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Temperature-dependence of alkyl peroxy and alkoxy radicals reactions

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The oxidation of volatile organic compounds (VOCs) in the atmosphere leads to a number of products of potential environmental concern, including ozone and carbonyl compounds. Alkyl peroxy (RO₂) and alkoxy radicals (RO) are key intermediates in the atmospheric degradation of VOC and determine the impact of the oxidation of a given VOC, in terms of both the immediate effects of closed-shell products, and as a result of the further chemistry of free radical products. Recent field measurements in the upper troposphere/lower stratosphere (UTLS) region have revealed higher than expected concentrations of partially oxidized hydrocarbons. In addition, ozone has been identified to be an important greenhouse gas in the UTLS, thus it is important to understand how temperature affects the relative rates of RO₂ and RO reactions.

The yields of pentyl nitrates, from the reaction of pentyl peroxy radicals with NO, have been investigated over a range of temperatures relevant to the troposphere (250320 K) using a flow system coupled to a GC-FID. Also, the temperature dependence of the competition between the reactions of selected RO, including 1butoxy, has been studied by relative-rate methods using a combination of analytical techniques (GC-FID and FTIR). Our results will be presented in the context of the role that the oxidation of VOC plays in the chemistry of the troposphere over a range of altitudes.