

2.011 Investigation of the oxidation of methyl vinyl ketone (MVK) by OH radicals in the atmospheric simulation chamber SAPHIR.

Presenting Author:

Hendrik Fuchs, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany, h.fuchs@fz-juelich.de

Co-Authors:

Sascha Albrecht, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Ismail-Hakki Acir, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Birger Bohn, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Martin Breitenlechner, School of Engineering and Applied Sciences and Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA

Hans-Peter Dorn, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Georgios Gkatzelis, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Andreas Hofzumahaus, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Frank Holland, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Martin Kaminski, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Frank N. Keutsch, School of Engineering and Applied Sciences and Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA, USA

Anna Novelli, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

David Reimer, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Franz Rohrer, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Ralf Tillmann, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Luc Vereecken, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Robert Wegener, Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Alexander Zaytsev, School of Engineering and Applied Sciences and Department of Chemistry and Chemical Biology, Harvard University, Cambridge,

MA, USA

Astrid Kiendler-Scharr, Institute of Energy and Climate Research, IEK-8:
Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Andreas Wahner, Institute of Energy and Climate Research, IEK-8:
Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Abstract:

The photooxidation of methyl vinyl ketone (MVK) was investigated in the atmospheric simulation chamber SAPHIR for conditions at which organic peroxy radicals (RO_2) mainly reacted with NO ("high NO" case) and for conditions at which other reaction channels could compete ("low NO" case). Measurements of trace gas concentrations are compared to calculated concentration time series applying the Master Chemical Mechanism (MCM version 3.3.1). Product yields of methylglyoxal and glycolaldehyde are determined from measurements. Direct quantification of OH radicals in the experiments shows the need for an enhanced OH radical production at low NO conditions similar to previous studies investigating the oxidation of the parent VOC isoprene and methacrolein, the second major oxidation product of isoprene. For MVK the model-measurement discrepancy is up to a factor of 2. Product yields and OH observations are consistent with assumptions of additional RO_2 plus HO_2 reaction channels as proposed in literature for the major RO_2 species formed from the reaction of MVK with OH. This study, however, shows that also HO_2 radical concentrations are underestimated by the model, suggesting that additional OH is not directly produced from RO_2 radical reactions, but indirectly via increased HO_2 . Quantum chemical calculations show that HO_2 could be produced from a fast 1,4-H shift of the second most important MVK derived RO_2 species. However, additional HO_2 from this reaction is not sufficiently large to bring modelled HO_2 radical concentrations into agreement with measurements due to the small yield of this RO_2 species. An additional reaction channel of the major RO_2 species would be required that produces concurrently HO_2 radicals and glycolaldehyde to achieve model-measurement agreement. A set of H-migration reactions for the main RO_2 radicals were investigated by quantum chemical and theoretical kinetic methodologies, but did not reveal a contributing route to HO_2 radicals or glycolaldehyde.