

# Partially oxidized radicals – crucial intermediates during atmospheric aerosol formation

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The dynamics of reactive mixtures under conditions being typical for important environmental issues and technical applications are driven by chemical kinetics being related to the elementary reaction steps of a zoo of stable and transient species. This complexity limits our current understanding of important phenomena like the atmospheric formation of secondary organic aerosol.

Reactions of partially oxidized, transient species like alkoxy and peroxy radicals or Criegee intermediates (CIs) represent key mechanistic branch points in hydrocarbon degradation schemes. However, for some crucial reaction steps like the atmospheric oxidation of SO<sub>2</sub> by CIs the rate coefficient was not accessible until recently (see Welz et al., 2012). Such knowledge gaps are critical since incorrect data for sensitive elementary steps can drastically mislead predictions of atmospheric models with regard to aerosol formation.

In recent years we applied and combined different experimental and modeling techniques for dealing with the complexity being inherent to atmospheric and combustion chemistry. This overall examination approach helped us to derive e.g. a compact and consistent kinetic model with fully validated peroxy radical chemistry (Zeuch et al., 2008). For the study of atmospherically relevant reactions we apply a specially

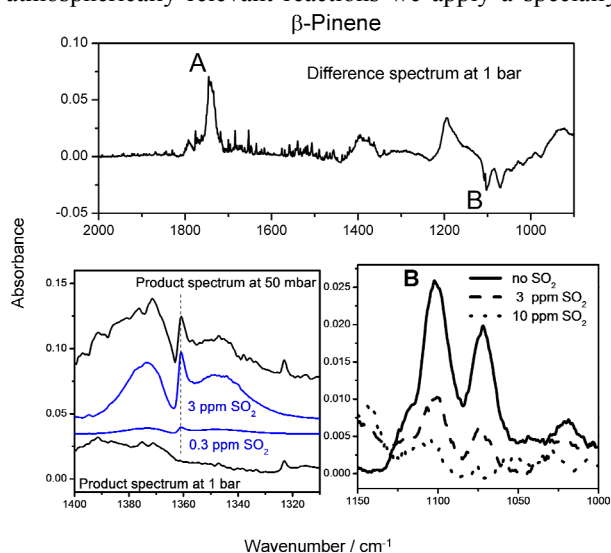


Figure 1. IR spectra of final products from  $\beta$ -pinene ozonolysis at 1 bar and 50 mbar. The difference spectrum in the upper panel shows the suppression of secondary ozonide formation (feature B) and highly increased nopinone formation (A). The lower panels

show the consumption of SO<sub>2</sub> at high pressure and the suppression of secondary ozonide formation by SO<sub>2</sub>. The designed reactor experiment featuring fast initial reactant mixing and aerosol characterization at the end of main reactive processes (Carlsson et al., 2012). The final product analysis at the end of  $\beta$ -pinene ozonolysis in the presence and absence of SO<sub>2</sub> revealed the high influence of SO<sub>2</sub> on mechanistic branching in the chemistry of CIs (Figure 1) and aerosol formation (Figure 2).

The combined use of time resolved infrared spectroscopy and kinetic modeling gives reliable constraints for the rate coefficient of SO<sub>2</sub> + CI from biogenic terpenes under ambient conditions. In (cis and trans) 2-butene ozonolysis experiments the measured particle numbers in the presence of SO<sub>2</sub> show a slope of  $\sim 2$  in a double logarithmic plot against predicted sulfuric acid concentrations in support of atmospheric and smog chamber observations (Carlsson et al., 2012), which represent much different reactive environments.

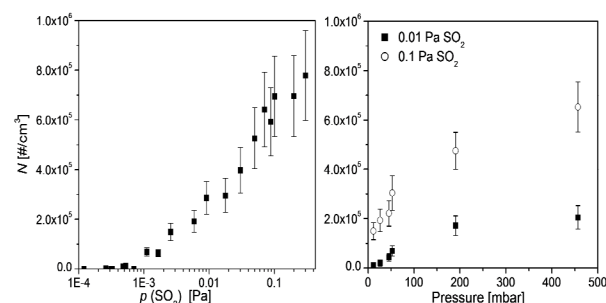


Figure 2. Aerosol formation during 2-butene ozonolysis as a function of SO<sub>2</sub> concentration and pressure.

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