

Feasibility of a selective epoxidation technique for use in quantification of peracetic acid in air samples collected on sorbent tubes

Detailed Methods and Materials

General Considerations

Peracetic acid (PAA) (32% in acetic acid), cyclohexene ($\geq 99.7\%$), anhydrous acetonitrile (ACN) (99%), *n*-hexane (98%), 1-bromohexane (98%), hydrogen peroxide (HP) (30% in H₂O), glacial acetic acid (AA), and cyclohexene oxide (CHO) (98%) were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Pre-loaded XAD-7 glass sorbent tubes (350 mg (Part No. 226-211) and 175 mg (Part No. 226-97 C)) were purchased from SKC, Inc. (Eighty Four, PA). Water was distilled, deionized to a resistivity of 18 MW cm (DI H₂O), and filtered using a Milli-Q® filter system (Billerica, MA). Helium and nitrogen gas (UHP grade) were supplied by Butler Gas (McKees Rocks, PA) and used as received.

PAA Liquid-Phase Experiments

Liquid-phase PAA experiments were conducted for determination of initial reaction conditions as well as for use in constructing calibration curves. PAA stock solutions with concentrations ranging from 0.041–3.27 M were prepared in DI H₂O. Freshly prepared PAA solution (2 μ L) was added to a clean 7-mL glass septum-capped vial containing 1 mL of anhydrous ACN such that the amount of PAA in the sample is equivalent to that of the gas-phase experiments. Specifically, 6, 12, 25, 50, 100, 199, 249, 373, and 498 micrograms (μ g) of PAA were chosen, which are equivalent to 25, 50, 100, 200, 400, 800, 1000, 1500, and 2000 ppb gas phase concentrations when dispersed into 80 L of air, respectively. An excess of cyclohexene (100 μ L, 0.99 mmol) was added to the vial, which was then capped and vortexed for 1 minute. The mixture reacted for approximately 24 hours at 297 ± 3 K (defined as room temperature in this study (RT)) without further agitation. Following this, 1.5 mL of 0.178 mM 1-bromohexane (internal standard, IS) in *n*-hexane was added. The solution was once again vortexed for 1 minute to promote even mixing. The layers were allowed to settle for 5 minutes, and then 100 μ L of the hexane layer was removed to a 2-mL amber vial with a 250- μ L glass insert, which was subsequently analyzed via GC-MS.

Control experiments were performed in the absence of added PAA solution as well as with the addition of HP or AA stock solutions prepared in DI H₂O at various concentrations and ratios as described in results. Additional control experiments were performed with CHO solutions, prepared by combining neat CHO purchased from Sigma-Aldrich with ACN in concentrations of 0.041–3.27 M (matching concentrations of PAA solutions as described above). For each experiment, 2 μ L of CHO solution was added to 5 mL ACN, extracted with hexane as described above, and analyzed by GC-MS. For comparison to the CHO samples, PAA samples were also prepared in 5 mL of ACN. Five mL of ACN were used in initial experiments, but after testing indicated that the use of 1 mL ACN improved recovery, all remaining experiments were performed as such. Experiments pertaining to the use of 5 mL are presented in the manuscript strictly when relative comparisons were made between treatments using 5 mL.

PAA Chamber Creation and Sorbent Tube Sampling

PAA solutions with concentrations ranging from 0.041–3.27 M were prepared as described above. A 2- μ L aliquot of the prepared PAA solution was dispersed into 80 L of air, resulting in concentrations of 25–2000 ppb. Chamber experiments were performed at RT in a collapsible Teflon® 100-L reaction chamber, the construction of which is described elsewhere.³⁹ Briefly, the chamber was equipped a 6.4-mm Swagelok (Solon, OH) Teflon® tee fitting, into which 2 μ L of prepared PAA solution was delivered. The aliquot of PAA was delivered to the chamber to create the PAA atmosphere as follows: compressed air from the NIOSH facility passed through

anhydrous calcium sulfate (CaSO_4) (Drierite, Xenia, OH) and 4-Å molecular sieves (Sigma Aldrich, St. Louis, MO) to remove moisture and flowed into a humidifying chamber where it was mixed to the predetermined relative humidity (RH) of $50 \pm 3\%$. A mass flow controller (MKS, Andover, MA) regulated the air flow rate to 5 L/min entering the chamber, and each chamber was filled to 80 L.

Following creation of the PAA atmosphere, 60 L out of the 80 L total of PAA-containing air was pulled through a 350-mg XAD-7 sorbent tube (SKC Inc., PA) via a personal sampling pump (Pocket Pump Touch, SKC Inc., PA) for 4 hours at 250 mL/min. For data shown in Table 4, PAA-containing air was collected at 1 L/min for 15 minutes (URG-3000-02Q, Chapel Hill, NC). After collection, the sorbent tube was broken, and the entire amount of XAD-7 sorbent in the tube (350 mg total) was transferred to a clean 7-mL clear glass vial equipped with a Teflon[®] septum cap. ACN (1 mL) and an excess of cyclohexene (100 μL , 0.99 mmol) were added, and the sample was vortexed for 1 minute. The mixture reacted for 24 hours at room temperature with no further agitation, after which 1.5 mL of 0.178 mM 1-bromohexane (IS) in *n*-hexane solution was added. The sample was vortexed for 1 minute and was allowed to settle for approximately 5 minutes. A 100- μL aliquot of the hexane layer was then transferred to a 2-mL amber vial with a 250- μL glass insert for GC-MS analysis as described below.

Calibration Curve Experiments

Calibration Curve A (Liquid-Phase)

Calibration Curve A was constructed using the data obtained from the liquid-phase experiments discussed above (0.041–3.27 M). Aliquots containing 6, 12, 25, 50, 100, 199, 249, 373, and 498 μg of PAA were used for the experiments, and three replicates were performed for each μg quantity.

Calibration Curve B (Liquid + Sorbent)

Samples for generation of Calibration Curve B were prepared in triplicate for each μg quantity as follows. Sorbent from a blank 350-mg XAD-7 sorbent tube, 1 mL of ACN, and 2 μL of PAA solution with a known concentration were added to a clean 7-mL glass vial equipped with a septum cap. This mixture was vortexed for 1 minute to promote even distribution of solvent and analyte throughout the sorbent. Following this, 100 μL of cyclohexene was added, and the sample was vortexed for 1 minute. This mixture reacted for 24 hours at RT without further agitation and then was extracted by adding 1.5 mL of 0.178 mM 1-bromohexane in *n*-hexane and vortexed for 1 minute. After the layers settled, 100 μL of the hexane layer was removed to a 2-mL amber vial with a 250- μL glass insert and was analyzed via GC-MS. Aliquots containing 6, 12, 25, 50, 100, 199, 249, 373, and 498 μg of PAA were used for the experiments.

Fortified Sampler Experiments

A 350-mg XAD-7 sorbent tube was loaded with 2 μL of a PAA solution with a known concentration (prepared as described above), and clean air at 50% RH from a Teflon chamber was pulled across the spiked sorbent tube for 4 hours at a rate of 250 mL/min. Following sampling, the sorbent tube was processed as described above and analyzed via GC-MS. Aliquots containing 6, 12, 25, 50, 100, 199, 249, 373, and 498 μg of PAA were used for the experiments, and three replicates were performed for each μg quantity.

Sorbent Capacity Experiments

A solution of PAA (2 μL , 3.27 M, 498 μg) was injected into a Teflon tee and was subsequently combined with 80 L of 50% RH air to create an atmosphere containing 2000 ppb of PAA within the chamber, as described above. An additional XAD-7 sorbent tube (containing 175 mg of sorbent) was inserted into the sampling train behind the initial 350-mg XAD-7 sorbent tube. A personal sampling pump was then attached to the opposite end of the second sorbent tube via

tubing, and 250 mL/min of PAA-spiked air from the chamber was pulled onto sorbent tubes for 4 hours. After sampling, the tubes were processed separately as described above and were analyzed by GC-MS.

Sorbent Tube Storage Experiments

Chambers containing 50, 100, and 199 μg of PAA were prepared, corresponding to 200, 400, and 800 ppb, respectively, in 80 L of 50% RH air as described above in "PAA Chamber Creation and Sorbent Tube Sampling." The PAA-containing air was sampled through a 350mg XAD-7 sorbent tube via a personal sampling pump for 4 hours at 250 mL/min (total of 60 L). The sorbent tube was then tightly capped, sealed with parafilm, and stored at RT or -20°C in the absence of light for 72 hours. Following storage, the sample was processed as described above, with the exception that 5 mL of ACN was used, and the corresponding data were normalized using data from experiments without storage that used the 5-mL extraction protocol described in "PAA Liquid-Phase Experiments."

Stability and Variable Sampling Time Experiments

The stability of PAA and the flexibility of sampling time were evaluated using 800 ppb chambers containing 199 μg of PAA and 80 L of 50% RH air (preparation described above). Two different treatments were conducted: 1) collection of a 15-L sample over the course of 1 hour at a rate of 250 mL/min ($n = 2$ chambers) and 2) collection of a 15-L sample over the course of 15 minutes at a rate of 1 L/min ($n = 3$ chambers). Four samples were collected from each chamber prepared. Following the allotted time periods, each of the samples was processed as described above.