

Atmospheric breakdown chemistry of the new green solvent 2,2,5,5- tetramethyloxolane via gas-phase reactions with OH and Cl radicals

Overall, general comment

This study has determined the gas-phase rate coefficients for the removal of tetramethyloxolane (TMO) with either hydroxyl (the main atmospheric oxidant) or chlorine radicals. Direct monitoring of OH in the presence TMO and TMO removal compared to another reagent – relative rate - provided two complimentary methods for determining the OH + TMO rate coefficient at room temperature. Excellent agreement was observed. The direct monitoring experiments were able to study the reaction over a range of elevated temperatures, up to 502 K, and the relative rate method also determined the Cl + TMO rate coefficient at room temperature. This experimental work has been carried out with enough suitable checks to give good confidence in their results. *Ab initio* calculations have been performed to indicate the site of H-abstraction, mainly at the CH₃ is suggested. Based on these experiments, I have no problem recommending this paper for publication. But the presentation of the calculations should be improved: show the potential energy surface and give the vibrational frequencies of the species in the SI.

Specific comments

To add further interpretation to the OH + TMO experimental results *ab initio* calculations have been carried out, where H-abstraction from either the CH₃ or the CH₂-ring was investigated. It is suggested that H-abstraction from the CH₃ is dominant at room temperature. In principle, enough information from these calculations is present to then carry out reaction rate theory calculations but this has not been done. Such calculations would better highlight the branching between CH₃ and CH₂ abstraction. It is conventional when doing such calculations to present the potential energy surface, but instead the free energy surface at 298 K has been presented. Also, no vibrations of the identified species of the reaction have been given in the SI. I recommend this be given in the supporting information.

In the discussion, it is highlighted that the observed OH + TMO rate coefficient is significantly smaller than predicted from the literature structural activity relationship, SAR, which is based on H-abstraction from the CH₂. Recognizing that abstraction is mainly via H-abstraction at the CH₃ allows a modified SAR to be constructed that is a better representation of the data, but still far from good. It is well-known that SAR struggle to fully describe experimental data over a range of temperatures when the reaction involves H-bonded complexes. As well as the *ab initio* calculations, further evidence of the involvement of H-bonded complexes in the reaction is supported by the “U-shaped” curved in the kinetic data, where at 340 K the minimum rate coefficient is observed. Based on Figure 6, the SAR and the modified SAR are straight-lines, but the experimental data is “curved”. Is it possible for a SAR to be “curved”?

As noted by RC1, is it reasonable to claim that “TMO is less problematic VOC than toluene”? Is this statement based on its rate coefficient alone? If this is the case then in an environment where Cl initiated oxidation dominants, then it is worse than toluene, as $\text{Cl} + \text{toluene}$ is 5.8×10^{-11} ! More of the full oxidation pathway needs to be taken into account. While it is suitably known for toluene, is it known for TMO beyond Figure 1?

Line by Line: technical

16 “*computational experiments*”?

49 “*with a photochemical lifetime of around two days*” I presume you mean wrt to OH, R3?

57 “*In air heavily impacted by atmospheric chlorine (Ariya et al., 1999; Atkinson and Aschmann, 1985; Thornton et al., 2010), TMO loss may be augmented by reaction with Cl atoms (R2).*” Are the likely sites of toluene / TMO emissions going to coincide with areas where [Cl] are significant?

107 “*situated downstream from a MFC and thus operating at close to reactor pressure*” How do you estimate how much this adds to the total flow through the system? You need to know this.

174 “ $S(t) = S_0 \exp(-Bt)$ ” Was there a baseline to worry about. Sometimes this is a probe induced problem, and sometimes there is an offset in the signal because of your measurement device.

178 “ $[\text{H}_2\text{O}_2] \cdot 1 \cdot 10^{14} \text{ molecule cm}^{-3}$ ” Is this concentration based on the intercept in Fig. 4? Using this and a typical photolysis energy allows an estimate of [OH]. My estimate is $\leq 10^{12} \text{ molecule cm}^{-3}$.

199 “*A mean of four values obtained at around room temperature yielded $k_1(296 \text{ K}) = (3.07 \pm 0.04) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$* ” If I look at Table 3, the 4 reported errors in the rate coefficients determination are close to 10%. So it is not clear how you have taken this data and assigned close to 1% error. Were the errors in Table 1 used? The uncertainty in flows and reagent concentrations normally means the accuracy of the measurement is higher than the quoted error.

236 “*A weighted mean value from these four relative rate determinations was $k_1, \text{RR}(296 \text{ K}) = (3.07 \pm 0.05) \times 10^{-12} \text{ cm}^3$* ” As noted above, weighted mean seems to lead to unrealistically small errors. If I look and Figures 7 and 8, the data in Figure 8 appear to have less systematic variation but has an error in k_2 of ~ 8%, while the k_1 has a quoted error of ~2%!

Are the errors quotes in this paper 1 or 2 sigma? Later in the discussion the above points are addressed by stating the overall uncertainty as just over 10%. This seems reasonable.

252 “*explore the hydrogen abstraction pathways (R1a) and (R1b) set out in Figure 1 and thus predict the products of (R1).*” To be clear, the *ab initio* calculations have only explored the abstraction. The potential products from these radicals are based on comparison other reactions? Was there evidence of the formation of these carbonyl products in the relative rate studies?

261 *“The free energy profiles of the reaction channels are presented in Figure 10”* These calculations could be presented in a more informative way. There should be enough information from these calculations to then do rate theory calculations, but was not attempted here. In order for someone else to make use of this data they would need the vibrations of all the species. This information is not given; please add it to the SI; also give the rotational constants. It is more conventional to show potential energy surfaces, PES, i.e. the energy of the reaction, enthalpy at zero K, rather than the free energy. By presenting free energy you are omitting giving the vibrational frequencies of the species.

Rate theory is statistical and only considers the turning points on the PES, so the distance between the species is not particularly that important. So, I do not consider the distance between the TS and pre-reaction complexes and *r* that important:

262 *mass-weighted distances (MWDs) quantifying the separation in Cartesian space between the TS and pre-reaction complexes, and key structural parameters (r_{O-H} , $r_{O \cdots H}$, and $a_{H-O \cdots H}$) are tabulated for each of the TS in Table 6.*

If the PES was shown, then I suspect there would be a strongly bound Pre-RC – ca. 20 kJ mol⁻¹ – and less strongly bound Pre-RC. And at low *T*, it will probably proceed mainly via strongly bound Pre-RC. But without rate theory this is conjecture.

278 *“The intimation is that the hydrogen-bound pre-reaction complex acts as a funnel on the free energy surface to bias the reaction towards preferential production of the kinetic (via R1b)”*

Yes, this will be generally the case at low *T*, but as *T* is increased the influence of the complex will be lost and the reaction will be controlled by TS. I think this is what your free energy is suggesting. If you calculated the free energy at say 200, 300, 400 and 500 K, it might show that the influence of the pre-RC is lost and the reaction rates are controlled almost solely by TS. I suspect, the fact that the rate coefficient start to increase above 350 K is where the influence of the complex is lost.

P313 *“the other two being direct non-stabilised (no H-bonds) abstractions.”* In Fig10 and SI, Pre-RC are given for all reactions? If there is direct abstraction, is there a Pre-RC?

The claim in the abstract that TMO is a less problematic solvent than toluene and **364**:

It is clear, therefore, that TMO has a longer lifetime than the solvent it is proposed to replace. A superficial assessment would indicate that, once emitted, TMO would have more time to disperse, leading to a less spatially-concentrated build-up of harmful products such as O₃, HCHO, and other aldehydes.

Should be further qualified. It is just based on its slower OH + TMO rate coefficient (“superficial”) rather than considering the full oxidation pathway, which I presume is not so well known for TMO compared to toluene.