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Chirality Retention in Aqueous Propylene Oxide Hydration: Chirality of the Transition State

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Abstract: The hydration kinetics of enantiomerically pure propylene oxide (PO, CH₃*CHCH₂O) to chiral propylene glycol (PG, CH₃*CH(OH)CH₂OH) in aqueous solution have been studied using FTIR while simultaneously monitoring the net chirality of the reaction mixture. The hydration reaction appears to be first-order in the PO concentration with a rate constant of $k \cong 0.05$ hr⁻¹. More importantly, the reaction is enantioselective; the product PG retains the chirality of the 2C carbon in PO with $\sim 2:1$ selectivity. The fact that there is some inversion of the chirality suggests that the dominant transition state is one in which the 2C–O bond in PO is cleaved, resulting in a close to planar transition state capable of inversion during hydration. If the transition state involved 1C–O cleavage it would retain the rigid chiral center of the PO reactant, preventing significant inversion.

Keywords: chirality · propylene oxide · propylene glycol · hydration · transition state

1. Introduction

Propylene oxide (PO, CH₃CHCH₂O, Figure 1A) is currently a high-demand chemical with a global demand that is increasing by 4–5% annually. This global demand is primarily due to the use of PO for production of polyether polyols and propylene glycol (PG, CH₃CH(OH)CH₂OH, Figure 1B). Polyether polyols are used in applications such as coatings, adhesives, sealants, elastomers and thermoplastic resins. PG is used for manufacturing unsaturated polyester resins. These resins have a wide range of commercial applications in the manufacturing of pipes, ducts, fixtures, tanks and panels.^[1]

Recently, the presence of PO has been discovered in the interstellar medium.^[2] This observation has prompted scientists to investigate the chemistry of PO formation under low temperature conditions.^[3] In addition, the chirality of PO makes it an interesting molecule for study of its stereo-chemistry. Its rigid structure makes it an ideal candidate for study by vibrational spectroscopy.^[4–7] Solvation of PO has been studied using vibrational circular dichroism (VCD) and optical rotatory dispersion (ORD) to understand hydrogen bonding with chiral molecules.^[8]



Figure 1. A) PO and B) PG with the chiral 2C carbon atoms indicated by the red circles.

In this work, we have studied PO hydration to PG in pure water. It is well known that with chiral catalysts, this reaction can be catalyzed with very high enantioselectivity.^[9–11] Hydration occurs by opening of the epoxide ring and is known to happen slowly without the need for a catalyst. The epoxide ring opening can occur at either of the C–O bonds and depending on the acidic or basic conditions, primary or secondary alcohols are formed.^[12] Herein, we focus on the degree to which the chirality of the PO is preserved in the product PG without the need for a chiral catalyst. The results lead to insights regarding the nature and chirality of the transition state for PO hydration.

2. Experimental

Two sets of FTIR experiments were conducted in this work. The first set were calibrations, focused on FTIR measurements of aqueous solutions containing R-PO, S-PO, R-PG and S-PG at concentrations in the range 0.1 to 1.0 M. The second set were kinetics experiments focused on the temporal evolution of the FTIR spectra of R-PO, S-PO and RS-PO at 1 M initial concentration and measured versus time for up to 30 hrs. The temperature used for this set of experiments was 60 °C and the

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FTIR spectra were obtained every 2 hrs for a duration of 30 hrs. The following procedure was used. First, a water bath was heated to 60 °C. Then aqueous solutions of R-, S- or RS-PO at initial concentrations of 1 M were prepared in scintillation vials. The vials containing PO were placed in the hot water bath for 2 hrs. The vials were then removed from the hot water bath, and placed into an ice bath for rapid cooling before analyzed using FTIR. PO is volatile so it is important to reduce any evaporation. The vials were also placed in the refrigerator at 4 °C overnight as needed to prevent further reaction over night. The vials were then returned to the hot water bath and the process was repeated until the total time at 60 °C reached 30 hrs.

The FTIR spectra were obtained by placing 25 μ l of R-, S-, or RS-PO solution on the surface of a diamond attenuated total reflectance FTIR cell. All FTIR spectra were measured using a Nicolet Nexus 670 spectrometer with a deuterated triglyceride sulfate (DTGS) detector. Vibrational spectra were obtained using 4 cm⁻¹ resolution and 32 scans were obtained for statistical averaging. FTIR measurements were conducted in the region of 950–1500 cm⁻¹. After each measurement, the diamond surface of the FTIR spectrometer was wiped with isopropanol and then cleaned with DI water to prevent any contamination.

Similar to the FTIR experiments, two sets of optical rotation measurements were conducted. The first set of calibration experiments measured the optical rotation of R-, S-, RS-PO and R-, S-, RS-PG at concentrations in the range 0.1 to 1 M. A second set of calibration experiments measured the optical rotation by solutions containing 0.1 to 1 M R-, S-, or RS-PO plus 0.5 M RS-PG and a set of solutions containing 0.1 to 1 M R-, S-, or RS-PO plus 0.5 M RS-PG plus 0.5 M RS-PO. These measurements were performed in order to detect any interactions between PO and PG in solution that might influence their optical rotation. Finally, the temporal evolution of the optical rotation was measured for a total time of 30 hrs for solutions initially containing 1 M R-, S-, or RS-PO and heated at 60 °C.

A Rudolph Research Analytical Autopol VI (Hackettstown, NJ, USA) was used for all optical rotation measurements. This polarimeter can measure optical rotation of samples at controlled temperatures and at six different wavelengths. In a typical optical rotation measurement, 3 mL of sample solution was put into a Temptrol polarimeter sample cell and placed in the polarimeter. All optical rotation measurements in this work were carried out using 436 nm wavelength light and at a temperature of 23 °C.

The R- and S-PO (>98%), and racemic RS-PO (>98%) used in these experiments were purchased from Alfa-Aesar Corp. Propylene glycol (96%) was bought from Sigma Aldrich. All chemicals were used without further purification. All solutions in these experiments were prepared in DI water. Added precaution was taken to make solutions of racemic RS-PO with no observable optical activity. The RS-PO was first analyzed with the polarimeter to ensure that its optical rotation was undetectable.

3. Results

3.1 FTIR of PO and PG

The 2C atoms in PO and PG are chiral (Figure 1) and one of the primary objectives of this work has been to determine the extent to which the 2C chirality of PO is preserved during its hydration to PG. The role of FTIR in this work has been to quantify the time-dependence of the compositions of an aqueous solutions of 1 M PO (R-, S-, and RS) as they spontaneously convert to PG at 60 °C. Given the compositions of the solutions at all times, polarimetry can then be used to quantify the enantiomeric excess in the product PG. Due to the epoxide ring structure with one pendant methyl group, the vibrational modes of PO are quite distinct from those of PG. Figure 2 shows the FTIR spectrum of 1 M S-PO (blue), the evolution of its spectrum while held at 60 °C for 30 hrs (black), and finally the FTIR spectrum of 1 M S-PG (red). Similar experiments conducted with R-PO and RS-PO (see section SI1), reveal the same evolution of their FTIR spectra from that of pure PO into that of PG, as observed in Figure 2.

The FTIR absorbance intensities for PO and PG related peaks in Figure 2 can be used to quantify the compositions of aqueous solutions containing mixtures of PO and PG. As shown in Figure 2, the strongest peaks observed for pure PO are at 1026 cm^{-1} , 1102 cm^{-1} , 1269 cm^{-1} , and 1408 cm^{-1} . Assignments of the various modes for PO and PG are given in Table 1.

The peaks at 1026 cm⁻¹ and 1408 cm⁻¹ are due to CH₃ wagging and CH₃ deformation modes in PO.^[3,5,13,14] The peaks at 1102 cm⁻¹ and 1269 cm⁻¹ correspond to ring-CH₃ stretching and ring deformation.^[13] Solvation of PO has also been studied using vibrational circular dichroism and optical rotation dispersion spectroscopy.^[8] That study suggests formation at room temperature of PO-(H₂O)_n complexes in which water interacts with PO via a hydrogen bond and lies on either the *syn* or *anti* side of the epoxide ring. That study also suggests that there is no epoxide ring opening at room temperature. FTIR spectra of PO at room temperature have also been investigated in solvents such as CCl₄, liquid xenon and in a

 Table 1. Assignments of the principle FTIR modes observed in

 Figure 2 and the time-dependence of their intensities.

Wavenumber (cm ⁻¹) Propylene oxide (PO)	Assignment	I(t)	Ref.
1026 1102 1269 1408	CH ₃ wagging Ring–CH ₃ stretching Ring deformation CH ₃ deformation	$\downarrow \\ \downarrow \\ \downarrow \\ \downarrow$	3,5,11,12 13 13 3,5,11,12
Propylene glycol (PG)			
990 1042 1080 1137	C–C stretching CO Stretching CO Stretching CH wagging	↑ ↑ ↑	17–19 17–19 17–19 17–19



Figure 2. FTIR spectra from 950–1500 cm⁻¹ of solutions starting with 1 M S-PO (blue) and after being held at 60 °C for 6, 12, 18, 24, and 30 hrs (black). The top spectrum is obtained from 1 M S-PG (red). The FTIR spectra evolve with time revealing the disappearance of peaks at 1026, 1102, 1269, and 1408 cm⁻¹ associated with the S-PO and the appearance with time of peaks at 990, 1042, 1080, and 1137 cm⁻¹ associated with PG. It is clear that after 30 hrs at 60 °C, the S-PO spectrum is virtually identical to that of 1 M S-PG.

solid argon matrix.^[4] The low wavenumber FTIR spectra in these solvents were all similar to the PO spectrum observed in water. Therefore, the initial FTIR spectrum of PO in water confirms that the epoxide ring structure of PO is intact.

The FTIR spectra in Figure 2 reveal clear evolution of the absorption intensities over the course of the 30 hr experiment monitoring PO in water at 60°C. After 6 hrs, we see the appearance of additional peaks at 990 cm⁻¹, 1042 cm⁻¹, 1080 cm⁻¹, and 1137 cm⁻¹. At this point, the peak at 1042 cm⁻¹ is roughly equal in intensity to the 1026 cm⁻¹ mode of PO. With time, the 1042 cm⁻¹ grows in intensity and after 30 hrs is the dominant peak, leaving the 1026 cm^{-1} peak of PO undetectable. The additional new peaks at 990 cm^{-1} , 1080 cm⁻¹, and 1137 cm⁻¹, which are first observable after 6 hrs also continue to grow monotonically over the duration of the experiment. It is clear from Figure 2 that, in aqueous solution, the FTIR spectrum of 1 M S-PO evolves over time to approach the spectrum of 1 M S-PG. The FTIR spectra are independent of molecular chirality and exhibit the same behavior when starting with R-PO or RS-PO (see section SI1).

There is an existing literature on the epoxide ring opening of PO to form $PG^{[12,17]}$ in the presence of water or acidic conditions.

$$CH_3CHCH_2O + H_2O \xrightarrow{<200 C} CH_3CH(OH)CH_2OH$$

In addition, PG formed during this reaction can react to form higher molecular weight poly-PG.

$\begin{array}{l} CH_{3}CHCH_{2}O+ \hspace{0.1cm}HOCH_{2}CH(OH)CH_{3}\rightarrow\\ CH_{3}CH(OH)CH_{2}OCH_{2}CH(OH)CH_{3} \end{array}$

In a commercial setting, the reaction is conducted in excess water (12 to 20 mol H_2O/mol PO) to minimize poly-PG formation.^[18] By this standard, our solutions are dilute (55 mol H_2O/mol PO) so, poly-PG formation can be neglected. The prominent vibrational peaks of S-PG at 990 cm⁻¹, 1042 cm⁻¹, 1080 cm⁻¹, and 1137 cm⁻¹ are associated with C–C stretching, CO stretching, and CH wagging modes.^[19–21] The FTIR spectra of S-PG as shown in Figure 2 (red) is almost identical to that of S-PO after 30 hrs at 60 °C, suggesting that the S-PO is spontaneously hydrated to PG in the presence of water. The net conclusion from the FTIR spectra is that PO is hydrated quantitatively to PG with near 100% selectivity.

3.2 Calibration of FTIR and Polarimetry Signals for PO and PG $% \left({{\mathbf{FT}} \right)$

To quantify the kinetics of PG formation via PO hydration and the extent to which the chirality of PO is preserved in the PG product, we conducted several calibration experiments to determine both the FTIR absorbance and the optical rotation



Figure 3. A) Calibration curves for the intensities versus concentration of the vibrational modes of PG at 1042 cm^{-1} (right axis) and PO at 1408 cm⁻¹ (left axis). B) Calibration curves for optical rotation versus concentration of R- and S-PG (left axis) and R- and S-PO (right axis). Sensitivities (slopes) are indicated numerically on the plot.

versus concentration for the species and enantiomers involved in the reaction. In order to quantify the concentration of PO and PG in solution we collected FTIR spectra from solutions prepared with concentrations of both enantiomers of PO or PG spanning the range 0 to 1.0 M. Figure 3A plots the intensity of the 1408 cm⁻¹ peak of PO versus concentration for both R-PO and S-PO. It also plots the intensity of the 1042 cm⁻¹ peak of PG versus concentration for both R-PG and S-PG. These yield sensitivity factors of $I_{1408}^{PO} = 0.0082$ [M]⁻¹ and $I_{1042}^{PG} = 0.052$ [M]⁻¹. These allows us to estimate the compositions of solutions containing both PO and PG based on their FTIR spectra.

In addition to calibrations of the FTIR spectra, calibrations of polarimetry data are needed to estimate the enantiomeric excess in solutions of PO and PG. Figure 3B plots the optical rotations of R- and S-PO versus concentration spanning the range 0 to 1.0 M. It also plots the optical rotations of solutions of R-PG and S-PG versus concentration spanning the range 0 to 1.0 M. The data for PO yields an intrinsic optical rotation of $\alpha_R^{PO} = -0.084^{\circ}/[M]$ and $\alpha_S^{PO} = 0.084^{\circ}/[M]$. These have been symmetrized $(-\alpha_R^{PO} = \alpha_S^{PO})$ based on the data and have yielded values that are very similar to those that we have determined previously.^[22–25] Finally, the intrinsic optical rotation of PG is found to be $\alpha_S^{PG} = -\alpha_R^{PG} = 3.3^{\circ}/[M]$.

In addition to calibrating the FTIR peak intensities and the optical rotations by using aqueous solutions of pure components, it is important to ascertain that the calibrations are accurate for use with mixtures of PO and PG. In other words, we need to demonstrate that there are no interactions between PO and PG that influence either their IR absorbance or their optical rotation. This has been verified by obtaining FTIR and

optical rotation measurements of the four possible solutions containing 0.5 M each of the enantiomers of PO and PG. The comparison of measured and predicted values of concentration and optical rotation are shown in Table 2. The concentrations determined based on the FTIR calibration are within 10% of 0.5 M and the optical rotations predicted on the basis of calibration are within 2% of the measured values.

3.3 Kinetics of PO Hydration to PG

The kinetics of PO hydration to PG in aqueous solution at $60 \,^{\circ}$ C have been monitored using the FTIR intensities of the peaks at 1408 cm⁻¹ (PO) and 1042 cm⁻¹ (PG) to estimate the concentrations of both species over a 30 hr time interval. These time-dependent concentrations have been measured using R-, S- and RS-PO as reactants. Figure 4 reveals that, as expected, the reaction kinetics for all three reactants are indistinguishable. It is worth noting that while R-PO and S-PO

Table 2. Predicted and measured optical rotations and concentrations of two-component aqueous solutions containing 0.5 M of both PO and PG, as determined using FTIR and Optical Rotation (OR) calibrations.

Solution	[PG] based	[PO] based	Measured	OR based on $\alpha^{\rm PO}$ and $\alpha^{\rm PG}$
components	on I ^{PG} ₁₀₄₂	on <i>I</i> ^{PO} ₁₄₀₈	OR	
R-PO + R-PG $R-PO + S-PG$ $S-PO + R-PG$	0.48	0.51	-2.01	-2.02
	0.45	0.54	1.29	1.24
	0.48	0.52	-1.21	-1.19
S-PO+S-PG	0.44	0.54	2.05	2.07



Figure 4. Time dependence concentrations of A) PO and B) PG during PO hydration to PG at 60 °C. Similar behavior is observed when starting with R-PO, S-PO, and RS-PO. The PO concentration was determined based on the intensity of the FTIR peak at 1408 cm⁻¹. The PG concentration was based on the intensity of the 1042 cm⁻¹ FTIR peak. The solid cyan lines are plots of exponential decay (A) and growth (B) curves with similar time constants of 0.046 and 0.055 hr⁻¹, respectively.

should have the same behavior in an achiral environment; RS-PO could be quite different, if there were strong heterochiral interactions at play. That does not appear to be the case.

The concentrations of PO display a first-order exponential decay (Figure 4A), while the concentrations of PG follow a first-order accumulation curve (Figure 4B). Fitting the data to first-order decay and accumulation curves yields estimates of the first-order rate constants for PO depletion, $k_{PO} = 0.046 \pm 0.002 \text{ hr}^{-1}$, and PG accumulation, $k_{PG} = 0.055 \pm 0.002 \text{ hr}^{-1}$, at 60 °C. These are comparable in magnitude, as they should be for a simple hydration reaction with no byproducts or secondary reaction products.

3.4 Enantioselective PO Hydration to PG

The enantioselectivity of PO hydration to PG in aqueous solution at 60 °C, has been observed by using polarimetry measurements concurrently with the FTIR measurements. Figure 5 shows the evolution of the optical rotations by solutions starting with R-, S-, or RS-PO at 1 M concentrations. The first thing to note is that the solution starting with RS-PO at 1 M remains achiral throughout the course of the reaction, as it should when starting from an achiral state with no chiral bias. Secondly, the behavior of the solutions starting with R- and S-PO yields optical rotations that are equal but opposite throughout the duration of the reaction, as they should given that they start with equal and opposite chirality and no other chiral bias is present. The most important observation is that the magnitude of the optical rotations by the solutions starting with R- and S-PO increase over the course of time, rather than



Figure 5. OR measurements versus time during the hydration of R-, S-, and RS-PO to PG. The fact that the optical rotations starting with R- and S-PO do not decay to zero implies that the reaction preserves the initial chirality of PO, to some extent. Optical rotation measurements were made using $\lambda =$ 436 nm. Initial solution concentrations were all 1 M.

tending towards zero. If the hydration of PO yielded racemic RS-PG, then at 100% PO conversion the solution should

exhibit no optical rotation. Clearly, the final state exhibits optical rotation and the hydration of PO must preserve the chirality of the reactant, to some extent. The degree to which chirality is preserved remains to be determined.

4. Discussion

4.1 Preservation of Chirality in PO Hydration to PG

Having determined the composition versus time of the reaction solution, we can define an extent of reaction or conversion, x, in terms of the concentration or amount of reactant consumed. For the hydration of S-PO, we have

$$[S - PO] = (1 - x) \cdot [S - PO]_0 \tag{1}$$

$$[PG] = x \cdot [S - PO]_0 \tag{2}$$

We can define the fraction, f, of S-PO hydrated into S-PG by

$$[S - PG] = f \cdot [PG] = f \cdot x \cdot [S - PO]_0 \tag{3}$$

$$[R - PG] = (1 - f) \cdot [PG] = (1 - f) \cdot x \cdot [S - PO]_0$$
(4)

The optical rotation by the solution, at any value of the conversion, $\alpha(x)$, can be described in terms of the calibrated values of the intrinsic optical rotations of all three species in the solution.

$$\frac{a(x)}{[S - PO]_0} = \bar{a}_{PO}^S \cdot (1 - x) + \bar{a}_{PG}^S \cdot f \cdot x + \bar{a}_{PG}^R \cdot (1 - f) \cdot x$$
(5)

A similar expression holds for the reaction starting with R-PO. Since the optical rotation, $\alpha(x)$, has been measured over a wide range of conversions, f can be evaluated versus conversion.

The values of f, the selectivity towards chirality preservation, are plotting in Figure 6 versus conversion for S-PO hydration to S-PG (solid black dots) and for R-PO hydration to R-PG (solid red dots). The data for the two enantiomers of PO agree with one another and reveal a selectivity that is roughly constant at f = 0.7 and independent of conversion. This corresponds to an enantiomeric excess of ee = 0.4 without any external chiral bias such as a catalyst.

4.2 Chiral Transition State for PO Hydration to PG

The net retention of chirality during the hydration of PO to PG suggests some constraints on the nature of the reaction transition state. Referring to the structure of PO in Figure 1A, the transition state presumably involves the initial opening of the epoxide ring by cleavage of either the 1C–O or 2C–O bond. Cleavage of the 1C–O bond leaves the initial chirality



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Figure 6. Values of f (the selectivity towards retention of PO chirality, eq. 5) versus conversion, x, for S-PO hydration into S-PG (solid black circles) and for R-PO hydration into R-PG (solid red circles). The degree of chirality retention is ~70% independent of x.

around the 2C carbon unchanged. Subsequent protonation of the 2CO[•] radical and hydroxylation of the 1C[•] carbon yields PG with the chirality of the 2C carbon atom preserved with 100% fidelity. The fact is, however, that we observe chirality preservation only ~70% of the time, and chirality inversion for the remaining 30% of the PO hydrations. If the initial step of the reaction is cleavage of the 1C–O bond, chirality inversion implies inversion of the chiral 2C center, which must have a significant energy barrier and seems unlikely.

The alternate scenario is that the reaction is initiated by the cleavage of the 2C-O bond and results in a planar, prochiral transition state around the 2C° atom. In principle, this would result in complete loss of chirality, if the planar 2C[•] were hydroxylated with equal probability from either side. Instead, the 2:1 bias that we observe might result from a small preference for H₂O binding to one side of the PO ring relative to the other. This is consistent with the results of recently published DFT calculations by Jin et al.^[26] Their calculations focus on the mechanism and the transition state for PO hydration in the gas phase and in solution but do not address issues of transition state chirality or enantioselectivity. Nonetheless, they show that in the solution phase the barrier to reaction via 1C-O scission is 30 kJ/mole higher than that for 2C-O scission. In the gas phase this difference drops to 16 kJ/ mole, still favoring 2C-O scission. The structures of the transition states (taken from^[26]) are shown in Figure 7. These reveal a fairly planar C-CH-C structure in the transition state



Figure 7. The structures of PO and its transition states for hydration to PG via scission of either the 1C-O or the 2C-O bond. The barrier to 2C-O cleavage is 16 kJ/mole lower than the barrier to 1C-O cleavage (30 kJ/mole in the solution phase). Cleavage of the 2C-O bond results in a transition state that is prone to chirality inversion around the 2C atom. (Figure modified with permission from ref. 26.)

for 2C–O scission; one that would be prone to inversion during hydration of PO.

5. Conclusions

The aqueous phase hydration of chiral propylene oxide to propylene glycol occurs with 70% retention of reactant chirality in the product, independent of a chiral catalyst or any chiral bias, other than the chirality of the reactant itself. The fact that there is 30% chirality inversion suggests that the transition state occurs via preferential cleavage of the 2C–O bond in PO and through a transition state that has a close to planar C–CH–C structure.

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