

Atmospheric degradation of methyl methacrylate initiated by OH radicals: Mechanistic study and quantification of methyl pyruvate in NO_x free air

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Polymeric materials constructed from methyl methacrylate monomers are used in large amounts by a variety of industries due to their wide domestic and industrial uses like cast sheet, advertising signs and displays, lighting fixtures, building panels and sidings, and coatings (latex paints, lacquer, and enamel resins).¹ Recent studies revealed that an optimized system for recycling methyl methacrylate waste is still required because it produces more than twice the amount of Greenhouse Gas (GHG) emissions than other commodity resins.²

The present work deals with the study of the gas-phase reaction of OH radicals with methyl methacrylate (MMA) in the absence of NO_x. Product quantification under atmospheric conditions was performed using the internal standard technique. The organics were monitored by gas chromatography–flame ionization detector and mass spectrometry to identify the species. In the absence of NO_x, methyl pyruvate was determined for the first time with a yield of 76 ± 13% according to the decomposition of the 1,2-hydroxyalkoxy radicals formed.

In addition, a computational study using Density Functional Theory is presented to describe for the first time the formation of alkoxy radicals and the differences observed on the degradation of MMA in mechanisms and yields of reaction pathways with the chemistry of polluted (with large amounts of NO_x) and remote areas (where the concentration of NO_x is scarce). Quantum mechanical calculations were performed with the Gaussian 09 suite of programs.³ Geometry optimization of the reactants, products, and transition states was made at the MPWB1K19 level of theory using 6-31+G(d,p) basis set. Theoretical analysis provides insight into the prevalence of C₁–C₂ scission at electronic level, suggesting that the formation of methyl pyruvate is kinetically and thermodynamically more favorable than that of alternative channels. Furthermore, according to our results it is possible to explain the difference in the yield of methyl pyruvate observed in the presence or absence of NO_x. In NO_x-free conditions, the reaction between RO₂ radical and OH radical is expected to be slightly exothermic and to be the dominating reaction pathway in the formation of RO radical because the most commonly accepted peroxy radical self-reactions proved to be strongly endothermic. In NO_x rich environments, the reaction RO₂ radicals + NO is calculated to be even more exothermic, expressed as a higher product yield due to a chemical activation effect.

References

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