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The Oxidation of Ethylene-1,2-d_2 over a Silver Catalyst Studied by Microwave Spectroscopy

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Stereospecific ethylene-1,2-d_2 was oxidized to ethylene oxide-1,2-d_2 over Ag catalysts in a flow reactor at 180–280°C. The epoxide products did not completely randomize for any of the reaction conditions explored. Using a catalyst with good selectivity, $57.5 \pm 1\%$ of the epoxide had the same configuration as the starting material; with a less selective catalyst $54.0 \pm 1\%$ was found. Variation of temperature did not affect the results for either catalyst. It was possible to increase slightly the percentage retention by decreasing the catalyst bed or increasing the flow rate through the reactor. Types of surface processes that can be eliminated by these observations were discussed as well as several hypotheses that can account for the deviations from complete randomization.

INTRODUCTION

The utility of microwave spectroscopy as a method both to distinguish geometric isomers and to determine quantitatively their concentration in mixtures has led to its development as an important technique for the study of mechanisms of heterogeneously catalyzed reactions. The position of inclusion of an isotopic atom in the reaction products can provide information on the structure of the surface intermediates. The relative proportions of the isomers can often suggest or rule out specific reaction pathways. Hirota *et al.* (*1–6*) have applied microwave spectroscopy to mechanistic studies of catalytic hydrogenation and exchange reactions of olefins and acetylenes with transition metals. Exchange reactions of propene with transition metal complexes have also been studied (*7–9*). Kondo *et al.* (*10*) have obtained more detailed mechanistic information about catalytic hydrogen transfer and exchange of propene by examining the distribution of isomers during the course of the reaction. The study reported here is the first application of microwave spectroscopy to a heterogeneous catalytic oxidation.

The oxidation of ethylene (ET) to ethylene oxide (ETO) on a silver catalyst is a reaction which has been studied from many perspectives. It is unique among olefin oxidations in formation of an epoxide in high yields. Silver is the only material which has been found effective to catalyze this reaction. The nature of the active oxygen species on the silver surface, the silver surface itself, the effect of moderators on the surface, as well as kinetic and other measurements, have been reviewed by Voge and Adams (*11*), Sachtler (*12*), and Kilty and Sachtler (*13*). Species present on the surface under reaction conditions have been observed by infrared spectros-

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copy (*14–16*) and mechanisms have been suggested by which adsorbed oxygen and ethylene combine to form reaction products.

Richey (*17*) has used infrared spectroscopy to analyze the deuterated ethylene oxides produced from the oxidation of *cis*- or *trans*-ET-d_2 in a recycle reactor. He reported that 70% of the ETO-d_2 had the same configuration as the original ET-d_2 and suggested that a concerted reaction followed by readsorption of the ETO to form a primary free radical would account for this. Hall has reported (*18*) that the mixture of *cis*- and *trans*-ETO-d_2 is equimolar or nearly equimolar. He has pointed out that this would be expected if the reaction were to pass through a biradical intermediate.

In view of these different observations, we considered it worthwhile to reexamine the question using microwave (MW) spectroscopy to determine the *cis/trans* distribution of the ETO-d_2 formed upon oxidation of *cis*- or *trans*-ET-d_2. This technique is attractive because its high resolution eliminates any ambiguities from interfering absorptions. Moreover both species have a number of MW transitions which could provide checks on internal consistency. Finally, the high sensitivity of the method permits investigation of whether small amounts of unexpected isotopic species were formed in the reaction, e.g., ETO-1,1-d_2 or ETO-d_1.

METHODS

Apparatus. A Hewlett–Packard 8460A microwave spectrometer was used for measurement of the relative intensities of the rotational absorption lines. Catalytic reactions were carried out in a Pyrex glass flow reactor system. The reactor consisted of the following: an inlet system for the introduction of air followed by a cold trap (−160°C) to remove water and carbon dioxide impurities, a second trap containing the ET-d_2 reagent at a temperature dictated by the $C_2H_2D_2/O_2$ mixture desired, the catalyst bed held in a 1.5-cm-o.d. tube on a fritted disk with glass wool packing above the catalyst, and a system of cold traps following the catalyst bed for removal of products. A heating unit surrounded the region containing the catalyst and glass wool. The entire system could be evacuated and the catalyst could be reduced in H_2 while in the reactor.

Reagents. Two precipitated silver catalysts were prepared as described by Wilson *et al.* (*19*) and further cleaned by washing in concentrated NH_4OH. Approximate BET surface areas of the two silver powders were obtained using Kr. The surface areas of both catalysts fell within the range of 0.02 to 0.2 $m^2\ g^{-1}$ generally reported for silver powders. The surface area of catalyst 2 differed from that of catalyst 1 by about a factor of 3. Hydrogen used for the silver reduction was Linde prepurified grade which was passed through a liquid N_2 trap before use. Linde dry air was used for the oxidations. *Cis*- and *trans*-ET-d_2 were obtained from Merck Sharpe and Dohme, Canada, Ltd. Their deuterium compositions were determined by mass spectral and infrared analysis; the results are listed in Table 1.

The silver catalyst powders were placed in the reactor and reduced in H_2 at 310°C before initial usage. Prestabilization also consisted of passage of air over the catalyst at 200–250°C for several hours prior to the reaction. To conduct a reaction, air at 8 psig and a known flow rate was passed through the ET-d_2 saturator trap (−136 to −145°C) and into the heated catalyst bed. The flow rate and feed mixture were originally chosen to produce sufficient yield of products to separate and analyze by the methods described. The products, $C_2H_2D_2O$, CO_2, H_2O, and some of the unreacted $C_2H_2D_2$, were trapped at −160°C. After completion of the reaction, the products were separated by low-temperature fractional condensation and yields were determined with a calibrated vacuum line. Com-

TABLE 1

Total Isotopic Composition of Ethylene and Ethylene Oxide for Two Representative Reactions at 245°C on Catalyst 1[a]

	Isotopic composition (%)	
	Reaction 1	Reaction 2
Reactant		
Cis-$C_2H_2D_2$	77.2–80.0	0.0 ± 0.2
Trans-$C_2H_2D_2$	2.0–5.0	98.6 ± 0.2
C_2H_3D	14.7 ± 0.7	1.4 ± 0.2
C_2H_4	3.1 ± 0.3	0.0 ± 0.1
Product		
Cis-$^{12}C_2H_2D_2O$	45.9 ± 0.3	41.8 ± 0.4
Trans-$^{12}C_2H_2D_2O$	33.0 ± 0.2	54.8 ± 0.3
Cis-$^{12}C^{13}CH_2D_2O$	1.1 ± 0.1	0.6 ± 0.1
Trans-$^{12}C^{13}CH_2D_2O$	0.8 ± 0.1	1.1 ± 0.1
$^{12}C_2H_3DO$	16.5 ± 0.3	1.5 ± 0.1
$^{12}C_2H_4O$	2.9 ± 0.1	Absent

[a] Flow rate: 14 cm^3 min^{-1} (STP); $C_2H_2D_2/O_2 \approx 0.25$.

pleteness of separation was determined by infrared spectroscopy. Microwave measurements were made on the fraction containing the $C_2H_2D_2O$ mixtures.

Microwave intensity analysis. The signal, S, observed from a microwave spectrometer is linearly related to the absorption coefficient for the rotational line (*20*),

$$S = G\gamma L_e, \qquad (1)$$

where γ is the absorption coefficient, L_e is the effective absorption path length of the radiation, and G is a constant instrument gain factor for a particular set of operating conditions. The absorption coefficient is defined as follows:

$$\gamma_{\max} = N \frac{8(\pi h)^{\frac{3}{2}}}{3c(kT)^{\frac{5}{2}}} f_{\mathrm{v}}(ABC)^{\frac{1}{2}} \exp(-W_{\mathrm{j}}/kT) \times (2J + 1)|u_{\mathrm{ij}}|^2 \frac{\nu^2}{\Delta\nu} g_{\mathrm{n.s.}}, \qquad (2)$$

where N is the number of molecules per cubic centimeter; h is Planck's constant; k is Boltzmann's constant; T is the temperature Kelvin; f_{v} is the fraction of molecules in the vibrational state from which the transition originates; A, B, and C are the molecular rotational constants; W_{j} is the rotational energy; J is the rotational angular momentum quantum number; $|u_{\mathrm{ij}}|$ is the dipole matrix element for the transition; ν is the frequency of microwave radiation; $\Delta\nu$ is the half-width at half-maximum of the absorption line; and $g_{\mathrm{n.s.}}$ is the nuclear spin statistical weight factor.

It is convenient to measure the ratio of the signals arising from two different molecules in a mixture of gases which gives directly the ratio of the number of molecules of the two species. In our case,

$$\frac{S_{cis}}{S_{trans}} = \frac{N_{cis}}{N_{trans}} R, \qquad (3)$$

where R is the ratio of all the remaining quantities in $\gamma_{\max}$ for the two species. For the two $C_2H_2D_2O$ isomers, the quantities necessary to compute R can all be unambiguously calculated or measured, except for f_{v}, since the rotational spectra of the isomers have been analyzed by Hirose (*22*). The ratio of $f_{\mathrm{v}}(cis)/f_{\mathrm{v}}(trans)$ was chosen to be 1 in our analysis and the effect of different assumptions for this value is analyzed in the results section. For additional discussions of microwave theory and analysis, see Refs. (*20*) and (*21*).

All intensity measurements were made at room temperature. Sample pressure in the region of 40 mTorr was used. The intensity of a given line varied linearly with pressure in this region. All measurements were made on fully modulated lines with an arbitrarily selected crystal current of 57.6 μA. This low power level was chosen in a region where the intensity is a linear function of crystal current and saturation effects were believed to be minimal. Repeated measurements of $\Delta\nu$ for the *cis*- and *trans*-$C_2H_2D_2O$ species failed to indicate a difference in the half-width which exceeded the experimental uncertainty when lines of the same transition were compared. The method of measurement adopted, therefore, was to observe the absorption maximum of a particular transition for the *cis*-$C_2H_2D_2O$ and *trans*-$C_2H_2D_2O$ alternately, for a period of not less than 100 time constants, making a total of ten separate measurements on each line. The location of the baseline was determined after each individual measurement. Both symmetric and antisymmetric transitions were measured as a check on the correct assignment of the nuclear statistical weight factors.

In addition to the intensity measurements on *cis*- and *trans*-$C_2H_2D_2O$, a search was made of the 30- to 40-GHz region on samples of the products of some of the catalytic reactions for lines due to 1,1-$C_2H_2D_2O$, C_2H_3DO, C_2HD_3O, C_2D_4O, and C_2H_4O. The spectra of those isotopically substituted species which were not reported by Hirose (*22*) were calculated with rotational constants derived from the data in his paper. The procedure involved determining the r_0 coordinates which fit best the rotational constants of the ten reported isotopes. This indicated that low J transitions for the unreported species should be predictable to ±50 MHz and easily searched for.

RESULTS

Catalysts

Figure 1 summarizes the behavior of the two silver powder catalysts over the temperature range explored in these experiments. Difficulties with temperature control over the course of each catalytic reaction require the assignment of an uncertainty of at least ±5°C to each point plotted. There is also a large uncertainty (~10%) attached to the ordinate values at the low end of the temperature range for catalyst 1 where total yields were less than 0.02 mmole and CO_2 was very near the detection limits.

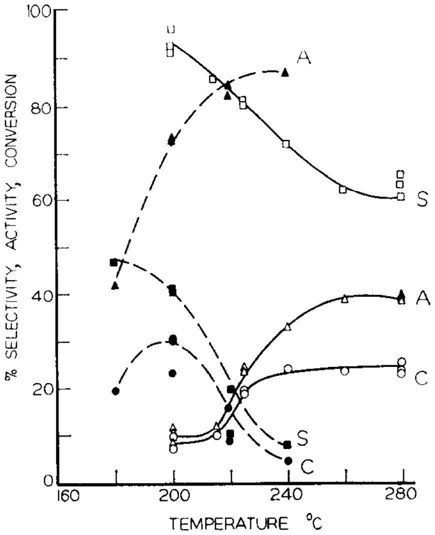

FIG. 1. Selectivity (S), activity (A), and conversion (C) as a function of temperature for 9.7 g each of silver powder catalysts 1 (open symbols) and 2 (darkened symbols). Flow rate: 14 cm^3 min^{-1} (STP); $C_2H_4/O_2 \simeq 0.25$. Each point represents a single measurement. $\%S = 100\, n_{ETO}/(n_{ETO} + 0.5\, n_{CO_2})$; $\%C = 100\, n_{ETO}/n_{ET(initial)}$; $\%A = 100\, C/S = 100\, (n_{ETO} + 0.5\, n_{CO_2})/n_{ET(initial)}$.

The pronounced inverse relationship of activity and selectivity vs temperature for catalyst 2 suggests that consecutive oxidation of ETO to CO_2 at higher temperatures is a more important process for this catalyst than catalyst 1 at this low flow rate. The decrease in selectivity with temperature for both catalysts may suggest undesirable concentration and/or temperature gradients in the reactor (*11*). However the data seem equivocal in this regard since the temperature/selectivity characteristics of the catalysts are generally consistent with those reported by Spath *et al.* (*23*) for a reactor design which minimized such gradients.

Analysis of Ethylene Oxide: Total Isotopic Composition

A microwave analysis of all ethylene oxide species present in two representative samples of catalytic reaction products is presented in Table 1. The uncertainties are assigned by allowing the statistical variations in the experimental data to assume maximum values. An additional uncertainty is introduced by the lack of information from which to evaluate the vibrational partition functions for all the species observed. Use of partition functions calculated with the vibrational frequencies determined by the force field of Cant and Armstead (*24*) does not result in changes in the percentage composition beyond the range of the uncertainties already assigned. It is to be noted that, aside from the distribution of the *cis*- and *trans*-$^{12}C_2H_2D_2O$, the composition of the oxides parallels that of the starting materials. Searches in the region of 30–40 GHz for lines due to $^{12}C_2D_4O$, $^{12}C_2HD_3O$, and 1,1-$^{12}C_2H_2D_2O$ failed to provide evidence that any of these species were present in the samples. Therefore, they were less than 0.01% of the mixture. Also, ir analysis of unreacted ET-d_2 recovered after the catalytic reaction showed no indication of changes from the starting material.

The good agreement between the composition of the starting materials and their oxides (apart from the ETO-d_2 species) indicates that the microwave analysis has an accuracy of about 1%. In support of this, the ^{13}C abundances in the ETO-d_2 are also close to the expected natural abundances.

Dideuteroethylene Oxide: Cis/trans Composition

Tables 2 and 3 contain representative data on the ratios of the *cis*- and *trans*-ETO-d_2 produced in reactions on catalysts 1 and 2, respectively. The uncertainties in the intensity ratios represent the random errors in the series of ten measurements from which the average value presented was derived. The uncertainties in the percentage *cis*-$C_2H_2D_2O$ are obtained from those of the intensity ratios by simple

TABLE 2

Cis- and *Trans*-Dideuteroethylene Oxide Composition for Reactions with Catalyst 1[a]

Starting material	Reaction temperature °C	Transition	S_{cis}/S_{trans}[b] (average)	R[c]	*Cis*-$C_2H_2D_2O$[d] (%)
Trans-$C_2H_2D_2$	208	$4_{31} \leftarrow 4_{22}$	0.806 ± 0.003	1.09	42.5 ± 0.1
	225	$1_{11} \leftarrow 0_{00}$	0.907 ± 0.011	1.18	43.5 ± 0.6
	225	$2_{21} \leftarrow 2_{12}$	0.598 ± 0.003	0.799	42.8 ± 0.2
	245	$1_{11} \leftarrow 0_{00}$	0.893 ± 0.003	1.18	43.1 ± 0.1
	245	$2_{21} \leftarrow 2_{12}$	0.578 ± 0.002	0.799	42.0 ± 0.1
	280	$4_{31} \leftarrow 4_{22}$	0.804 ± 0.006	1.09	42.5 ± 0.2
Cis-$C_2H_2D_2$	200	$4_{31} \leftarrow 4_{22}$	1.46 ± 0.01	1.09	57.3 ± 0.1
	225	$1_{11} \leftarrow 0_{00}$	1.63 ± 0.01	1.18	58.0 ± 0.2
	225	$2_{21} \leftarrow 2_{12}$	1.07 ± 0.01	0.799	57.2 ± 0.1
	225	$4_{31} \leftarrow 4_{22}$	1.46 ± 0.01	1.09	57.3 ± 0.1
	245	$1_{11} \leftarrow 0_{00}$	1.63 ± 0.01	1.18	58.0 ± 0.1
	245	$2_{21} \leftarrow 2_{12}$	1.08 ± 0.004	0.799	57.5 ± 0.1
	280	$4_{31} \leftarrow 4_{22}$	1.46 ± 0.01	1.09	57.3 ± 0.1

[a] Amount of catalyst: 9.7 g; flow rate: 14 $cm^3 min^{-1}$ (STP); $C_2H_2D_2/O_2 \approx 0.25$.

[b] Observed *cis/trans* intensity ratio for microwave transition.

[c] Calculated from absorption coefficients; see Eq. (3).

[d] Percentage *trans* + percentage *cis* = 100. Uncorrected for the small amount of *trans*-ethylene present in the *cis* starting material since its exact concentration was not precisely known. Inclusion of 2–5% *trans*-ethylene will raise the percentages by 0.2 to 0.9% for the *cis*-ethylene oxidations. This was considered in estimating the overall uncertainties.

TABLE 3

Cis- and *Trans*-Dideuteroethylene Oxide Composition with Catalyst 2[a]

Starting material	Reaction temperature °C	Transition	S_{cis}/S_{trans}[b] (average)	R[c]	*Cis*-$C_2H_2D_2O$[d] (%)
Trans-$C_2H_2D_2$	180	$4_{31} \leftarrow 4_{22}$	0.925 ± 0.008	1.09	45.9 ± 0.2
	200	$4_{31} \leftarrow 4_{22}$	0.924 ± 0.005	1.09	45.9 ± 0.1
	200	$2_{21} \leftarrow 2_{12}$	0.674 ± 0.004	0.799	45.8 ± 0.2
	200	$1_{11} \leftarrow 0_{00}$	1.03 ± 0.01	1.18	46.6 ± 0.3
	220	$2_{21} \leftarrow 2_{12}$	0.681 ± 0.002	0.799	46.0 ± 0.1
Cis-$C_2H_2D_2$	200	$4_{31} \leftarrow 4_{22}$	1.26 ± 0.01	1.09	53.6 ± 0.2
	200	$2_{21} \leftarrow 2_{12}$	0.932 ± 0.002	0.799	53.8 ± 0.2
	200	$1_{11} \leftarrow 0_{00}$	1.41 ± 0.014	1.18	54.4 ± 0.2

[a–d] See Table 2.

propagation of error analysis. A systematic error is present due to the lack of vibrational partition functions for *cis*- and *trans*-$C_2H_2D_2O$. To determine the magnitude of this error, three possibilities were examined. Using the data in Ref. (*24*) and treating all the observed frequencies as fundamentals, a ratio of partition functions $f_v(cis)/f_v(trans) = 0.993$ is obtained. If the frequencies from the two force field calculations in this same reference are used the ratios become $f_v(cis)/f_v(trans) = 1.017$ (rocking vibrations assumed higher than twisting) and $f_v(cis)/f_v(trans) = 1.000$ (twisting vibrations assumed higher than rocking). The factor $f_v(cis)/f_v(trans) = 0.993$ changes the percentage *cis*-$C_2H_2D_2O$ only within the limits of uncertainty already assigned. $f_v(cis)/f_v(trans) = 1.017$ decreases the percentage *cis*-$C_2H_2D_2O$ by a few tenths of a percent. Therefore a ratio of unity for the partition functions was taken in the calculations.

No correction has been made for power saturation effects. The small differences (less than a percent) between the values obtained in measurements on the same sample using different transitions may be due to saturation effects, slight changes in effective cell path length due to residual standing waves, or some other unknown effect. Nevertheless, the high consistency for different transitions is gratifying and makes a compelling case that the true percentages differ by less than 1% from the values reported in Tables 2 and 3. Furthermore, the consistency obtained for the same rotational transition measured for different samples (reaction temperatures) is even better in almost every case. This gives us confidence that small changes in the relative amounts of the species can be detected for different reaction samples if the same transition is employed; differences of about 0.5% would appear to be significant.

The data in Tables 2 and 3 indicate that there is no variation with temperature of the product distribution on either catalyst 1 or 2 although selectivity varies to some extent with temperature over the range studied for both catalysts. In addition, it is seen that the less selective catalyst (catalyst 2) produces a higher degree of randomization of the product.

The effect on product distribution of variation in the mass of catalyst and flow rate is presented in Table 4. Decreasing the amount of catalyst or increasing the flow rate, using either catalyst, decreases the amount of randomization. Since the small changes are systematic and appear significant by the criteria just discussed, we believe they are not artifacts. The last two reactions listed in Table 4 for catalyst 2

TABLE 4

Product Distribution with Variation in Flow Rate and Catalyst Mass at 200°C[a]

Catalyst	Catalyst mass (g)	Flow rate [cm^3 min^{-1} (STP)]	Transition	S_{cis}/S_{trans} (average)	*Cis*-$C_2H_2D_2O$ (%)
2	9.7	14	$2_{21} \leftarrow 2_{12}$	0.932 ± 0.002	53.8 ± 0.2
2	4.9	14	$2_{21} \leftarrow 2_{12}$	0.953 ± 0.010	54.4 ± 0.2
2	4.9	42	$2_{21} \leftarrow 2_{12}$	0.969 ± 0.004	54.8 ± 0.1
2	1.5	14	$2_{21} \leftarrow 2_{12}$	1.08 ± 0.02	57.5 ± 0.4
1	9.7	14	$2_{21} \leftarrow 2_{12}$	1.07 ± 0.01	57.3 ± 0.2
1	4.8	42	$2_{21} \leftarrow 2_{12}$	1.11 ± 0.004	58.1 ± 0.1
1	2.4	14	$2_{21} \leftarrow 2_{12}$	1.11 ± 0.003	58.1 ± 0.1

[a] Starting material: *cis*-$C_2D_2H_2$; $C_2H_2D_2/O_2 \approx 0.25$.

were also checked for changes in selectivity. Increases of about 10% were obtained relative to that presented for the same catalyst and temperature in Fig. 1.

DISCUSSION

The ratios of the dideuteroethylene oxides formed with both catalysts used in this study show that the epoxide products did not completely randomize for any of the reaction conditions explored. [Although the zero-point energies of *cis*- and *trans*-$C_2H_2D_2O$ are not precisely known, vibrational data (*24*) indicate that the *cis/trans* ratio in an equilibrium mixture will be 1.00 ± 0.02.] Using catalyst 1 (higher selectivity), 57.5 ± 1% of the epoxide had the same configuration as the starting material; with the less selective catalyst 2, 54.0 ± 1% was found. Variation of reaction temperature or configuration of starting material did not affect the results for either catalyst. It was possible, however, to increase the percentage retention slightly by decreasing the catalyst bed length (i.e., catalyst mass) or increasing the flow rate through the reactor.

The temperature insensitivity of the *cis/trans* randomization ratio while selectivity changed markedly implies that temperature and temperature gradients were not influencing the randomization kinetics. The small dependence of the randomization ratio upon a sixfold change in catalyst mass and a threefold change in flow rate suggests some mass transfer effects on the randomization kinetics. The effect appears small but deserves additional exploration in further studies.

Although some kinetic ambiguities remain, nevertheless, the principal observation is noteworthy, viz., that the *cis/trans* ratios deviate somewhat from the statistical values and vary for the two catalysts. In this regard it is also interesting that the observed *cis/trans* ratios in this study are intermediate to those reported by Richey (*17*) and Hall (*18*). This suggests that catalyst properties are an important element in determining the extent of randomization. Certainly the observations indicate that some caution should be exercised before concluding that a reaction pathway with loss of stereo configuration about the carbon–carbon bond of ethylene completely defines the epoxidation mechanism.

In considering rationalizations on a more molecular level for this deviation from complete randomization, it is apparent that the temperature insensitivity places several constraints on possible proposals. A simple reaction pathway seems unlikely, which invokes an activation energy or barrier, for example, an intermediate with restricted rotation about a C–C bond. In a similar vein, two parallel competing surface reactions at the same site, leading to randomization and retention, respectively, are only possible if they have nearly the same activation energies. Such a situation could apply to formation of a radical intermediate on the surface (Ag–O–CH_2–$CH_2\cdot$) (*16*, *18*) permitting ring closure to occur sometimes before C–C bond rotation. Also the possibility of two parallel competing reactions, even with somewhat different activation energies but at different reaction sites, cannot be excluded until a more thorough investigation is undertaken into the possibility that diffusion-limited reaction conditions may have occurred.

The high and variable conversions (or selectivities) with temperature changes for both catalysts, while flow rate and partial pressures remained unchanged, indicate conditions for which readsorption and further oxidation of ETO were important. These marked changes in conversion with temperature, while *cis*/*trans* ratios were invariant, indicates that certain consecutive processes are not likely to be related to the deviations from complete randomization. Hence, processes involving readsorption of unrandomized ETO formed by a concerted process followed by desorption of randomized ETO, as proposed by Richey (*17*), do not easily conform to the observations nor does a scheme in which unrandomized ETO is readsorbed followed by competitive desorption of either randomized ETO or CO_2.

Additional constraints are imposed from negative isotopic labeling results for species other than ETO-1,2-d_2. Pathways can be eliminated which involve intermediates which could desorb to even a small extent to give ETO-1,1-d_2, ETO-d_1, etc. Also, the absence of change in the *cis*/*trans* ratio of the ET-1,2-d_2 as monitored by ir reduces the likelihood of an ET adsorption/desorption step prior to oxidation as a major source for randomization. This observation is not as compelling in eliminating the following process: $C_2H_2D_2O$(random) + $C_2H_2D_2$(*cis*) → $C_2H_2D_2O$(*cis*) + $C_2H_2D_2$ (random). Such oxygen exchange has been observed (*25*) and only a small contribution is necessary to account for our data; the concomitant change in the ET could go undetected by ir. However, this process is not very attractive in view of the insensitivity of the randomization ratio over a wide temperature range while the adsorptivities of the ETO(random) and ET(*cis*) are presumsbly changing as well as their relative concentrations as evidenced by the variable selectivities and conversions.

The above considerations indicate a number of reaction processes on the surface that can be eliminated. Several hypotheses that can account for the incomplete randomization were also discussed. Some of these proposals can be investigated by additional labeling experiments using MW spectroscopy. Additional experiments are also suggested for further delineating the sensitivity of the *cis*/*trans* ratio to variables such as reaction composition, catalyst properties, and reactor parameters. Such experiments should lead to additional insights regarding the mechanism of oxidation of ethylene.

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