5%  $\text{O}_2$ , and 86.5%  $\text{N}_2$ . A series of experiments were carried out in which the concentration of ET was varied from 3 to 90% at a constant concentration of oxygen (10%). In another series, the concentration of oxygen was varied from 0.2 to 10.5% with 3%  $\text{C}_2\text{H}_4$ . In both series,  $\text{N}_2$  gas made up the balance of the mixture. In some experiments, 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$  was also included in the feed gas. This was achieved by flowing the oxygen over a small amount of the material condensed in a trap at  $-63$  or  $-78^\circ\text{C}$ .

The oxidation of ethylene by  $\text{N}_2\text{O}$  was conducted over the Ag-sponge catalyst at  $280^\circ\text{C}$  by using the reactant composition of 2%  $\text{C}_2\text{H}_4$ , 2–13%  $\text{N}_2\text{O}$ , and 85–96%  $\text{N}_2$ . The reductions of  $\text{Ag}_2\text{O}$  and AgO with ethylene were carried out at 150 and  $140^\circ\text{C}$ , respectively, with the reducing gas comprised of 2%  $\text{C}_2\text{H}_4$  and 98%  $\text{N}_2$ .

The amount of  $\text{C}_2\text{H}_2\text{D}_2$  reacted in a stereochemistry experiment was usually 0.5–1.0 mmol. In these runs, the  $\text{N}_2$  stream was diverted over small amounts of  $\text{C}_2\text{H}_2\text{D}_2$  condensed in a trap at  $-145$  to  $-125^\circ\text{C}$  after the  $\text{C}_2\text{H}_4$  flow had been stopped.

Reaction products were sampled by a syringe inserted into the effluent for gc analysis or collected in a sample loop at  $-160^\circ\text{C}$  for spectroscopic analysis. The latter samples were trap to trap distilled to concentrate either the ET or the ETO. A Varian 920 gas chromatograph was employed to analyze reactant and product gases. Three columns were used: 10% Carbowax 1000 on Chromosorb W-HP (2.5 m,  $45^\circ\text{C}$ ) for the analysis of ETO, Porapak Q (2.5 m, 25 or  $60^\circ\text{C}$ ) for  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and ET, and Molecular Sieve 5A (1.5 m,  $60^\circ\text{C}$ ) for  $\text{O}_2$  and  $\text{N}_2$ . The conversion/selectivity data for the oxidation of ET- $d_2$  were also ob-

tained. It was reliable only for the ratio of CO<sub>2</sub> and ETO formation, that is, the selectivity of reaction, because the reaction time for ET-*d*<sub>2</sub> was usually less than 10 min.

A Hewlett-Packard 8460A microwave spectrometer was employed to determine *cis/trans* ratios in the product epoxide C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>O. This analytical technique has been discussed extensively and the previous report can be consulted for further details (3). In most cases three to five pairs of rotational transitions were compared to obtain estimates of precision and accuracy. The deviation of each percentage *cis*-ETO-*d*<sub>2</sub> value from the average was less than ±0.5%. In this paper, data from only one transition (1<sub>11</sub> ← 0<sub>00</sub>) which was closest to the average are presented. The absolute accuracy in the intensity ratios is believed to be better than ±1.0% including consideration of a possible systematic error due to the lack of vibrational partition functions for *cis*- and *trans*-C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>O (3). The factor *R*, converting the microwave intensity ratio *I*<sub>*cis*</sub>/*I*<sub>*trans*</sub> into the ratio of the number of molecules of the two species, is 1.18 (3).

## RESULTS

*Reactor Variables*

The previous report (3) suggested a slight increase in the percentage of retention of the original stereochemical configuration upon decreasing the catalyst mass or increasing the flow rate through the reactor. The flow rate employed was 14 cm<sup>3</sup> min<sup>-1</sup> where breakdown of plug flow or diffusion effects might become noticeable. In order to test whether such conditions might have an effect on the randomization kinetics, experiments were carried out over catalyst Ag(2) while the flow rate was varied in the range 15–90 cm<sup>3</sup> min<sup>-1</sup> at a constant contact time, *W/F* = 5.0 g · sec · cm<sup>-3</sup> (*W* = catalyst weight, *F* = flow rate). The results at 190–250°C show effects at flow rates less than 40 cm<sup>3</sup> min<sup>-1</sup>; at 210°C, for example, total conversion of ET at 15 cm<sup>3</sup> min<sup>-1</sup> was 23.2% while 33.4% at 60 cm<sup>3</sup> min<sup>-1</sup>. Also, an increase in selectivity is observed in Table 1 (and Table 2) while conversions were also rising contrary to expectations for the usual triangular kinetic scheme where CO<sub>2</sub> is formed in reactions parallel and consecutive to ETO. No ready expla-

TABLE 1

The Effect of Flow Rate on the Stereochemistry of Epoxidation of Ethylene over Ag(2) at a Constant Contact Time *W/F* = 5.0 g · sec · cm<sup>-3</sup> (C<sub>2</sub>H<sub>4</sub> = 3%, O<sub>2</sub> = 10.5%, N<sub>2</sub> = 86.6%)

Reaction temp. (°C)	Flow rate <i>F</i> (cm <sup>3</sup> · min <sup>-1</sup> )	Oxidation of C <sub>2</sub> H <sub>4</sub>		Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
		X <sub>ET</sub> <sup>a</sup> (%)	S <sub>ETO</sub> <sup>b</sup> (%)	S <sub>ETO</sub> (%)	<i>I</i> <sub><i>cis</i></sub> / <i>I</i> <sub><i>trans</i></sub> <sup>c</sup>	% <i>cis</i> -ETO <sup>d</sup>
210	15	23.2	33.1	47.0	1.440	54.7
	60	33.4	36.5	48.5	1.393	54.1
250	15	55.1	33.4	37.1	1.389	54.0
	60	72.9	37.5	44.0	1.392	54.1

<sup>a</sup> X<sub>ET</sub> = conversion of ET = 100 (n<sub>ETO</sub> + 0.5n<sub>CO<sub>2</sub></sub>)/n<sub>ET(Initial)</sub>.

<sup>b</sup> S<sub>ETO</sub> = selectivity to ETO = 100n<sub>ETO</sub>/(n<sub>ETO</sub> + 0.5n<sub>CO<sub>2</sub></sub>).

<sup>c</sup> Observed *cis/trans* intensity ratio for MW transitions.

<sup>d</sup> Percentage *cis* + percentage *trans* = 100. To estimate the randomization, a correction should be made for the small amount of *trans*-ET-*d*<sub>2</sub> present in the *cis* starting materials (3). These corrections will raise the randomization values slightly (from 0.1 to 0.9%) from those estimated by ignoring them for the data in all tables except Table 10. These corrections were normally not made in the text except for Table 10, since the precise amount of *trans*-ET was not known. The text estimates are therefore lower bounds.

TABLE 2

The Effect of Contact Time on the Stereochemistry of Epoxidation over Ag(2) ( $C_2H_4 = 3\%$ ,  $O_2 = 10.5\%$ ,  $N_2 = 86.5\%$ ,  $F = 60 \text{ cm}^3 \cdot \text{min}^{-1}$ )

Reaction temp. (°C)	W/F (g · sec · cm <sup>-3</sup> )	Oxidation of C <sub>2</sub> H <sub>4</sub>		Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
		X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO
210	0.7	8.8	28.9	38.6	1.433	54.8
	1.25	14.5	33.3	41.1	1.408	54.4
	5.0	33.4	36.5	48.5	1.393	54.1
250	0.7	28.0	30.4	43.3	1.408	54.4
	5.0	77.9	37.5	44.0	1.392	54.1
	7.5	86.0	37.8	45.2	1.361	53.5

nation is apparent for the increase in selectivity. However, these effects were not found to noticeably affect the randomization kinetics of epoxidation as shown in Table 1.

Table 2 shows the effect of contact time or catalyst mass at the constant flow rate of  $60 \text{ cm}^3 \text{ min}^{-1}$  on the stereochemistry over Ag(2). A slight increase in the randomization was again observed with increasing contact time or conversely an increase in the conversion level of ET. The slight decrease in retention at longer contact times could arise from increased randomization in the feed ET. It was previously shown (2) (and confirmed in this study) that 2–4% of the reactant ET-*d*<sub>2</sub> has randomized. This is not enough to account for the much greater randomization in the ETO but could explain the weak dependence of the *cis/trans* ratios with contact time.

In some high-temperature olefin oxidations (e.g., propylene over bismuth molybdate at 400°C (9)) epoxides are formed by a surface-initiated homogeneous reaction in a postcatalytic zone. If such a reaction was occurring in the ET oxidation, its effect on the stereochemistry data would need clarification. However, no significant changes in the reaction kinetics were observed when the postcatalytic volume was varied from 1.0 to 12.5 cm<sup>3</sup>, indicating the absence of any homogeneous reaction effects in this case.

#### Stereochemistry over Six Silver Catalysts

In order to determine whether the randomization process depends upon the properties of the silver catalyst, stereochemical experiments were conducted over four unsupported and two supported catalysts whose activities and selectivities varied considerably. The results over the reduced catalysts are listed in Table 3 with their surface area, total oxidation rate, and selectivity to ETO. Table 3 also includes the temperature-dependence experiments.

In comparing the catalytic properties of Ag(1), Ag(2), and Ag-sponge to the earlier reports (2, 3), the following aspects were noted. The catalytic behavior of Ag(1) was the most disparate from the earlier study. The catalyst was noticeably more active with total conversions ranging from 1.5 to 2 times greater. The selectivity to ETO was slightly lower and remained effectively unchanged at about 68% in the temperature range 180 to 250°C, above which the consecutive oxidation to CO<sub>2</sub> became noticeable. The difference is attributable partly to the different flow rate as mentioned before and also to the catalyst pretreatment since catalyst performance closer to the previous study could be obtained if H<sub>2</sub> reduction was not undertaken. The activity of Ag(2) was not greatly different from the previous study. Selectivity was again low and increased from 32 to 38% in the temperature

TABLE 3

Comparison of the Stereochemistry of Epoxidation over Some Silver Catalysts ( $C_2H_4 = 3\%$ ,  $O_2 = 10.5\%$ ,  $N_2 = 86.5\%$ ,  $F = 60 \text{ cm}^3 \cdot \text{min}^{-1}$ )

Catalyst	Reaction temp. (°C)	W/F (g · sec · cm <sup>-3</sup> )	Oxidation of C <sub>2</sub> H <sub>4</sub>			Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>			
			X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	Oxidation rate (μmol · min <sup>-1</sup> · g <sup>-1</sup> )	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO	
Ag(1) <i>S</i> = 0.14 m <sup>2</sup> · g <sup>-1</sup>	180	7.5	7.7	67.6	0.74	72.6	1.364	53.6	
	210	7.5	21.7	68.0		73.2	1.366	53.6	
	250	2.0	23.2	67.1		72.4	1.396	54.2	
		7.5	54.3	68.0		73.2	1.382	53.9	
	280	2.0	30.0	67.8		73.9	1.420	54.6	
		7.5	76.6	62.3		69.8	1.397	54.2	
Ag(2) <i>S</i> = 0.19 m <sup>2</sup> · g <sup>-1</sup>	180	5.0	11.0	34.5	1.58	53.6	1.409	54.4	
	210	5.0	33.4	36.5		48.5	1.393	54.1	
	250	5.0	77.9	37.5		45.2	1.392	54.1	
Ag-sponge <i>S</i> = 0.43 m <sup>2</sup> · g <sup>-1</sup>	180	2.0	6.1	72.1	2.29	78.2	1.399	54.2	
	210	2.0	20.9	73.7		78.8	1.411	54.4	
	250	2.0	58.9	67.6		—	1.410	54.4	
Ag(3) <i>S</i> = 0.77 m <sup>2</sup> · g <sup>-1</sup>	140	0.93	5.4	46.6	4.12	55.9	1.443	55.0	
	150	0.93	10.3	44.3		7.90	55.4	1.424	54.7
	180	0.93	69.8	39.1		46.0	52.5	1.442	55.0
Ag-Al <sub>2</sub> O <sub>3</sub> (1.5%)	180	10.0	1.8	41.0	0.13	—	1.359	53.5	
	210	10.0	3.5	40.4		50.7	1.367	53.6	
	250	10.0	8.4	32.3		41.8	1.378	53.9	
Ag-SiO <sub>2</sub> (1.5%)	180	0.5	8.2	34.1	11.7	46.5	1.410	54.4	
	210	0.5	25.8	29.5		45.1	1.441	54.9	
	250	0.5	43.7	27.8		—	1.448	55.1	

range 170–250°C while total conversion of ET increased from 7 to 78%. The Ag-sponge behaved similarly to the promoted Ag-sponge in Ref. (2), having nearly constant selectivity of about 72% from 170 to 240°C. The Ag(1) and Ag-sponge catalysts in Table 3 show selectivities somewhat greater than the 40–50% typical of relatively pure silver. The catalysts were not analyzed for the content of promoters such as Cl. It appears, however, from the increased selectivity that some accidental promotion had occurred.

The Ag(3) catalyst was the most active of the unsupported catalysts examined and the stereochemistry runs were made at 140 and 150°C. The two supported catalysts were not as thoroughly studied over as many temperatures. It was clear that the Ag/Al<sub>2</sub>O<sub>3</sub> was relatively inactive while conversely the Ag/SiO<sub>2</sub> had a quite high activity. Selectivity for both catalysts was in the range of 28–41%.

The selectivity to ETO from *cis*-C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> is always larger than that from C<sub>2</sub>H<sub>4</sub>, an observation also seen in most data in other tables. This isotopic effect can be explained in the manner similar to Cant and Hall (2) who indicated that the enhancement in selectivity for C<sub>2</sub>D<sub>4</sub> resulted from a reduction in the rate of complete oxidation.

Regarding the stereochemistry, it is clear that the variability in randomization at a given temperature is no larger than 1.5% when all catalysts are given the same H<sub>2</sub> reduction treatment and even results for Ag(3) which was reduced differently fall in this range. This relative constancy for the percentage *cis*-ETO in the range 53.5–55.1 is the most striking result except to further observe that there is no systematic correlation between the degree of randomization and the catalytic properties or activity/selectivity data. It should be recognized that this constancy does not represent equilibration. It was shown previously

(2, 3) that use of *trans*-ET would result in about 53.5–55% *trans*-ETO. (See also Table 8.) The minor variation in percentage *cis*-ETO among the six catalysts may be attributable to different extents of randomization, although small, in the recovered ET- $d_2$  due to the different contact time as mentioned before, or to the different surface state of the catalyst which will be discussed later.

The effect of temperature is hardly well defined, and most randomization variations with temperature are within the experimental precision. Hence, the data indicate that there is essentially no temperature dependence on the randomization kinetics in the range 140–280°C, as also reported in the previous study (3).

The stereochemistry results for reduced Ag(2) and Ag-sponge are identical to the previous studies (2, 3) within experimental error. For reduced Ag(1), the results differ for percentage *cis*-ETO and are 3–4% lower than the earlier results where values of 57.2–58.0% were observed and where air was passed over the catalysts at 200–250°C for several hours prior to reaction runs.

### Pretreatment of Catalyst

The difference between the present and the earlier result on Ag(1) suggests that the pretreatment procedure for the catalysts plays an important role in the randomization process. The effect of air treatment was systematically examined over Ag(1) and Ag(2). As shown in Table 4, air treatment caused a noticeable increase in the retention of the ETO conformation. In this way the earlier stereochemistry results on Ag(1) could be nearly reproduced. Also, the activity markedly decreased and the selectivity increased somewhat to approach values more similar to the earlier study. This indicates a significant correlation between the surface state of silver and the randomization process.

### Composition of Reactant

The stereochemistry results at low concentrations of O<sub>2</sub> with a fixed concentration of ET are listed in Table 5. The selectivity to ETO was markedly decreased by lowering the concentration of O<sub>2</sub>, which is likely caused by the predominant formation of atomic species O<sup>-</sup> or O<sup>2-</sup> on the surface

TABLE 4

The Effect of Catalyst Pretreatment on the Stereochemistry (C<sub>2</sub>H<sub>4</sub> = 3%, O<sub>2</sub> = 10.5%, N<sub>2</sub> = 86.5%, T = 250°C)

Catalyst	Pretreatment	W/F (g · sec · cm <sup>-3</sup> )	Oxidation of C <sub>2</sub> H <sub>4</sub>		Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
			X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO
Ag(1)	H <sub>2</sub> reduction, 310°C	7.5	54.3	68.0	73.2	1.382	53.9
	Room-temperature air flow for 16 hr	7.5	8.5	74.8	77.6	1.508	56.1
	Room-temperature air flow for 64 hr	7.5	5.7	75.1	72.6	1.520	56.3
Ag(2)	H <sub>2</sub> reduction, 310°C	5.0	77.9	37.5	44.0	1.392	54.1
	As stored in air	6.5	10.3	64.6	68.0	1.528	56.4
	Room temperature air flow for 72 hr	6.5	2.4	54.5	53.5	1.590	57.4

TABLE 5

The Effect of O<sub>2</sub> Concentration on the Stereochemistry (C<sub>2</sub>H<sub>4</sub> = 3%, O<sub>2</sub> = 0.22–15.5%, N<sub>2</sub> = 86.5–96.8%, T = 250°C, W/F = 7.5 for Ag(1) and 5.0 g · sec · cm<sup>-3</sup> for Ag(2))

Catalyst	Concentration of O <sub>2</sub> (%)	Oxidation of C <sub>2</sub> H <sub>4</sub>			Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
		X <sub>O<sub>2</sub></sub> <sup>a</sup> (%)	X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO
Ag(1)	10.3	20.5	54.5	67.9	73.2	1.382	53.9
	0.51	96.6	7.3	32.5	51.7	1.312	52.6
	0.22	~100	3.0	31.4	35.8	1.309	52.6
Ag(2)	10.5	44.4	77.9	37.5	44.0	1.392	54.1
	1.16	98.0	13.9	13.0	25.8	1.342	53.2

<sup>a</sup> X<sub>O<sub>2</sub></sub> = conversion of O<sub>2</sub> = 100 (0.5n<sub>ETO</sub> + 1.5n<sub>CO<sub>2</sub></sub>)/n<sub>O<sub>2</sub></sub> (initial).

(5, 10, 11). The corresponding percentage *cis*-ETO values also decreased by about 1–1.5%, a small but still significant decline.

Table 6 shows the effect of ET concentration on the stereochemistry. The purpose of this experiment was to repeat the earliest study (1), which employed a reactant mixture of 80% ET and 20% O<sub>2</sub> and reported about 70% *cis*-ETO from *cis*-ET-*d*<sub>2</sub>. However, we found that the percentage *cis*-ETO was almost independent of the concentration. This indicates no significant, direct contribution from the gaseous ethylene molecule to the stereochemistry data. The slight decrease at higher ET concentrations may be due to the lowered effective concentration of oxygen which is indicated by its high conversion level.

These results may suggest the sig-

nificance of adsorption sites for ET in the randomization process. Since organic halogen compounds are well known to modify the surface state and produce higher selectivity, some experiments were carried out on a catalyst heavily moderated with chlorine (12, 13). Results are listed in Table 7 where 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> was added to the basic feed gas at concentrations of 0.004 and 0.01%. The poisoning of the catalysts with C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> is seen to result in an increase in the retention of the original olefin conformation as in the case of the air catalyst (Table 4). A pronounced decrease in activity and relative increase in selectivity are also observed. The lower selectivity for *cis*-C<sub>2</sub>H<sub>2</sub>D<sub>2</sub> compared to C<sub>2</sub>H<sub>4</sub> for the last entry in Table 7 appears anomalous and has no readily apparent

TABLE 6

The Effect of ET Concentration on the Stereochemistry over Ag(1) (C<sub>2</sub>H<sub>4</sub> = 3.0–90.2%, O<sub>2</sub> = 10%, N<sub>2</sub> = 0–87%, T = 250°C)

ET concentration (%)	W/F (g · sec · cm <sup>-3</sup> )	Oxidation of C <sub>2</sub> H <sub>4</sub>			Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	
		X <sub>O<sub>2</sub></sub> (%)	X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO
90.2	20.0	95.7	6.4	55.4	1.326	52.9
20.3	20.0	74.4	24.7	63.4	1.352	53.4
3.0	7.5	20.5	54.5	67.9	1.382	53.9

TABLE 7

The Stereochemistry of Epoxidation over Ag-Sponge Heavily Moderated by 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (C<sub>2</sub>H<sub>4</sub> = 3%, O<sub>2</sub> = 10.5%, N<sub>2</sub> = 86.5%, T = 280°C)

Concentration of C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> (%)	W/F (g · sec · cm <sup>-3</sup> )	Oxidation of C <sub>2</sub> H <sub>4</sub>		Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
		X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO
0.0	0.15	40.0	55.0	58.9	1.340	53.2
0.004	3.0	9.1	78.5	80.1	1.639	58.1
0.01	3.0	8.4	78.5	73.5	1.622	57.9

explanation. However, only one run at this concentration of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> was made.

#### Oxidation by N<sub>2</sub>O

Table 8 compares the results of N<sub>2</sub>O versus O<sub>2</sub> as the oxidant over Ag-sponge at 280°C. It was found that the oxidation of *cis*- or *trans*-ET-d<sub>2</sub> by N<sub>2</sub>O resulted in more randomization than in the normal oxidation by O<sub>2</sub>. The randomization increased slightly with the decreasing concentration of N<sub>2</sub>O. However, complete randomization was not quite reached even at the lowest

concentration of N<sub>2</sub>O. The amount of isomerization in reactant ET also seemed somewhat larger (~4–5%) for these runs compared to a normal oxidation with O<sub>2</sub>.

It was also noted that N<sub>2</sub>O caused a pronounced decrease not only in conversion levels of ET but also in selectivity to ETO particularly at the lower concentrations of N<sub>2</sub>O. The decrease in activity and selectivity can be ascribed to the slow activation step of N<sub>2</sub>O and to the predominant formation of atomic oxygen species on the surface, respectively (5).

TABLE 8

Comparison of the Stereochemistry of Epoxidation by N<sub>2</sub>O and by O<sub>2</sub> over Ag-Sponge at 280°C (C<sub>2</sub>H<sub>4</sub> = 1.9%, W/F = 3.0 g · sec · cm<sup>-3</sup> for oxidation by N<sub>2</sub>O, and C<sub>2</sub>H<sub>4</sub> = 1.5%, W/F = 0.15 g · sec · cm<sup>-3</sup> for oxidation by O<sub>2</sub>)

Reaction	Concentration of oxidant (%)	Oxidation of C <sub>2</sub> H <sub>4</sub>		Oxidation of <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
		X <sub>ET</sub> (%)	S <sub>ETO</sub> (%)	S <sub>ETO</sub> (%)	I <sub>cis</sub> /I <sub>trans</sub>	% <i>cis</i> -ETO
N <sub>2</sub> O + <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> or C <sub>2</sub> H <sub>4</sub>	13.3	18.1	23.5	36.2	1.275	51.9
	7.5	15.2	18.7	28.1	1.265	51.7
	2.1	6.4	12.8	19.3	1.261	51.6
N <sub>2</sub> O + <i>trans</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> or C <sub>2</sub> H <sub>4</sub>	13.5	20.4	23.2	35.5	1.126	48.8
	7.5	15.1	19.2	27.9	1.132	48.9
	2.0	6.8	12.2	19.9	1.139	49.1
O <sub>2</sub> + <i>cis</i> -C <sub>2</sub> H <sub>2</sub> D <sub>2</sub> or C <sub>2</sub> H <sub>4</sub>	10.2	42.2	51.2	58.9	1.340	53.2
	7.1	45.2	55.0	62.4	1.347	53.3
	3.6	33.1	50.0	58.6	1.329	53.0
	1.0	16.9	36.7	48.0	1.302	52.4



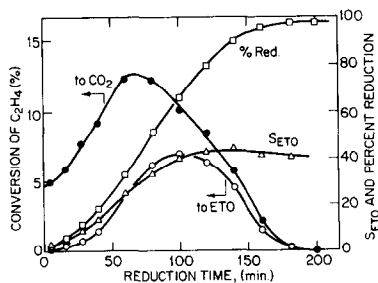


FIG. 1. Reduction of  $\text{Ag}_2\text{O}$  (1.0 g) with  $\text{C}_2\text{H}_4$  at  $150^\circ\text{C}$  ( $\text{C}_2\text{H}_4 = 2\%$ ,  $\text{N}_2 = 98\%$ ,  $F = 60 \text{ cm}^3 \cdot \text{min}^{-1}$ ).

### Reduction of Silver Oxides with ET

It has been reported (14) that the reactions of some silver oxides with ET produced ETO even in the absence of gaseous oxygen. The stereochemistry during these reactions was also investigated since it could provide insights on the effect of the oxidation state of the catalyst on the randomization process. Results of the reduction of  $\text{Ag}_2\text{O}$  with  $\text{C}_2\text{H}_4$  at  $150^\circ\text{C}$  are shown in Fig. 1, where oxidation products from  $\text{C}_2\text{H}_4$  are plotted versus the reduction time. Figure 1 also shows the percentage reduction of bulk oxide, calculated from the rate of incorporation of oxygen into products. One hundred percent reduction corresponds to the complete reduction of  $\text{Ag}_2\text{O}$  into metallic Ag. These results are in good agreement with the earlier study (14). The stereochemistry results which were conducted at four stages of the reduction cycle are listed in Table 9. The percentage *cis*-

TABLE 9

The Stereochemistry of Exoxidation during the Reduction of  $\text{Ag}_2\text{O}$  (1.0 g) with *cis*-ET-*d*<sub>2</sub> at  $150^\circ\text{C}$

Percentage reduction	$S_{\text{ETO}}$ (%)		$I_{\text{cis}}/I_{\text{trans}}$	% <i>cis</i> -ETO
	From $\text{C}_2\text{H}_4$	From $\text{C}_2\text{H}_2\text{D}_2$		
0-4	2-6	3-11	1.473	55.5
40-44	28-31	—	1.555	56.8
73-78	42-43	49	1.569	57.1
92-96	41-44	47-50	1.545	56.7

ETO obtained is very close to the results over the air-treated  $\text{Ag}(1)$  and  $\text{Ag}(2)$  catalysts.  $\text{Ag}_2\text{O}$  itself seems to be inactive for epoxide formation, because the selectivity was very low at the beginning and gradually increased up to 40–45%, a level characteristic of a plain silver catalyst. Therefore, the formation of ETO should not be ascribed to catalysis by  $\text{Ag}_2\text{O}$  but rather by Ag itself. Thus, one could reasonably expect a good coincidence between the stereochemistry for this reduction experiment and the usual oxidation run over the air catalyst in Table 4.

A similar study over AgO at  $140^\circ\text{C}$  is shown in Fig. 2. The behavior of AgO was very different from  $\text{Ag}_2\text{O}$ , again in agreement with the earlier report (14). It is apparent from Fig. 2 that AgO itself has a good catalytic activity for epoxidation with a selectivity of 40%. The selectivity gradually decreased with the progress of reduction and became closer to the initial value for  $\text{Ag}_2\text{O}$ , which is not reduced very fast at this temperature. Thus, the reduction of AgO in Fig. 2 is due to the change of AgO into  $\text{Ag}_2\text{O}$  with 50% reduction corresponding to the completion of this change. The stereochemistry results obtained at two different degrees of reduction are listed in Table 10. The results were markedly different from the usual oxidation runs in Table 3. The percentage *cis*-ETO from *cis*-ET-*d*<sub>2</sub> was about 70%, which implies  $43 \pm 3\%$  retention of original olefin configuration (for an ET composition of  $96 \pm 2\%$  *cis*- and  $4 \pm 2\%$  *trans*-*d*<sub>2</sub>).

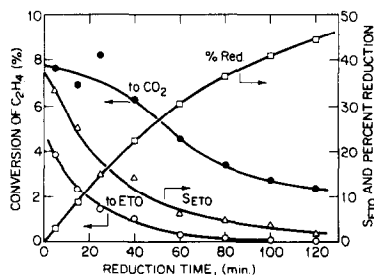


FIG. 2. Reduction of  $\text{AgO}$  (0.5 g) with  $\text{C}_2\text{H}_4$  at  $140^\circ\text{C}$  ( $\text{C}_2\text{H}_4 = 2\%$ ,  $\text{N}_2 = 98\%$ ,  $F = 60 \text{ cm}^3 \cdot \text{min}^{-1}$ ).

TABLE 10

The Stereochemistry of Epoxidation during the Reduction of AgO with *cis*-ET-*d*<sub>2</sub> at 140°C

Percentage reduction	<i>S</i> <sub>ETO</sub> (%)		<i>I</i> <sub>cis</sub> / <i>I</i> <sub>trans</sub>	% <i>cis</i> -ETO
	From C <sub>2</sub> H <sub>4</sub>	From C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>		
0-5	40-30	36	2.711	69.7
11-17	21-15	12	2.734	69.8

## DISCUSSION

The important observations from this study are summarized as follows.

(i) Four unsupported and two supported catalysts when given similar reduction pretreatments displayed similar stereochemical behavior in the oxidation of ET-*d*<sub>2</sub> to ETO-*d*<sub>2</sub>, independent of their wide variability in catalytic properties. 53.5-55% of the product epoxide had the same configuration as the starting material, i.e., about 90-93% equilibration occurred upon epoxidation. The isomerization of ethylene-*d*<sub>2</sub> during reaction runs was only a few percent, which is not enough to account for the much higher randomization in the product ETO.

(ii) Randomization was independent of temperature over the range 140-280°C.

(iii) Mass transfer limitations did not affect the stereochemistry based on results from flow rate variations although a slight dependence on catalyst mass or contact time was observed.

(iv) No effect on the randomization was observed upon varying the ET-*d*<sub>2</sub> concentration in the range of 3-90%. However, decreasing the O<sub>2</sub> concentration increased the randomization. For concentrations of O<sub>2</sub> ≤ 1%, when the O<sub>2</sub> was essentially consumed, values of *cis*-ETO-*d*<sub>2</sub> from *cis*-ET-*d*<sub>2</sub> decreased to 52.4-52.6% (~95% equilibration).

(v) Air treatment of the catalysts at room temperature raised the percentage *cis*-ETO from *cis*-ET-*d*<sub>2</sub> to 56.5-57.5% (85-87% equilibration). Similar stereochemical results were also obtained for the epoxida-

tion occurring during the reduction of Ag<sub>2</sub>O with ET in the absence of any gaseous oxygen. However, a much higher retention (70% *cis*-ETO from *cis*-ET-*d*<sub>2</sub>, i.e., ~57% equilibration) was observed in the reduction of AgO with ET.

(vi) A catalyst heavily modified with 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> also resulted in a decrease of 9-10% in the equilibration compared to runs without it in the feed mixture.

(vii) The use of N<sub>2</sub>O in place of O<sub>2</sub> as the oxidant increased the randomization although complete randomization was not quite attained (~98-99% equilibration).

The stereochemistry results with Ag catalysts summarized under (i) and (ii) are essentially the same as those of Cant and Hall (2) and of Larrabee and Kuczkowski (3). However, the result of Richey (1), who reported about 70% *cis*-ETO-*d*<sub>2</sub> from *cis*-ET-*d*<sub>2</sub>, could not be reproduced in the present study for any reaction conditions using Ag catalysts and will not be included in the further discussion.

The above findings show insensitivity of the stereochemistry to temperature and catalytic properties such as selectivity but a dependency on the catalyst pretreatment or reactant composition. These latter variations show a qualitative correlation of the stereochemistry with the state of oxidation of the surface. This is summarized in Table 11.

In Table 11, the highest retention is ob-

TABLE 11

A Correlation of the Stereochemistry of Epoxidation and the Surface State of Silver Catalysts

% <i>cis</i> -ETO from <i>cis</i> -ET- <i>d</i> <sub>2</sub>	Reaction	Oxidation state of surface
~70	Reduction of AgO by ET	High
~58	Oxidation over Ag modified with C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	
56.5-57.5	Reduction of Ag <sub>2</sub> O by ET	↑ ↓ Low
53.5-55	Oxidation over air catalyst	
52.5-53	Oxidation at low concn of O <sub>2</sub> over reduced Ag	
51.5-52	Oxidation by N <sub>2</sub> O over reduced Ag	

served for the epoxidation occurring during the reduction of AgO into Ag<sub>2</sub>O. AgO consists of Ag<sup>+</sup>, Ag<sup>3+</sup>, and O<sup>2-</sup> and can be written as Ag<sup>+</sup>Ag<sup>3+</sup>(O<sup>2-</sup>)<sub>2</sub> (15). Alternatively, Kagawa *et al.* (14) indicated by electron diffraction that the activity of AgO toward epoxidation arose from the formation of a superoxide AgO<sub>2</sub> with the NaCl structure on the surface (16). A recent ESR study (17) also indicated the existence of the O<sub>2</sub><sup>-</sup> species in AgO. Regardless of the oxidizing species, it is apparent that the surface exists in a high oxidation state during the reduction since the main product from AgO was not Ag but Ag<sub>2</sub>O.

In the case of the reduction of Ag<sub>2</sub>O by ET, the stereochemistry was quite analogous to the standard oxidation over the air-treated catalyst in spite of the formally higher oxidation state of the former. However, as discussed before, the formation of ETO in the reduction of Ag<sub>2</sub>O is ascribable to the catalytic function of metallic silver produced which is likely to have many oxygen ions available at nearby sites. One can therefore reasonably expect a similar trend for the reduction of Ag<sub>2</sub>O and the oxidation over the air catalyst.

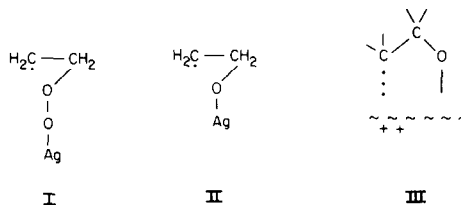
The influence of 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> is to modify or block surface sites by the adsorption of chlorine atoms presumably as Cl<sup>-</sup> (18). Consequently, the surface would become more oxidized and randomization results similar to air-oxidized catalysts could be expected.

The surface must be considered as partially oxidized even for the reduced Ag catalysts. It has been reported (4, 10, 19) that catalysts reduced with H<sub>2</sub> have oxygen species on their surfaces under reaction conditions. Kagawa *et al.* (20) indicated the formation of AgO<sub>2</sub> on the surface by electron diffraction whereas Sato and Seo (21) observed that the adsorption of oxygen on silver resulted in the formation of Ag<sub>2</sub>O with O<sub>2</sub><sup>-</sup> adsorbed on it. In fact, the adsorption of ethylene is possible only on a Ag surface having preadsorbed oxygen. The oxidation state of the Ag should be lower

than for the air-treated or C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>-modified catalysts and should also depend upon the partial pressure of oxygen under operating conditions. Thus, runs with low concentrations of oxygen or the employment of N<sub>2</sub>O as the oxidant, whose decomposition is so slow as to become the rate-determining step, would lead to a lower overall oxidation state for the catalyst.

These experimental findings and the constraints they impose will be examined in terms of three general categories of reaction models that have received attention in the literature: (a) Nonconcerted process—radical intermediate; (b) concerted process—symmetric intermediate; (c) two-site or competitive reactions.

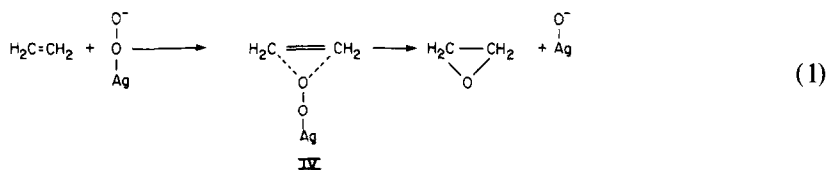
One approach to the epoxidation process has been to emphasize an initial, nonconcerted adsorption process. Gereš *et al.* (22) suggested from their ir study that ET adsorption occurred with rupture of the double bond to form the peroxide I. Force and Bell (23) also proposed a similar type of



intermediate, II, but differing in the form of the active oxygen species. These two intermediates, with rotation permitted about the C–C link, can correlate with the stereochemistry results which show extensive equilibration usually between 90 and 93% and sometimes higher. Of course, the small degree of retention requires that ring closure to ETO can compete with full development of rotation about the C–C bond in the radical intermediate and that this competition is temperature independent. The small barrier leading to the partial equilibration and its variation with positive charge on the surface might be visualized through an interaction depicted by III.

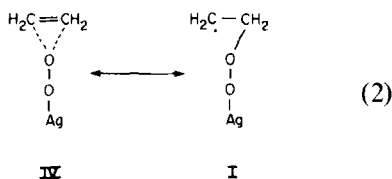
One of the epoxidation mechanisms pro-

posed by many authors (19, 20, 24) is the symmetric Rideal-Eley model involving a gaseous ethylene molecule and a diatomic oxygen species,  $O_2^-(ad)$  or  $O_2(ad)$ :



In the limit of a strictly concerted process, the epoxide would completely retain its starting configuration. Amendments to such a mechanism to incorporate the observed partial randomization might include (a) ascribing a finite lifetime to **IV** with occasional ring opening/closing/randomization processes before rupture of the O-O bond to give ETO and (b) subsequent steric isomerization in the epoxide. This latter possibility has been ruled out by Cant and Hall (2).

Process (a) was also discussed by them. They proposed a facile equilibrium between the peroxide **IV** and the open chain form **I** which would undergo rotation about the C-C bond before reforming the C-O bond and desorption to ETO:



To account for partial equilibration, this proposal would require that the equilibrium not always develop but that **IV** occasionally proceed directly to epoxide with retention or equivalently that species **I** not always sterically equilibrate before epoxidation or before returning to **IV**. Variations in extent of randomization with surface charge could be incorporated into the model through stronger interactions with a more negative oxygen species decreasing the forward rate of reaction (2) or with surface interactions similar to **III**. It would also be necessary

that the equilibration rates  $IV \leftrightarrow I$  (random) in competition with  $IV \rightarrow ETO$  (retention) have similar thermal dependencies.

Cant and Hall further speculated that **I** might also be the active species leading to  $CO_2$  via an intermolecular isomerization to form the species  $Ag-O-CH-CH_3$ . This aspect now appears less attractive in view of the relative insensitivity of the randomization to wide variations in catalyst selectivity. This presupposes that increasing loss of **I** through total oxidation, as expected for very active/low-selectivity catalysts, would decrease the production of randomized ETO by decreasing the reverse rate for reaction (2). The data, however, strongly suggest that kinetic processes leading to  $CO_2$  formation are uncoupled from those leading to partial randomization.

Larrabee and Kuczkowski (3) pointed out that the incomplete-randomization results might also be rationalized by a two-site mechanism with two competitive reactions occurring with randomization and retention, respectively. One of the simplest models would be a combination of the concerted and radical processes just discussed, for example, involving intermediates **II** and **IV**. The randomization ratio should then vary with any change in the number of  $-O-Ag$  and  $-O_2-Ag$  sites leading to intermediates **II** and **IV**.

Greater randomization was indeed observed when  $O_2$  concentrations decreased or when  $N_2O$  was the oxidant which might be consistent with increases in atomic O species and the intermediate **II**. However, some variation in the randomization ratio

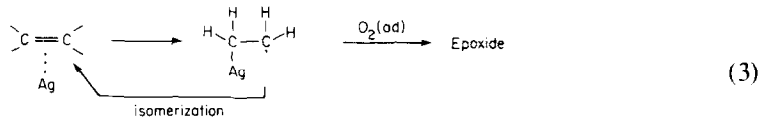
might also be expected as the Ag catalysts differ in surface area, selectivities, and activities, but this was not observed. Also, an effect on the randomization with ET pressure would normally be expected. The reaction is positive order in ethylene so coverage increases with ET pressure. If two sites are available, then their relative populations will change unless isotherms are identical which seems unlikely. It also appears problematical to expect that these two processes would have similar activation energies since their transition states are likely to be quite dissimilar. Hence, the plausibility of a proposal involving competition between intermediates II and IV is debatable and any two-site mechanism must be carefully formulated in view of the constraints imposed.

The above proposals all contain oxygen in the adsorbed species accounting for the randomization. Intermediates involving an ET-Ag species prior to epoxidation might



also be considered. This seems attractive since (a) species such as V and VI are plausible chemical species for isolated ET and Ag and could accommodate the variability in randomization with state of oxidation of the silver. (b) The observation of small amounts of randomization in the ethylene is also easily correlated with such adsorption intermediates that do not involve strong interactions with oxygen in the initial stages of the reaction. (c) Infrared studies by Force and Bell (23) suggested at least two different Et-Ag precursors. One set of bands strongly resembled that for ET coordinated to isolated silver ions (25) and they postulated structure V.

One possibility is described by reaction (3):



This process would assume identical initiating steps for epoxidation versus isomerization with their relative rates determined by site configuration differences. These latter two processes must also have similar activation energies.

Alternatively, a two-site proposal could involve different numbers of V and VI. If it is assumed that the two different adsorption sites react with an oxygen species and that the subsequent epoxidation process occurs with retention of configuration for species V, then the stereochemistry results might be reasonably explained. The extent of randomization or retention would depend upon the number of each site which is principally dependent upon the oxidation state of the surface and the rates at which the intermediates form and react.

The absence of any significant temperature dependence on the stereochemistry must be a constraint for such a process necessitating similar adsorption isotherms and activation energies for the epoxidation step. An invariance in numbers of sites with temperature is also necessary but this could be correlated with the oxygen data of Czanderna (10). He measured the O<sub>2</sub> adsorption isobar at -77 to 351°C at an O<sub>2</sub> pressure of 10 Torr. In the range of 140 to 280°C which was employed in the present work, the surface coverage of oxygen was very close to monolayer coverage. The coverage was nearly independent of the adsorption temperature in this range, showing only a small variation in  $\theta$  between about 1.1 to 1.0. If the oxidation state of the surface is an important variable affecting the degree of

randomization by affecting the ratio of sites, then temperature changes may not affect this ratio since the overall site coverage remains nearly constant.

In summary, various reaction mechanisms involving intermediates such as I-VI can be incorporated into the stereochemistry results. It is obviously difficult to infer the precise surface intermediates controlling the stereochemistry in isotopic experiments which do not directly examine the surface species. In particular, interpretation of the stereochemistry is hampered by lack of answers to the following questions. (i) Is the small amount of ethylene isomerization independent of randomization in the epoxide or directly related to it? (ii) Does randomization take place before, after, or during attachment of the oxygen? (iii) Is the temperature invariance of randomization brought about simply because two independent processes happen to have identical activation energies or as a consequence of an unusual mechanism? Hence, it is not easy to presently justify a strong preference among the various alternatives. Nevertheless, the randomization data for ethylene are intriguing and provide information on the reaction mechanism, albeit shadowy, that should help experimentalists and theorists ultimately evolve a better consensus on the details.

#### ACKNOWLEDGMENTS

The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the portion of this work conducted at the University of Michigan. The National Science Foundation (Washington, D. C.) provided funds to purchase and maintain the microwave spectrometer used in this work.

#### REFERENCES

1. Richey, W. F., *J. Phys. Chem.* **76**, 213 (1972).
2. Cant, N. W., and Hall, W. K., *J. Catal.* **52**, 81 (1978).

3. Larrabee, A. L., and Kuczkowski, R. L., *J. Catal.* **52**, 72 (1978).
4. Hucknall, D. J., "Selective Oxidation of Hydrocarbons," p. 8. Academic Press, London/New York, 1974.
5. Herzog, W., *Ber. Bunsenges. Phys. Chem.* **74**, 216 (1970).
6. Wu, J. C., and Harriott, P., *J. Catal.* **39**, 395 (1975).
7. Brauer, G., "Handbuch der Preparation Anorganischen Chemie," p. 771. Ferdinand Enke Verlag, Stuttgart, 1954.
8. Bailar, J. C., Jr. (Ed.), "Inorganic Syntheses," Vol. 4, p. 12. McGraw-Hill, New York, 1953.
9. Daniel, C., and Keulks, G. W., *J. Catal.* **24**, 529 (1971).
10. Czanderna, A. W., *J. Phys. Chem.* **68**, 2765 (1964).
11. Kilty, P. A., Rol, N. C., and Sachtler, W. M. H., in "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), Vol. 2, p. 928. North-Holland, Amsterdam, 1973.
12. Janda, J., and Kluckovsky, P., *Chem. Zvesti* **20**, 267 (1966); *Chem Abstr.* **65**, 3817a.
13. Metcalf, D. L., and Harriot, P., *Ind. Eng. Chem. Process Des. Develop.* **11**, 478 (1972).
14. Kagawa, S., Kono, K., Futata, H., and Seiyama, T., *Kogyo Kagaku Zasshi* **74**, 819 (1971).
15. Scatturin, V., Bellon, P. L., and Salkind, A. J., *J. Electrochem. Soc.* **108**, 819 (1961).
16. Vol, Y. T., and Shishakov, N. A., *Iz. Akad. Nauk SSSR Otd. Khim. Nauk*, 586 (1962); *Chem. Abstr.* **57**, 4088e (1962).
17. Tanaka, S., and Yamashina, T., *J. Catal.* **40**, 140 (1975).
18. Voge, H. H., and Adams, C. R., *Advan. Catal.* **17**, 151 (1967).
19. Kilty, P. A., and Sachtler, W. M. H., *Catal. Rev. Sci. Eng.* **10**, 1 (1974).
20. Kagawa, S., Tokunga, H., and Seiyama, T., *Kogyo Kagaku Zasshi* **71**, 775 (1968).
21. Sato, N., and Seo, M., *Denki Kagaku* **38**, 649, 768 (1970); **39**, 623 (1971); *J. Catal.* **24**, 224 (1972).
22. Gerei, S. V., Kholovenko, K. M., and Rubanik, M. Y., *Ukr. Khim. Zh.* **31**, 449 (1965).
23. Force, E. L., and Bell, A. T., *J. Catal.* **38**, 440 (1975); **40**, 356 (1975).
24. Kenson, R. E., and Lapkin, M., *J. Phys. Chem.* **74**, 1493 (1970).
25. Carter, J. L., Yates, D. J. C., Lucchesi, P. J., Elliott, J. J., and Kevorkian, V., *J. Phys. Chem.* **70**, 1126 (1966).