

The paper reports a detailed study of the oxidation of methyl vinyl ketone (MVK), initiated by reaction with OH and under atmospheric conditions, in the large, instrumented, outdoor chamber, SAPHIR, at Juelich. The study is based around measurements of [OH], using both the FAGE (laser induced fluorescence) technique and DOAS (differential optical absorption). In addition, the inverse lifetime of OH was measured, to facilitate assessments of the OH budget. HO₂ and RO₂ concentrations were measured by conversion to OH by reaction with NO and detection using FAGE. A wide range of advanced monitoring techniques were used to determine trace gases, including chemiluminescence (NO), cavity ring down (H₂O, CO), absorption spectroscopy (O₃) and proton time of flight MS (organic compounds). The experiments were limited to only four experiments, over an extended period of time, two at high [NO] and two at low [NO]. The quality and detail of the experimental characterisation were exceptional.

The experimental measurements are compared with simulations based on the master chemical mechanism (MCM, 3.3.1), which was selectively modified to test the mechanistic implications of model, measurement discrepancies. These modifications primarily relate to discrepancies observed at low [NO] and to peroxy, hydroperoxy radical chemistry. They are based on detailed quantum chemical calculations, using high level methods.

The high [NO] experiments show good agreement between model and measurement once problems arising from the time required to convert RO₂ species to OH, for detection by LIF, are recognised and accommodated. The agreement is much worse at low [NO] and significant changes to the MCM are needed; these relate primarily, but not exclusively to missing radical (OH and HO₂) sources – the inverse OH lifetime measurements show good model / measurement agreement. Quantum chemical calculations show that the discrepancies cannot be explained by identifiable unimolecular H-shift reactions of RO₂ radicals, which are calculated to be too slow. Note that the level of calculation used here is higher than that previously used to examine similar reactions for isoprene. The requirements for the missing reactions are given but none identified.

MVK is a key intermediate in the atmospheric oxidation of isoprene. This detailed, combined experimental and modelling study of its oxidation mechanism, provides a key step in the quest to understand detailed and ‘missing’ radical sources in the atmospheric oxidation of isoprene. It is an exemplary investigation that bridges field and mechanistic studies and is based on the very best aspects of both approaches. While not providing definitive answers to the mechanistic deficiencies observed, it provides a key step in the development of an accurate capability to understand and model the oxidation of a key organic compound under important and widely prevalent atmospheric conditions.

The paper is undoubtedly worthy of publication. I have no major criticisms. The authors should consider the following minor points:

General point. The authors should examine the tenses used in the paper. It is usual to use the past tense for experiments (e.g. p9 l1, should be “MVK...was injected..”) and the present tense for results etc.

P4, l9. Change to “...prevents ambient air entering...”

P4, l21. Change to “...detection limit of the instruments.”

P10, l21. Either square brackets or the word concentrations should be inserted. i.e. “..OH concentrations agree...”. This error occurs on a number of occasions (e.g. later on the same line)

P11,I10. The sentence beginning “The predicted rate constant .. “ would be helped by inserting a diagram into the SI – I presume the term “limited protruding section” means that part of the forward barrier that lies above the reactant energy, but it isn’t obvious. The comment on the reversibility of the alkoxy decomposition is not very clear – again this would be helped by a diagram of the PES and some additional comment in the SI.

P11, R7. The mechanism would be clearer if the underlined phrase below were inserted:

“....HMVKAO2 1,4 H migration ...-OH group, followed by H abstraction at the –OH site by O₂ forming HO₂...” Also the O₂ in reaction R7 is not involved in the rate determining step and so + O₂ should be placed in brackets. Generally speaking, it is necessary to have the MCM site open on reading the paper to appreciate the details of the reactions being discussed. While this is OK, it does slow reading down – the authors might consider putting the structures, with MCM names, in the SI P13, I4. The first sentence needs rephrasing – the word rates should be inserted and a reference made to the steady state (the reaction rates are equal – they are not genuinely in equilibrium.) I suggest “OH is in steady state because of its short lifetime, so that its rates of production and destruction are equal.”