

The Stereochemistry of Propylene-1,2-d₂ Epoxidation over Silver Catalysts

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Received December 4, 1980; revised February 16, 1981

The stereochemistry of the epoxidation of *cis*-propylene-1,2-d₂ to propylene oxide over three unsupported and one supported silver catalysts as well as over Ag₂O and AgO was studied by microwave spectroscopy. Variations of the stereochemistry with N₂O as the oxidant and with catalysts heavily moderated by C₂H₄Cl₂ were also explored. In the absence of Cl moderators, the equilibration in the product ranged between 66 and 99% and was similar to a previous study with ethylene. Unlike ethylene, the use of Cl moderators had a large effect and equilibration varied between 37 and 65%. Substitution of methyl hydrogen atoms with deuterium, where *trans*-propylene-1,2,3,3,3-d₅ was used, did not change the equilibration kinetics even though the selectivity was increased. Three theses are developed from the results. (1) The predominant epoxidation mechanisms for ethylene and propylene are similar for unmoderated catalysts. (2) The randomization kinetics upon epoxidation are uncoupled from the parallel production of CO₂. (3) Chloride moderation alters the randomization kinetics for propylene perhaps by stabilizing a secondary radical or otherwise increasing the rotational barrier about the C-C bond of an adsorbed intermediate.

INTRODUCTION

There have been three recent studies (1-3) of the oxidation of ethylene-1,2-d₂ (ET) to ethylene oxide (ETO) over a variety of silver catalysts. For an unmoderated Ag catalyst and typical conditions, the stereo equilibration in the ETO was 90-93%. It was unaffected by temperature changes over a range of 140°C. However, the equilibration could be varied between 84 and 97% depending on the catalyst pretreatment and reaction composition. It has also been shown that when ETO is produced over Ag₂O and AgO, in the absence of O₂(g), equilibrations of 85 and 60%, respectively, were obtained (3).

These results are amenable to interpretation by a variety of mechanistic models without auxiliary data from other studies

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(3). One aspect worthy of further investigation is to determine whether the results are unique to the epoxidation of ethylene or characteristic of other alkene epoxidations, as well. This motivated us to extend the experiments to the oxidation of stereolabeled *cis*-propylene-1,2-d₂ and *trans*-propylene-1,2,3,3,3-d₅.

The oxidation of propylene (PR) to propylene oxide (PRO) normally occurs with low selectivity over Ag (~2-4%) in contrast to ET. The large difference in the relative reaction kinetics provides the two systems with some substantive and interesting contrasts. At the same time, the low PRO yield makes a study of the stereochemistry more difficult. Since analysis by microwave (MW) spectroscopy requires about 1-10 μmol and since it can resolve transitions from different deuterated isomers of PRO, this technique was employed to determine the stereochemistry of the product epoxides.

EXPERIMENTAL

The work carried out was very similar to the recent study of ethylene (3). The same catalyst, reactor, and techniques were employed. A brief repetition of some of the experimental procedures is appropriate although the previous reference should be consulted for more of the details.

Reagents. Three nominally unmoderated silver powders (Ag-sponge, Ag(1), and Ag(2)) and one supported catalyst (5% Ag/SiO₂) were used. Their preparation, surface areas, and variable activities to ethylene oxidation were previously reported (3). Parallel reactivity differences were found for the oxidation of PR in most cases. For example, Ag(2) had significantly lower selectivities for both epoxides compared to Ag-sponge and Ag(1). The preparation and characterization of the Ag₂O and AgO used in this work was also described in the earlier study (3).

Matheson CP-grade C₃H₆ and N₂O, extra dry O₂, and prepurified N₂ were employed. *Cis*-propylene-1,2-d₂ and *trans*-propylene-1,2,3,3,3-d₅ were obtained from Merck, Sharp and Dohme Co. with stated deuterium enrichments of 98 and 98.9 at%, respectively. The isomeric purity of the *cis*-PR-d₂ was checked by MW spectroscopy. Transitions could not be observed for *trans*-PR-d₂ (4). When the *cis*-PR-d₂ was stereospecifically oxidized with *m*-chloroperbenzoic acid (5), the transitions of *trans*-PRO-d₂, which are more intense than for PR-d₂, were also absent (6). This set the limit for the presence of *trans*-PR-d₂ in the starting material below 0.1%. The same procedure was employed for the *trans*-PR-d₅ sample using transitions predicted for *cis*-PR-d₅ from its structure (7) and the known transitions for *trans*-PR-d₅ and the

cis and *trans* forms of PRO-d₅ (6). The amount of *cis*-PR-d₅ in the starting material was set below 0.4%.

Apparatus and procedure. A single pass flow reactor was employed. After pretreatment of the catalyst with H₂, reaction runs were conducted for 0.5–7.0 hr with PR before introduction of the deuterated species. Reaction runs were usually limited to the temperature range of 200–230°C. Below 200°C the activity was too low for easy recovery of PRO while above 230°C the selectivity to PRO decreased markedly.

The amount of deuterated propylene used in a typical experiment was 1 mmol. It was held in a trap at –95°C until it was swept over the catalyst by the O₂/N₂ mixtures. Reaction conditions are more extensively described in Table 1.

The products were sampled by gc analysis or collected for spectroscopic analysis as described previously (3). Conversion and selectivity data were monitored by gc to ascertain that changes in the catalytic activity occurred systematically. Only the selectivity data (ratio of CO₂ and PRO) are listed in Table 1 for the deuterated species since the results for conversions on the small amount of material are too unreliable.

The determination of the ratio, *cis*-PRO-d₂/*trans*-PRO-d₂ or *cis*-PRO-d₅/*trans*-PRO-d₅ required the measurement of the intensity of the same microwave transition for the two isomers. The intensity ratio (*I*_{*cis*}/*I*_{*trans*}) was converted to a molar ratio (and subsequently to %-*cis* or %-equilibration) with a conversion factor (called *R*) based on the transition line strengths as discussed previously (1). The reported structure of PRO (8) was used to predict the spectra of the four deuterated species needed in this work.

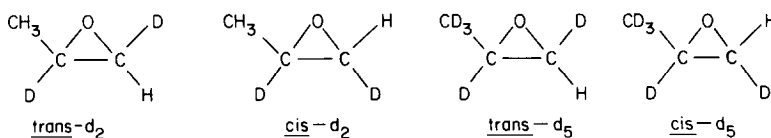


TABLE 1
 Stereochemistry of the Epoxidation of Propylene^a

Run	Catalyst	Reactants	Reaction variables		Oxidation of C ₃ H ₆		Oxidation of <i>cis</i> -CH ₃ CD=CHD	
			Temp. (°C)	Time ^b (hr)	X _{PR} ^c (%)	S _{PRO} ^d (%)	S _{PRO} (%)	% <i>cis</i> -PRO ^e
1	Ag-sponge	Standard ^f	200	0.6	31	2.7		56.1
2			200	1.7	32	2.6	2.6	56.3
3			200	3.0	26	2.6	2.4	56.0
4			200	3.3	32	2.6	2.8	55.4
5			200	6.0	38	2.8	2.5	55.0
6			215	2.2	48	2.9	3.0	57.3
7			230	0.6	72	2.7	3.3	55.7
8			230	1.7	77	3.1	4.0	56.7
9			230	7.0	75	2.1	3.1	55.1
10 ^g			230	2.0	83	2.9	3.0	56.4
11			280	1.8	100	1.2	1.3	57.4
12	Ag-sponge	<i>c</i> -C ₃ H ₄ D ₂ = 1.5% <i>t</i> -CD ₃ CDCHD = 0.5%	230	2.1	77	3.1	4.4	57.0
13		<i>c</i> -C ₃ H ₄ D ₂ = 1% <i>t</i> -CD ₃ CDCHD = 1%	230	2.0	78	2.3	6.0	57.6 57.4(trans) ^h
14		<i>t</i> -CD ₃ CDCHD = 2%	230	2.6	74	2.2	13.2	58.1(trans) ^h 58.3(trans) ^h
15	Ag-sponge	C ₂ H ₄ Cl ₂ 2 × 10 ⁻⁴ %	230	2.2	16	4.4	5.4	67.3
16		2 × 10 ⁻³ %	230	2.2	8	4.4	5.1	73.8
17		2 × 10 ⁻⁴ %	280	4.0	10	12.5	12.3	82.5
18	Ag-sponge	N ₂ O 10%, N ₂ 88%	280	1.8	29	0.3	0.6	50.7
19		N ₂ O 5%, N ₂ 93%	280	2.2	13	0.7	0.9	50.6
20	Ag(1)	Standard	230	3.3	40	2.9	2.9	55.4
21	Ag(2)	Standard	230	2.0	71	0.9	0.6	54.2
22	5% Ag/SiO ₂ (1 g)	Standard	230	0.6	9	1.6	2.3	59.1
23			280	9.3	76	3.4	2.8	61.9
24	AgO (2 g)	N ₂ = 98%	105	0.2	8	2.5	2.3	67.1
25			105	0.2	15	3.2	2.8	66.8
26	Ag ₂ O (1 g)	N ₂ = 98%	150	0.1				59.7

^a C₃H₆ = 2%, O₂ = 10%, N₂ = 88%, F = 60 cm³ min⁻¹, W (catalyst) = 2.5 g.

^b Duration of C₃H₆ flow preceding introduction of C₃H₄D₂.

^c X_{PR} = conversion of PR = 100 (N_{PRO} + 0.33 N_{CO₂})/N_{PR (initial)}.

^d S_{PRO} = selectivity to PRO = 100 N_{PRO}/(N_{PRO} + 0.33 N_{CO₂}).

^e Percentage *cis* + percentage *trans* = 100.

^f Standard proportions given in the table heading. Propylene held at 2% including deuterated oxidations.

^g The heated postvolume after catalyst bed was increased to 10 cm³ for this run.

^h Value for percentage of *trans*-PRO-d₅.

Their assignment was straightforward and more details of their spectra will be reported elsewhere (6).

In the initial stages of the investigation, I_{cis}/I_{trans} was determined for 13 pairs of transitions from the PRO obtained from run 8 in Table 1. These transitions were not perceptibly overlapped by nearby transi-

tions and had negligible internal rotation splittings as determined by calculation or experiment. This led to values for %-*cis*-PRO-d₂ between 56.1 and 57.7%. The average value was 56.9 ± 0.6% (1σ). In subsequent runs, only three transition pairs were used to measure I_{cis}/I_{trans} . The transitions (in MHz) were the 12(2,10)–12(1,11), (*cis*

28219.83, *trans* 27297.23); 13(2,11)–13(1,12), (*cis* 30463.89, *trans* 29869.81); and 15(2,13)–15(1,14), (*cis* 36906.07, *trans* 36991.77). The value of R for these transitions was 1.317, 1.300, and 1.272, respectively. The average of these 3 molar ratios was used to obtain the %*cis*-PRO-d₂ listed in Table 1.

The *cis/trans* ratios of PRO-d₅ were initially checked for seven transition pairs. This resulted in a precision very similar to the PRO-d₂ measurements. The %*trans*-PRO-d₅ for runs 16–18 in Table 1 were obtained by averaging the measurements from three transitions, 13(1,12)–13(0,13), (*cis* 35878.19, *trans* 35819.34); 15(2,13)–15(1,14), (*cis* 29189.13, *trans* 29497.67), and 16(2,14)–16(1,15), (*cis* 32118.14, *trans* 32150.35). R for these transitions were 1.274, 1.287, and 1.275, respectively.

The consistency in the *cis/trans* ratios for a number of transitions indicates that the precision in %*cis*-PRO is about $\pm 1\%$. Hence, relative changes in the %*cis*-PRO-d₂ (or %*trans*-PRO-d₅) in Table 1 of greater than 1% are considered meaningful. The accuracy of these values is estimated to be $\pm 2\%$. This is estimated by considering the experimental precision as well as sources of error in R which could systematically raise or lower all values. Such errors could arise from the ratio of dipole moments and/or vibrational partition functions which enter into R . The error from the dipole moments should be small. The values for $\mu_{\text{D}}(\text{cis})/\mu_{\text{D}}(\text{trans})$ measured for the PRO-d₂ and PRO-d₅ which enter R were both 1.10 ± 0.01 . The ratio of the vibrational partition functions for the two isomeric species of PRO-d₂ (or PRO-d₅) was assumed equal to 1.00 ± 0.02 . This is similar to the estimate used for ethylene oxide-d₂ where more extensive vibrational data are available (1).

RESULTS

The activities/selectivities of Ag, Ag₂O, and AgO for oxidation of propylene to CO₂ and PRO were determined. The results (Table 1) were generally consistent with

expectations based on the previous studies of propylene and ethylene using similar or identical catalysts (2, 3). Because of this regularity and also due to many similarities to ethylene in the stereochemistry results (*vide infra*), the effects of the reaction variables were not as extensively examined as in the earlier studies. The more limited amounts of stereolabeled propylene also required selectivity in the experiments. In presenting the experimental results which follow, it will be convenient to often note significant similarities and differences to ethylene (1–3).

Temperature, Oxidation Time, Postvolume

The effect on the stereochemistry with variations in temperature or the pretreatment time with C₃H₆ was studied using a standard catalyst. The silver sponge was employed since its total activity ($\sim 7 \mu\text{mol min}^{-1} \text{g}^{-1}$ at 200°C) and selectivity to PRO (generally 2.5–3.0%) provided a reasonable yield of material for spectral analysis. Runs 1–13 in Table 1 summarize the effects of these changes for normal PR and *cis*-PR-d₂.

At a fixed temperature, there was a small change of about 1% in the percentage of *cis*-PRO over a propylene pretreatment period of 6–7 hr. This was best identified for runs 1 vs 5 and 2 vs 4 where two deuterium samplings were taken at different times during a reaction cycle. The small change was marginally detectable and certainly small enough to conclude that the extent of stereo equilibration over this catalyst was not very sensitive to the length of pretreatment period. For these runs, the extent of equilibration was high (~ 80 – 90%) although complete randomization was not obtained. (An equilibrium mixture of the *cis* and *trans* isomers is presumably equimolar, an approximation unlikely to be in error by more than 1–2%.)

The effect of temperature changes was apparently negligible on the stereochemistry and selectivity although total conversion was markedly affected. Runs 1–

10 between 200 and 230°C (group 1) were carried out over 3 months and showed little change in the stereochemistry over the temperature range. Runs 11–13 between 230 and 280°C (group 2) were carried out 6 months later and again no variation in the stereochemistry was evident between these three runs. However, the amount of *cis*-PRO-d₂ was about 1% higher for group 2 compared to group 1. This difference probably arose from some changes in the experiment during the 6-month interval. For example, the residual chloride content in the catalyst may have changed due to runs 15 and 16 which were carried out in the interim.

Run 10 explored whether the formation of PRO by a surface-initiated homogeneous reaction might occur in a postcatalytic reaction zone. This was found to take place in some high temperature oxidations involving propylene over bismuth molybdate at 400°C (9). However, no significant changes were observed in the conversion, selectivity, or stereochemistry when the postcatalytic volume was increased from 1.0 to 10.0 cm³.

The most significant observation associated with runs 1–13 is the close similarity in the extent of stereo equilibration (85–90%) with that observed for ethylene under similar conditions (~91%). Also, no significant temperature dependence on the stereochemistry kinetics was observed for either alkene.

Methyl Deuteration

Runs 12–14 studied the effect on the stereochemistry from deuteration in the methyl group. This was of interest since it had been demonstrated that a pronounced kinetic isotope effect occurs for CD₃-PR which increases the selectivity to 10–14%. In run 14, the oxidation of PR-d₀ was followed by PR-d₅ so that the selectivity of the catalyst towards normal PR and *trans*-CD₃CD=CDH would be determined separately. The difference in selectivity for the two species was indeed substantial. Runs

12 and 13 used mixtures of the *cis*-PR-d₂ and *trans*-PR-d₅ so that the stereochemistry for species with CH₃ and CD₃ groups could be compared for the same reaction conditions. It was clear that the preference for retention of the original propylene stereochemistry in the product epoxide was virtually identical for CH₃-PR and CD₃-PR.

Chloride Moderation

Runs 15–17 were conducted to evaluate the effect that small amounts of organic chloride had in the reaction stereochemistry. A marked decrease in catalyst activity and an increase in the selectivity to PRO were observed. The large selectivity increase for run 17 was similar to a previous study of propylene using butyl chloride as the moderator (10). Runs 15–17 had the largest retention of configuration in the PRO-d₂; as little as 35% equilibration occurred in run 17.

In the case of ethylene, qualitatively similar changes in activity, selectivity, and stereochemistry were observed although the percentage of change was somewhat less, most notably in the stereochemistry. For example, the %*cis*-ETO for an unmoderated vs heavily moderated catalyst went from 53.2 to 58%. A check was made to ascertain that this contrast was not a result of different conditions for the earlier ET and present PR experiments. In run 17, the following alkenes were passed seriatim: PR-d₀, *cis*-PR-d₂, and *cis*-ET-d₂ along with C₂H₄Cl₂ in the feed. The selectivity to ETO was 72% and the %*cis*-ETO-d₂ was 58.9% which compare closely to the earlier results for ET (3) while the %*cis*-PRO-d₂ was 82.5%.

Oxidation by N₂O

Runs 18–19 illustrated the effect of N₂O(g) as the oxidant over the Ag-sponge. A large decrease in the conversion and selectivity was observed very similar to ethylene (3). A much higher randomization was also found, similar to ethylene where the equilibration was 96–97%. Only a *cis*-

PR-d₂ species could be studied and so it was not possible to determine if the observed values of 50.6% *cis*-PR-d₂ are the equilibrium value or still slightly away from equilibrium. Nevertheless, there was little reason to doubt that the extent of equilibration was virtually complete (99–100%).

Catalyst Variation

In the case of ethylene, it was found that the variability in randomization at a given temperature was no larger than 1.5% when a variety of silver catalysts with different properties were employed. This was obtained provided that their pretreatments were similar. The results for runs 20–23 for propylene indicated an almost similar behavior. The randomization for the Ag(1) and Ag(2) catalysts were virtually identical to those over the Ag-sponge. Two runs over the supported catalyst Ag/SiO₂ had a small but clear increase (3–6%) in the amount of *cis*-PRO-d₂. The runs with *cis*-ET-d₂ over this catalyst also occurred with slightly higher retention although the effect was less pronounced (0.5–1.5% increase in the *cis*-ETO-d₂) (3).

It was interesting to compare the conversion and selectivity changes for PR and ET over the four silver catalysts. The selectivity to ETO was Ag-sponge ≈ Ag(1) > Ag(2) ≈ Ag/SiO₂ (3). The same order was found for PRO except that the Ag/SiO₂ catalyst appeared to have a selectivity ≥ Ag-sponge. (The data to establish this are more extensive than found in Table 1.) For ET the total activity was Ag(1) < Ag(2) < Ag-sponge ≪ Ag/SiO₂. The same order occurred for PR except that the activity of Ag-sponge appeared to be somewhat closer to Ag(2).

Reduction of Silver Oxides with PR

It has been shown that silver oxides oxidize ET to ETO in the absence of O₂(g) and that less randomization occurred compared to the standard reaction over Ag (3). The results of propylene (runs 24–26) were similar.

The reactivities of AgO and Ag₂O to PR were not documented extensively because of experimental problems. Like for ET, the oxidation of PR occurred with low conversions and selectivities at temperatures near 150°C. The %*cis*-PRO-d₂ from Ag₂O was 3–5% higher and from AgO it was 10–12% higher compared to a typical run over the Ag-sponge. In the case of ET, the same relative comparison gave values ~3 and ~15% higher.

It was not possible to compare at similar temperatures the equilibrations over the silver oxides with those from silver powders. However, we suspect that the lower temperatures are not a significant factor behind the observation of less equilibration in the case of the silver oxides. This is inferred by analogy with ethylene where the differences in the extensive equilibration over silver oxides and silver powders still remained when the reactions were carried out at temperatures of 140–150°C.

Stereo Control Experiments

It was necessary to evaluate the extent of stereo randomization that might occur in unreacted PR and in PRO subsequent to formation. MW measurements on the unreacted PR found negligible *cis*–*trans* isomerization (<0.3%) for ordinary runs over the Ag-sponge (including the Cl moderated Ag-sponge runs). An exception occurred for N₂O as the oxidant where the recovered propylene contained 0.8% *trans*-PR-d₂.

Little or no isomerization occurred in *cis*-PRO-d₂ passed over the catalyst in the presence of C₃H₆/O₂/N₂. This was ascertained by MW spectroscopy. The result placed a limit for such a process below 3%. The stereolabeled PRO used in the repassage experiment was prepared by a stereospecific peroxy acid oxidation (5).

DISCUSSION

The principal stereochemical observations for PR and ET are summarized in Table 2. These data and related results

TABLE 2

Comparison of the Stereochemistry for Ethylene and Propylene Epoxidation over Silver Catalysts

Reaction	Equilibration	
	Ethylene	Propylene
Reduction of AgO by alkene	~60%	~66%
Oxidation over Ag modified with C ₂ H ₄ Cl ₂	~84%	~37–65%
Reduction of Ag ₂ O by alkene	85–87	~81
Oxidation over reduced Ag/SiO ₂	90–91	76–82
Oxidation over reduced Ag powder	91–93	85–90
Oxidation by N ₂ O over reduced Ag powder	96–97	98.6

suggest three plausible hypotheses which will be developed in this section. (1) The predominant mechanisms for the epoxidation of ET and PR are similar except in the case of heavily chloride moderated silver catalysts. (2) This similarity extends to the corollary that the randomization kinetics upon epoxidation are uncoupled from the parallel production of CO₂. (3) Chloride moderation, which has a marked effect on the stereochemistry and selectivity for PR, changes the epoxidation pathway for PR through an interaction which is less important or absent for ET.

Similar Mechanisms

The supposition of similar mechanisms for the epoxidation process is supported by the close similarity in the extent of stereo equilibration for ETO and PRO over the reduced Ag powders. This is remarkable since the catalysts' selectivities to the epoxides are so different. Nevertheless, it could be fortuitous so that other similarities between the two reactions are noteworthy. The similar stereochemistry also extends to the parallel changes observed in the equilibration for most other reaction conditions (Table 2). The absence of any temperature

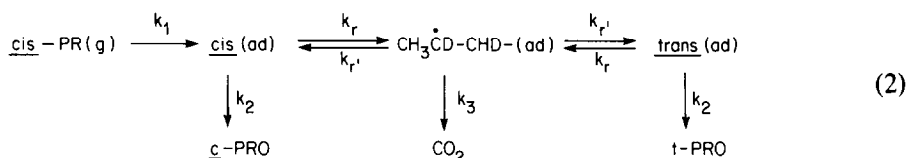
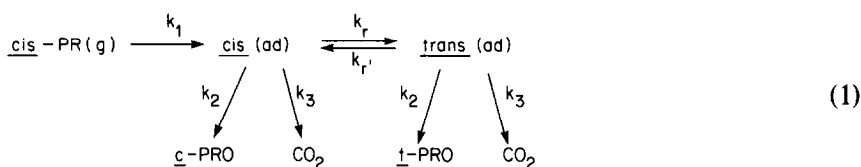
dependence on the stereochemistry is notable. The absence of connection between the randomization kinetics and the parallel production of CO₂ (*vide infra*) also applies to both ET and PR. The confluence of these data suggests epoxidation processes which are basically similar.

Randomization/CO₂ Kinetics

It was argued in the previous ET study (3) that the randomization kinetics are uncoupled from the parallel production of CO₂. This is also apparent for PR from the invariance in the stereochemistry for CD₃-PR and CH₃-PR. This is significant because the selectivity changes markedly for the two alkenes due to a kinetic isotope effect related to the production of CO₂ (2). This uncoupling is also consistent with the similar PRO equilibrations observed for reduced Ag powders having different activities and selectivities. It is suggested by the invariance in stereochemistry with temperature changes which affect the CO₂ kinetics, i.e., the activity. The similar stereochemistry for ETO and PRO in spite of large differences in a catalyst's selectivity to the two epoxides is also noteworthy.

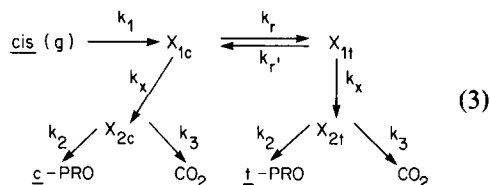
The relationship between the CO₂ and PRO kinetics and the randomization kinetics can be more clearly understood by examining some mechanisms. A plausible mechanism must uncouple the reaction kinetics from the randomization kinetics as just described. It must also account for the increased selectivity to PRO with CD₃-PR although the rate of CO₂ formation is apparently unchanged. As discussed elsewhere (2), a common intermediate for both CO₂ and PRO production can rationalize this apparent inverse isotope effect toward CD₃PRO production. This intermediate precursor must therefore be suitably isolated from the randomization kinetics. These constraints apparently rule out mechanisms involving a single intermediate precursor common to both randomization and reaction kinetics. Two schemes in this

category are:

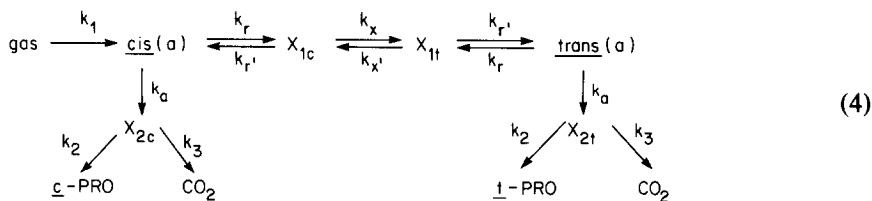


With a steady-state approximation, these models lead to $cis\text{-PRO}/trans\text{-PRO} \approx (1 + k_3/k_r)$. Since $k_{3H}/k_{3D} \approx 4$ is estimated from the apparent inverse isotope effect (2), $\text{CD}_3\text{-PR}$ should lead to greater randomization which is not consistent with the data. The above relationship for $c\text{-PRO}/t\text{-PRO}$ results from Scheme (1) if $k_2 \ll k_3$, $k_r \approx k_{r'}$ and $k_r \approx k_{r'}$, which is reasonable for propylene. The same inequalities are assumed in deriving $c\text{-PRO}/t\text{-PRO}$ for Scheme (2) except that it is no longer suitable to presume that $k_r \approx k_{r'}$.

It is apparent that an extension of these models to include two intermediates is necessary to accommodate the mechanistic constraints. One scheme could be:



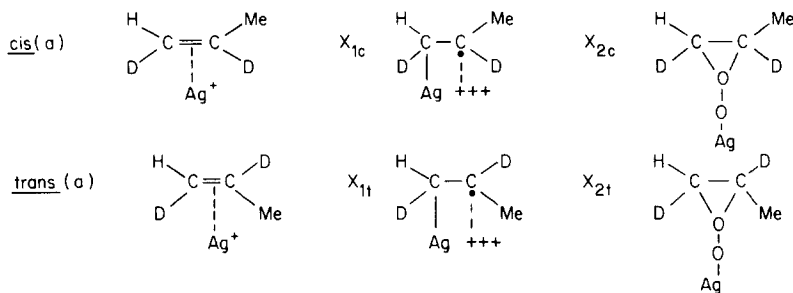
By applying a steady-state approximation and assuming $k_2 \ll k_3$ and $k_r \approx k_{r'}$, the expression is obtained, $c\text{-PRO}/t\text{-PRO} = (1 + k_x/k_r)$. This also requires that k_x , k_r , and $k_{r'}$ be the same for the cis and $trans$ species. Since $c\text{-PRO}/t\text{-PRO}$ are nearly equal for $\text{CD}_3\text{-PR}$ and $\text{CH}_3\text{-PR}$ then $k_x^D/k_r^D \approx k_x^H/k_r^H$. This is plausible since only secondary isotope effects are likely to affect k_x and k_r and they are expected to be small. Another model along similar lines would be



It is speculative to propose structures for X_{1c} , X_{1t} etc. based on the kinetic scheme alone and a more complete discussion of

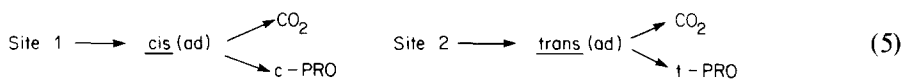
their possible structures can be found in a preceding study (3). Nevertheless, it may be salutary to illustrate some plausible in-

intermediates in order to help comprehend the implications of reaction, Scheme (3) and (4).



It is also possible to explain the CD₃ data and partial equilibration by "two site" reaction processes where the extent of randomization would depend on the number of

each site. One very simple mechanism includes two competitive, unconnected reactions which occur with retention and inversion, respectively.



A more attractive possibility would be two competitive reactions occurring with retention and randomization, respectively. A combination of the left hand side of Scheme (5) and Schemes (3) or (4) or even (1) or (2), if $k_r \gg k_3$ could represent the two independent processes.

Effect of Chloride

It was previously argued that the small effect on the stereochemistry of ET due to chloride moderation was consistent with a model which correlated the extent of equilibration with the surface oxidation state of the catalyst (3). However, such a model which posits a small, indirect effect on the stereochemistry does not seem compatible with the much larger change in the stereochemistry for PR under similar conditions (Table 2). This contrast is perplexing since so many other similarities between ET and PR are observed. Since the position has been put forward that these similarities are reflected in the microscopic mechanistic processes, then the most obvious alterna-

tive is to assume that chloride moderation affects the randomization mechanism by a combination of effects. Part of the change in randomization is associated with the higher surface oxidation state of the catalyst similar to the rationalization used for ET (3). Another contribution could arise from the greater stabilization of the secondary radical ($\text{CH}_3\dot{\text{C}}\text{D}-\text{CHD}-$) necessarily absent in ET. There could also be some contribution from a more direct interaction with adjacent surface sites, perhaps even a steric interaction, which could have a greater effect on the randomization kinetics of PR than ET.

To illustrate these rationalizations more concretely, consider Scheme (4). The isomerization between *cis(ad)* and *trans(ad)* would occur via a radical intermediate with double bond opening ($\text{CH}_3\dot{\text{C}}\text{D}-\text{CHD}-\text{Ag}$ and/or $\dot{\text{C}}\text{HD}-\text{CD}(\text{CH}_3)-\text{Ag}$). On the chlorinated (or oxidized) surface, the radical center of the intermediate should interact more readily with a positive site on the surface (3). Presumably, this would lead to

more stabilization of the secondary radical (see above, species X_{1c} and X_{1t}). Both k_x and k_x' would decrease leading to less randomization and an increase in *cis*-PRO/*trans*-PRO. Another possibility is that on the chlorinated surface the hindrance to rotation about the C–C bond is greater for PR than ET due to a more direct interaction, possibly steric-like, with adjacent Cl^- or R–C–Cl fragments. A partial contribution from some such direct interactions seems necessary to account for the contrast in the randomization kinetics of PR and ET over Cl moderated Ag catalysts compared to Ag_2O and AgO.

SUMMARY

The study of the stereochemistry of PR upon epoxidation has revealed many interesting similarities to ethylene. The phenomena of partial randomization is not unique to ET but may be more a general characteristic of the epoxidation process over Ag catalysts. In fact, it is attractive to assume that the intermediates and pathways for ET and PR epoxidation are basically similar. This similarity also includes the inference that the randomization kinetics must be uncoupled from the CO_2 kinetics. In conjunction with the inverse kinetic isotope effect for the production of CD_3PRO , additional constraints can be placed on the reaction process. Nevertheless, reactivity differences between ET and PR over Ag are well known and they also appear in the stereochemistry using heavily Cl moderated catalysts.

The data do not clearly distinguish between the plausibility of certain reaction intermediates and more specific kinetic processes such as the single site or two site mechanisms which were extensively discussed in a previous report (3). However, a single or a two site process must be carefully qualified if it is to agree with all the data, especially the temperature independence of the stereochemistry.

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.

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