Multiphase Reactivity of Benzotriazole Ultraviolet Stabilizers

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1. Introduction

1.1 Benzotraizole UV Stabilizers: Emerging Contaminant

- Benzotriazole UV stabilizers (BUVs) are a class of phenolic benzotriazole derivatives with a strong ability to absorb UV light (300-328 nm) [1].
- High production volume additives to consumer and industrial products such as paints, polymers, and adhesives [2].
- Persistent and bioaccumulative pollutant found in the environment since 1978 [3].
- Toxicological studies show potential risk to human health [4] and aquatic organisms [5].

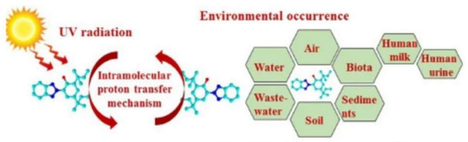
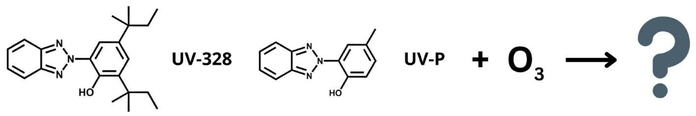


Figure 1. UV stabilization mechanism and environmental occurrence of BUVs [1].

Potential products with BUVs

1.2 Research Questions

1. **Can benzotriazole UV-stabilizers (UV-P and UV-328) undergo multiphase reactions with the gas phase oxidant ozone (O_3)?**
2. **What products are formed from this chemistry?**



2. Method

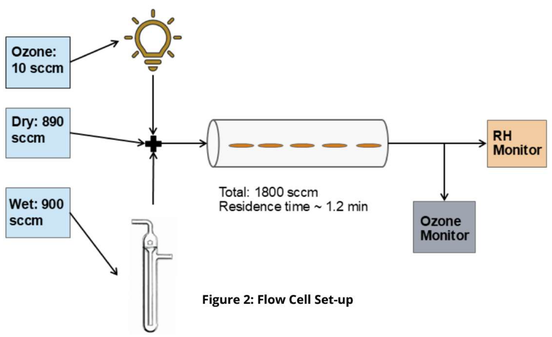


Figure 2: Flow Cell Set-up

- Flow tube experiments at 250 ppb, 1000 ppb, and 7000 ppb for up to 24h.
- UV-328 and UV-P deposited using chloroform solution with theoretical thickness of 2.5 nm on glass cover slip slides.
- Samples placed in real indoor environment for up to 4 weeks
  - Dark: office shelf covered by open cardboard box
  - Light: at window
- Starting compound decay quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS).
- Mass-to-charge ratio (m/z) of UV-328 products identified using high-resolution liquid chromatography mass spectrometry (LC-Orbitrap).

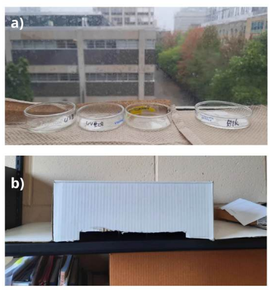


Figure 3: Indoor samples under light conditions next to window (a) and dark conditions in office (b).

3. Results & Discussion

3.1 UV-P and UV-328 Flow Tube Experiments

Ozone exposure 50 ppb equivalent = 20 days

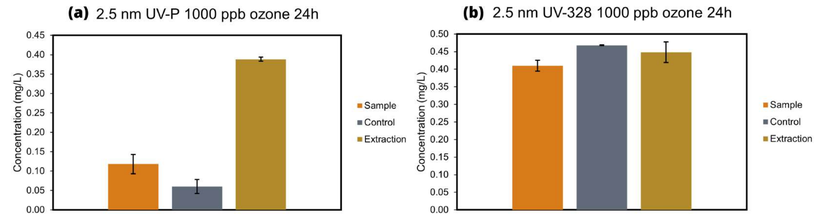


Figure 4. Concentration of UV-P (a) and UV-328 (b) following reaction at 1000 ppb for 24h. Control refers to samples within the flow tube for 24h without ozone. Extraction efficiency determined by extraction immediately following deposition on slide. Error bars represent standard deviation of triplicates.

Ozone exposure 50 ppb equivalent = 140 days

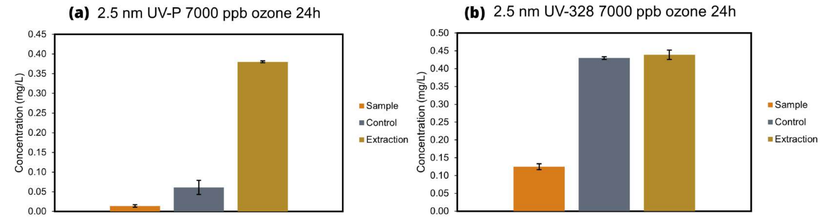


Figure 5. Concentration of UV-P (a) and UV-328 (b) following reaction at 7000 ppb for 24h. Control refers to samples within the flow tube for 24h without ozone. Extraction efficiency determined by extraction immediately following deposition on slide. Error bars represent standard deviation of triplicates.

BUVs are highly recalcitrant to multiphase ozone oxidation

- UV-328 and UV-P were similarly recalcitrant; 7000 ppb was needed in 24h to show a significant decay ($p < 0.05$) for both UV-328 and UV-P.
  - 77.3% UV-P, 71% UV-328 was reacted.
- UV-P evaporated significantly within the flow tube during 24h and was not used in indoor experiments.

3.2 UV-328 Reactions in Real Indoor Environments

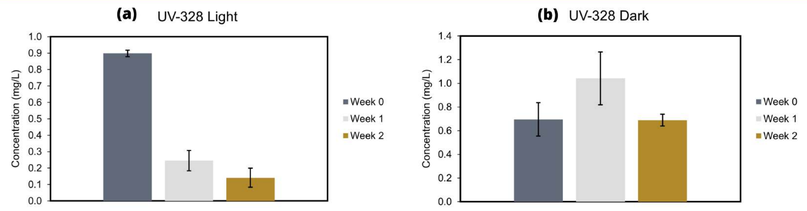


Figure 6. Weekly concentration of UV-328 in light (a) and dark (b) conditions. Error bars represent standard deviation of triplicates.

UV-328 reacts indoors under light but not in dark conditions

- Statistically significant decrease of UV-328 under light conditions ($p < 0.001$), with 84.3% lost by week 2.
  - Potential reactivity with OH radicals, ultraviolet light, and/or enhanced evaporation.
- No statistically significant difference in dark conditions ($p > 0.05$).
  - Consistent with flow-tube experiments showing slow reaction kinetics with only ozone.

3.3 UV-328 Ozonolysis Products

26 potential products identified from UV-328 in trial 1
16 of these 26 were detected in trial 2

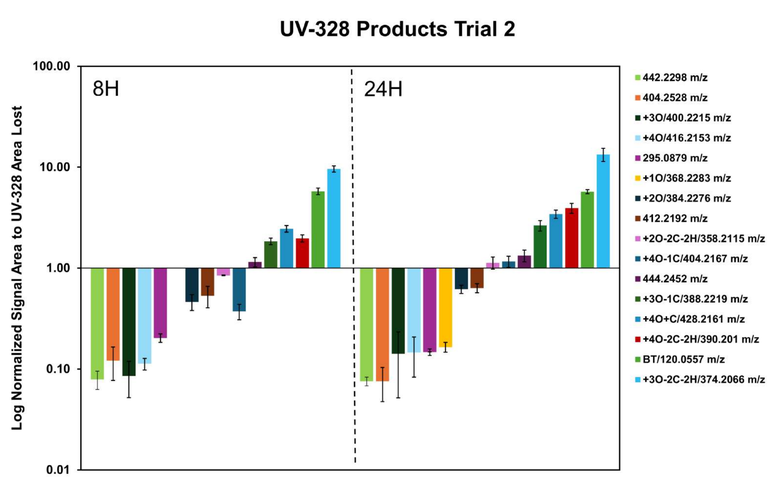


Figure 7. Integrated area of suspected products normalized to the difference in average signal area between 0h and 24h of UV-328. Error bars represent standard deviation of triplicates.

- Targeted analysis using generated m/z list of molecular formula with addition of 0-5 oxygen atoms, loss of 0, 2, 4, 6, 8 hydrogen atoms, and loss of 0 to 8 CH_2 groups with mass tolerance of 5 ppm.
- Non-targeted analysis using R program developed by the Peng group at the University of Toronto, with a mass tolerance of 2.5 ppm.
- Suspected molecular formula in relation to starting material listed when applicable. Benzotriazole (BT) was confirmed using MS^2 fragments and retention time based on standards.

5. Conclusion & Future Direction

- Benzotriazole UV stabilizers are recalcitrant to multiphase O_3 oxidation but may react faster with OH radicals or light.
- Preliminary analysis shows significantly oxidized products of UV-328 are produced after O_3 oxidation, resulting in more polar compounds than the starting material.
  - This may increase condensation into aerosol phase in the atmosphere or increase ability to be washed out from the atmosphere.
- Future Direction
  - Analysis and comparison of UV-328 ozonolysis products to UV-P products
  - Hydroxide (OH) radical oxidation, ultraviolet light exposure in flow tube experiments
  - Investigate reactive potential within consumer plastics

Acknowledgements

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References

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