

Atmospheric oxidation of new 'green' solvents part II: methyl pivalate and pinacolone

Major Comment

This paper is well written and gets across its results in a digestible way.

The photolysis calculation using MEK as the proxy can be improved/investigated further by using more up to date data, see reference below. This has a significant impact as the more up to date photolysis study reduced the photolysis rate significantly, factor of 2-3. The older experiments did not look at the T dependence and assumed it insignificant. It turns out that at the wavelength of interest > 300 nm photolysis has a significant T dependence

Indication of the potential photolysis products (at 266 nm) can be ascertained by seeing if $R + O_2 \rightarrow OH$ occurs at low pressure. $CH_3CO + O_2$ is well known to do this reaction. Has this been checked?

While I understand the need to do the absorption measurements in solution, and then use theory to back-out the "gas-phase" values? I would maybe concentrate on the wavelengths of atmospheric interest (>300 nm). What difference is there between calculated and measured in this range. Is the % difference similar over the whole wavelength range? I'm not clear of the PCO cross-sections you have used in the photolysis calculations.

The abstract mentions exploring " $(CH_3)_3CC(O)CH_3$ photolysis (R4)" but it is not really as you have assumed it behaves as MEK and scaled the absorption cross-sections appropriately. You have only really explored the absorption cross-sections (theory and expt) but not the photolysis, where you have assumed it behaves MEK-like.

Maybe it should be stated in abstract that methyl pivalate does not photolysis in the atmosphere and therefore its lifetime in the atmosphere is control by only reaction with OH.

Specific comments

Line 24

UV-vis. spectroscopy experiments and computational calculations were used to explore (CH₃)₃CC(O)CH₃ photolysis (R4).

The absorption spectrum was determined in the solution phase and via theory translated to the gas-phase. Theory does not explore photolysis.

Line 25

Absorption cross sections for (CH₃)₃CC(O)CH₃, $\sigma_4(\lambda)$, in the actinic region were larger and the maximum was red-shifted compared to estimates used in current state-of-science models. As a consequence, we note that photolysis (R4) is likely the dominant pathway for removal of (CH₃)₃CC(O)CH₃ from the troposphere.

Red-shifted compared to what? I presume you mean MEK. You need to point out that MEK is being used as a proxy for PCO, where you are assuming that photolysis yields are the same except that you are scaling the absorption cross-sections.

Line 81

is therefore concerning. This seems a little overdramatic.

Line 106

"log gas temperature" While you estimate 15% error in the [OVOC] what do you estimate the accuracy of the temperature? The thermocouple will not be in the same place as where the laser beams overlap. Maybe also give typical gas flow rates for a given pressure.

Line 119

"S(t) = S₀ exp(-Bt)" Is there any residual signal at long times, i.e. do you have to add a baseline to Equation 1.

Line 119

2.2 Absorption cross sections, $\sigma(\lambda)$, via UV-vis. Experiments

It is noted that you state that the spectrometer measures over the range 250 – 400 nm, but the longest wavelength reported is 337 nm. Can you state why this is the case. It could be that you have hit the minimum absorption that can be measured, but as you only report cross-sections I cannot tell if this is the case.

Line 207

"Such non-Arrhenius behaviour may be indicative of a change of mechanism, with direct hydrogen abstraction dominating at high temperatures, whilst pathways via hydrogen bonded pre-reaction complexes play an increasingly important role at lower temperatures."

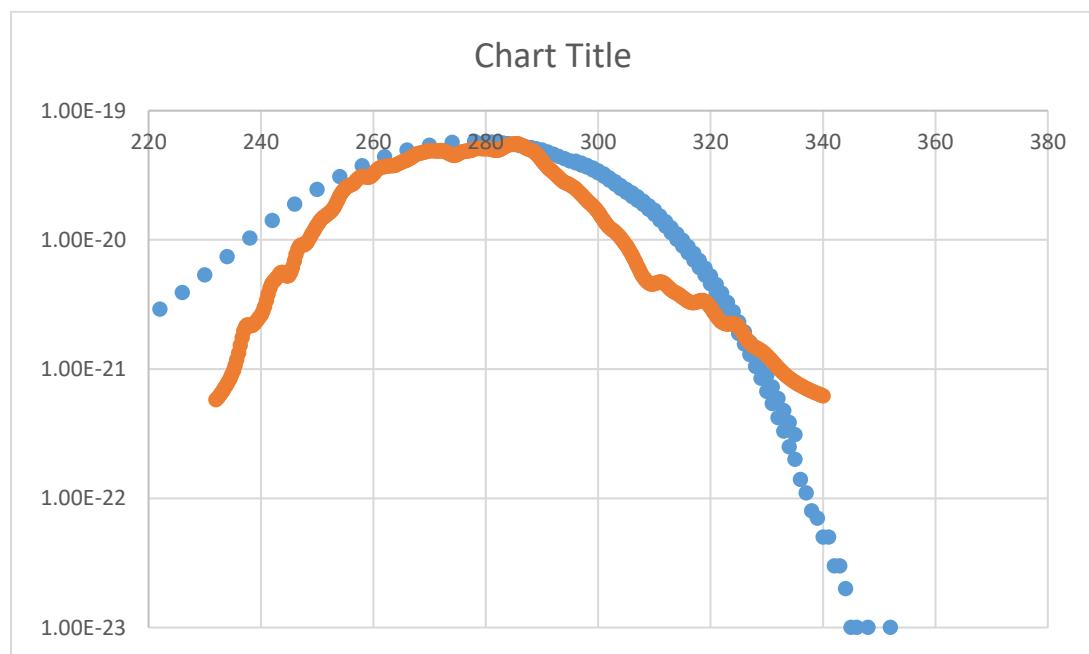
I do not think you have to invoke a different mechanism to explain this behaviour. It can be explained by the change in the rate determining step, from capture of the complex at low temperature to abstraction at high temperature, i.e., from outer to inner transition-state control as T is increased.

Line 263

“and as such does not reproduce the vibronic structure of a given electronic transition.” Is this related to problems in matching the experimental spectrum at long wavelength, > 300 nm? Does this mean the theory will not predict reliably the T dependence of the spectrum, which is often evident in the tail of the spectrum?

Line 269

“predicted by the NEA for MEK, again mimicking closely the shift observed experimentally when comparing the gas-phase cross-section with the MEK” While this is fair comment at the max of the spectrum, it is the values at in the actinic flux region that should also be considered. Below I have plot the MEK experimental and theoretical cross-sections (taken from the SI), where difference in the important 300-330 nm can reach a factor of ca. 5.



Line 276

“3.4 Estimation of photolysis rate coefficients (j values)” It is unclear what PCO cross-sections have been used in these calculations, theory or experimental? Please state.

Line 282

“Accordingly, the photolysis rate was calculated using $\varphi = 0.16$, the quantum yield determined by Pinho et al. (2005)” This reference is for isoprene degradation!

Line 288

The same procedure for the calculation of j for MEK leads to a quite different result (Fig. 6), with $j5 = 0.8 \times 10^{-6} \text{ s}^{-1}$ estimated using the cross sections determined in this work (see Fig. S6) and $j5 = 0.9 \times 10^{-6} \text{ s}^{-1}$ 290, determined using cross sections from Martinez et al. (1992) (Fig. 6).

A more recent study should also be considered:

DOI: [10.1039/B419160A](https://doi.org/10.1039/B419160A) (Paper) *Faraday Discuss.*, 2005, **130**, 73-88

Photolysis of methylethyl, diethyl and methylvinyl ketones and their role in the atmospheric HO_x budget

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Where the temperature dependence of the photolysis was explored. It is stated in this abstract that this reduces the photolysis rate by a factor of 2-3. This should be explored, especially when Table 3 has PCO's removal being dominated by photolysis.

Line 308

“confirmation of these results by e.g. the relative rate technique would be worthwhile in future.” Yes, it is noted that the 266nm laser will be photolysing the PCO. In fact, it is noted that if PCO photolyses to CH_3CO then at low pressures it can be tested via the well-known reaction $\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{OH}$. Was this considered?

Line 308 “anti-Arrhenius” It is more generally referred to as “non-Arrhenius”

Line 355

“Our UV-vis. results indicate a ratio of 0.95:1 between the integrated gas phase spectrum and the one recorded in solution (See SI for spectra integration).” Not sure where this 0.95 comes from. Is it theory gas-phase vs theory solution or theory vs experimental gas phase. Also, note that it is difference in the actinic flux region that is most important

Line 383

“However, this photolysis parameter appears to be based upon cross-section and quantum yield values from the MCM, determined for photolysis of MEK (R5).” Should also check the impact from the above paper on MEK, where T is considered.