

Supporting Information for

Rate Constants and Products of the OH Reaction with Isoprene-Derived Epoxides

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Synthesis of IEPOX-1. The synthesis of IEPOX-1 was previously reported by our laboratory¹ and is briefly summarized below. The synthesis of IEPOX-1 required the preparation of 3-methyl-1,2-epoxy-3-butene, which was produced according to a procedure first reported by Harwood et al.² 20 mL of methacrolein were added in 300 μ L increments every 3 minutes to a stirring 600 mL CH_2Cl_2 solution that contained 60 g of powdered NaOH and 50 g of trimethyl sulfonium methyl sulfate (Oakwood Products, Inc.). The resulting solution was washed thrice with 200 mL of DI H_2O and a majority of the CH_2Cl_2 was removed under reduced pressure yielding approximately 50 mL of a mixture of 3-methyl-1,2-epoxy-3-butene/ CH_2Cl_2 . The epoxide was hydrolyzed by adding 100 mL of 0.002 M H_2SO_4 and heating the solution to 80 $^\circ\text{C}$ for 1 hour. The hydrolyzed product was distilled in vacuo (46 $^\circ\text{C}$, 70 mtorr) yielding approximately 4 g of 3-methyl-3-butene-1,2-diol. Epoxidation of the alkene diol was performed by slowly adding 12.8 g of meta-chloroperbenzoic acid (mCPBA, Sigma-Aldrich) to a mixture of the distilled diol and 210 mL of CH_2Cl_2 and refluxing the solution for 24 hours at 42 $^\circ\text{C}$ followed by 24 hours of stirring at room temperature. After cooling (to 4 $^\circ\text{C}$) and filtering the solution, a 2 molar excess of KF (8.9 g) was added and the solution was stirred vigorously for 1 hour before again cooling and filtering the solution. The volume of the solution was reduced to 25 mL and IEPOX-1 was extracted from the organic phase by washing it with 25 mL of DI water three times. The aqueous solution was neutralized by adding 0.01 M NaOH solution. The water was removed under reduced pressure at 50 $^\circ\text{C}$, and the residue was purified by flash chromatography (SiO_2 , ether) to give the purified IEPOX-1, as described by Zhang et al.³ As

was the case for all syntheses, ^1H NMR was used to confirm the product's identity and to assess the purity of the product.

Synthesis of IEPOX-4. The synthesis of IEPOX-4 was also previously performed in our laboratory¹ and was based on the three step procedure of Shepard and Johnson.⁴ A mixture of 54 mL of Br_2 and 250 mL of CHCl_3 was added drop-wise over the course of 3 hours to a stirred mixture of 100 mL isoprene and 100 mL CHCl_3 that was kept below $-25\text{ }^\circ\text{C}$, yielding 2-methyl-1,4-dibromo-2-butene. NaHSO_3 was added to remove the unreacted bromine before reducing the volume of the mixture to 150 mL under reduced pressure. The concentrated dibromo species, 150 g of powdered potassium acetate and roughly 100 mL of glacial acetic acid were mixed, stirred and heated to $100\text{ }^\circ\text{C}$ for 18 hours yielding 2-methyl-1,4-diacetate-2-butene. 500 mL of DI H_2O were swirled three separate times into the reaction mixture forming a brown oily layer that was separated from the aqueous layer and collected. The crude diacetate was distilled in vacuo ($67\text{ }^\circ\text{C}$, 250 mtorr) yielding 134 mL of distilled product. 900 mL of 95% ethanol, 486 g of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and the distilled diacetate species were combined and refluxed for 5 hours at $90\text{ }^\circ\text{C}$. The solid was removed by filtration and the ethanol was removed under reduced pressure. Vacuum distillation ($95\text{ }^\circ\text{C}$, 250 mtorr) of the remaining product was performed twice and yielded 13.39 g of 2-methyl-2-butene-1,4-diol. 15.83 g of mCPBA were added slowly to a solution of 5.50 g of the distilled diol species and 185 mL of acetonitrile and the reaction was stirred for 1 week at room temperature. After cooling (to $-20\text{ }^\circ\text{C}$) and filtering the solution, the

acetonitrile was removed under reduced pressure and the residue was purified by flash chromatography (SiO₂, ether) to give the purified IEPOX-4.

Flow Tube Apparatus. The main flow tube was 100 cm in length and constructed with 2.2 cm inner diameter Pyrex tubing. A large flow of oxygen carrier gas (15 STP L min⁻¹) was introduced at the rear of the flow tube. The reactants necessary for the production of OH radicals were prepared in a 20 cm long, 1.25 cm inner diameter sidearm. The epoxides—which were added by flowing He gas through traps containing the liquid phase of the various species because of their low vapor pressures—and the competitor species were introduced together through an injector with a fan-shaped Teflon device placed at the end to enhance mixing. All gas flows were monitored with calibrated mass flow meters. A polonium-210 (²¹⁰Po) α -particle-emitting ionization source was placed between the flow tube and the entrance to the CIMS. Pressure was measured using a 0-1000 Torr capacitance manometer and was held at 100 ± 2 torr and temperature was measured with Cu-constantan thermocouples and held at 298 ± 2 K for most of the experiments. Most of the flow tube gasses were removed at the CIMS inlet using a 31 L s⁻¹ roughing pump.

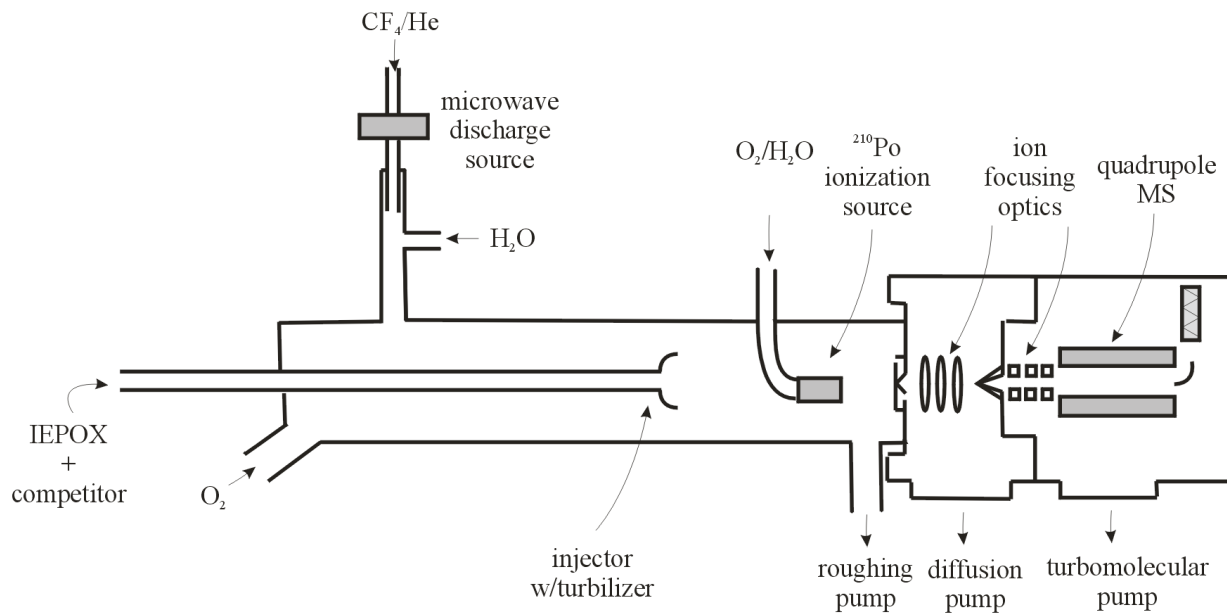


Figure S1. Experimental apparatus.

Derivation of Equation 6. Equation 5 applies to each competitor separately, which are generically labeled as competitors I and II below:

$$\ln \frac{[epoxide]_{t,0}}{[epoxide]_{t,OH}} = \frac{k_3}{k_4} \ln \frac{[competitor I]_{t,0}}{[competitor I]_{t,OH}} \quad (S1)$$

$$\ln \frac{[epoxide]_{t,0}}{[epoxide]_{t,OH}} = \frac{k_3}{k_{4'}} \ln \frac{[competitor II]_{t,0}}{[competitor II]_{t,OH}} \quad (S2)$$

Equating the right hand sides of Equations S1 and S2:

$$\frac{k_3}{k_4} \ln \frac{[competitor I]_{t,0}}{[competitor I]_{t,OH}} = \frac{k_3}{k_{4'}} \ln \frac{[competitor II]_{t,0}}{[competitor II]_{t,OH}} \quad (S3)$$

Defining competitor I as the normalized competitor and competitor II as the reference competitor and rearranging S3 gives equation 6:

$$\ln \frac{[\textit{normalized competitor}]_{t,0}}{[\textit{normalized competitor}]_{t,OH}} = \frac{k_4}{k_4'} \ln \frac{[\textit{reference competitor}]_{t,0}}{[\textit{reference competitor}]_{t,OH}} \quad (6)$$

References

- (1) Cole-Filipiak, N. C.; O'Connor, A. E.; Elrod, M. J. Kinetics of the hydrolysis of atmospherically relevant isoprene-derived hydroxy epoxides. *Environ. Sci. Technol.* 2010, *44*, 6718-6723.
- (2) Harwood, L. M. A simple laboratory procedure for preparation of (1-methylethenyl)oxirane (3,4-epoxyisoprene). *Synth. Commun.* 1990, *20*, 1287-1290.
- (3) Zhang, Z.; Lin, Y. H.; Zhang, H.; Surratt, J. D.; Ball, L. M.; Gold, A. Technical Note: Synthesis of isoprene atmospheric oxidation products: isomeric epoxydiols and the rearrangement cis and trans-3-methyl-3,4-dihydroxytetrahydrofuran. *Atmos. Chem. Phys.* 2012, *12*, 8529-8535.
- (4) Shepard, A. F.; Johnson, J. R. Rearrangement of unsaturated 1,4-glycols. 2-methyl-2-butene-1,4-diol. *J. Am. Chem. Soc.* 1932, *54*, 4385-4391.