

# New Insights on the Chemistry of Organic Peroxy Radicals from Speciated Monitoring with Chemical Ionization Mass Spectrometry: Application to RO<sub>2</sub> + Alkene Reactions under Atmospheric Conditions

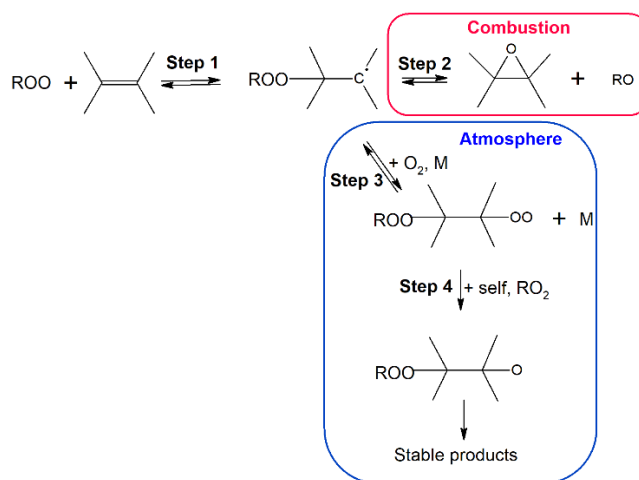
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The chemistry of organic peroxy radicals (“RO<sub>2</sub>”) in Earth’s atmosphere is complex. To improve its understanding we are developing Chemical Ionization (mostly, proton transfer) Mass Spectrometric approaches to monitor individual RO<sub>2</sub>. Here, we report an application of these approaches to the study of RO<sub>2</sub> + alkene reactions under atmospheric conditions in laboratory (T = 298 ± 5 K, P = 0.9 atm., in air). Until recently, these reactions had been exclusively studied under combustion conditions (T ≥ 360 K) [1], where the mechanism proceeds in two steps (Figure 1): a fast addition of RO<sub>2</sub> on the double bond (Step 1) followed by the slow and kinetically-limiting formation of epoxide and alkoxy radical (Step 2). Recently, we have investigated several of these reactions at room temperature in a flow reactor by monitoring the consumption of individual RO<sub>2</sub> by various alkenes [2]. The rate coefficients obtained were significantly larger than expected from the combustion data (×10 to ×100). To identify the cause for these discrepancies, new experiments were performed with the objective of obtaining the reaction rate coefficients from the stable reaction products, the later being monitored both by Proton-Transfer Mass Spectrometry and by Tenax sampling followed by Gas Chromatography/Electron Impact Mass Spectrometry analysis. The results showed that, under atmospheric conditions, Step 2 is not the main reaction pathway but is by-passed by the faster Step 3 (and subsequent fast Step 4) (Figure 1). Thus, under these conditions, RO<sub>2</sub> consumption is not kinetically limited by the epoxide formation but by the faster addition reaction (Step 1), which is consistent with the rate coefficients obtained in our previous study [2]. The RO<sub>2</sub> sinks due to their reactions with unsaturated compounds in Earth’s atmosphere should thus be more significant than expected until now based on the combustion data, at least for some RO<sub>2</sub>. This study underlines the importance of monitoring individual RO<sub>2</sub> rather than stable products when investigating RO<sub>2</sub> chemistry.



**Figure 1:** Mechanism for RO<sub>2</sub> + 2,3-dimethyl-2-butene reaction showing the different pathways dominating under different conditions.

[1] M. S. Stark, *J. Phys. Chem. A*, 1997, 101, 8296–8301, and references therein.

[2] B. Noziere & F. Fache, *Chem. Sci.*, 2021, 12, 11676–11683.