Manuscript entitled "Organic photolysis reactions in tropospheric aerosols: effect on secondary organic aerosol formation and lifetime"
by Hodzic et al.

Reviewer #1 (Comments to Author):

R1.1) This is -as far as I can tell, not being a chemist– an excellent work on a difficult subject. The manuscript shows the importance of photolysis reactions (both gas-phase and in-particle) on the formation rate and lifetime of secondary organic aerosols. The manuscript combines nicely some box model calculations with a global chemistry model simulation. I think however that the authors need to improve the presentation and language if they want to be understood by non-chemist aerosol scientists. Below is a list of comments:

Response R1.1) We thank the reviewer for recognizing the importance and merits of our work, and we have done our best to respond to reviewer's specific comments below.

R1.2) The conversion of lifetimes from permanent daylight conditions to equivalent summer or winter conditions is a little unclear (although I understand what the authors mean).

Response R1.2) The concept of the photolysis age in JNO2 equivalent summertime or wintertime days is already defined in the manuscript:
"We define the Photolysis Age in JNO2 equivalent days (Table 1) as the JNO2 exposure of the simulated SOA during our simulations normalized to a 1 day average summer (or winter) JNO2 exposure: Photolysis Age=(JNO2× time)/JNO2_average, where time is the duration of the simulation in days. Photolysis Age values are reported in Table 1 for our experiments. Typically, our 1 week simulations performed under constant lights at mid-latitudes and a solar zenith angle of 45° (JNO2 = 8.1×10^{-3} s^{-1}) are equivalent to about 2 equivalent weeks of exposure in the atmosphere at mid-latitudes during summer, or to about 38 equivalent days during winter."

We have also simplified Table 1 as discussed in R1.14.

R1.3) There is no reason to mix 45 SZA and mid-latitude conditions as it is done in a number of places (eg line 10 in the abstract, line 7 on page 8120, or in caption of figure 1). Likewise on line 25 on page 8120, why mention the 45 SZA here? A solar zenith angle of 45 is a solar zenith angle of 45 and can occur at many latitudes. So I would simply say that the effects of JNO2 for a SZA of 45 under permanent light conditions corresponds to (roughly) twice the effects of a varying JNO2 in summer mid-latitude conditions. Or maybe the "mid-latitude conditions" correspond to something else than the SZA but that's not clear in the manuscript. It is required also to say how the equivalence was done (or in what sense it is an equivalence) and what the uncertainty on this equivalence is.

Response R1.3) The reason for specifying both the solar zenith angle and the latitude in the paper is that the overhead ozone column changes at different locations which impacts the photolysis calculations. See Table 1 for the corresponding ozone overhead column values. This is now clarified in the manuscript:

"Typical ozone overhead values are used at different locations based on the Total Ozone Mapping Spectrometer data (http://disc.sci.gsfc.nasa.gov/acdisc/TOMS)."

R1.4) Some chemical terms and notations would benefit from being explicited. In particular the notation on line 21 page 8122 (and also in Fig 2) is not clear to me. Sorry if I sound stupid, but what does the H add to a K functional group that already has two R groups?

Response R1.4) H, K, N, O, etc. refer to various functional groups that may be present in a particular molecule, as detailed in lines 17-19 on that same page 8122. For example, HHKKK refers to a molecule that contains two hydroperoxide and three ketone groups. This is now more clearly explained in the manuscript:

"Ketone (K) and alcohol (O) moieties are present in a majority of the molecules, while hydroperoxides (H) are seen mainly at low NOx and nitrates (N) mainly at high NOx. Gas-phase photolysis leads to a decrease in most species, which seems to be particularly important for highly functionalized compounds containing multiple carbonyl and nitrate groups (e.g. HKKKK, HHKK, HHKKK, HKKK, NNKK, NNKO where e.g. HHKK refers to a molecule that contains two hydroperoxide and two ketone groups)."

R1.5) What is an activation value (line 10, page 8123)? Is this a dimensionless quantity?

Response R1.5) We have changed the term "activation value" to "activation factor" which is defined in the manuscript on page 8118:

"Kinetic data for OH / hydroperoxide reactions are sparse in the literature, and previous versions of GECKO-A assumed an activation factor (i.e. an enhancement of the rate constant due to the presence of the functional group) of 14 on the basis of data for the OH/CH3OOH reaction."

R1.6) It would be interesting to show what actinic wavelengths are involved. Can the effects of the photolysis (calculated here at pretty low concentrations) saturate with the amount of organics present in the atmosphere? or be amplified in the presence of aerosols and clouds? I would think that a figure showing the distribution and strengths of absorbed wavelengths would be useful to the reader.

Response R1.6) We interpret this question as saying: Can absorption by organics (gas or particle phase) affect the radiation field itself, and therefore provide a negative (saturating) feedback on the photochemistry? Typical aerosol optical depths (scattering + absorption) rarely exceed 2 even in highly polluted urban settings, and only a fraction (1 minus the single scattering albedo) is absorbed. Taking a very polluted conditions with total AOD = 2 and SSA = 0.9 gives an absorption optical depth of 0.2, corresponding to about 20% reduction in radiation (Beer-Lambert, $F(z,\lambda)/F_{TOA}(\lambda)=\exp(-AOD(z, \lambda))$ for overhead sun). This is a significant but not overwhelming reduction, so that even under these highly polluted conditions the photochemistry is expected to proceed vigorously. Regional and global effects are expected to be smaller.

This is now explained in the manuscript:

"We note that the absorption by organic gases and/or particles is not expected to substantially affect the radiation field itself. Even in highly polluted conditions, aerosol optical depth (AOD) rarely exceeds 2, and only a fraction (1 minus the single scattering albedo (SSA)) is absorbed e.g. AOD=2 and SSA=0.9 gives an absorption optical depth of 0.2, corresponding to about 20% reduction in radiation. This is a significant but not overwhelming reduction, so that even under these highly polluted conditions the photochemistry is expected to proceed vigorously. Regional and global effects are expected to be smaller."

R1.7) In section 3.1 the whole discussion is in terms of formation rate, why not discuss the effects on concentrations as well?

Response R1.7) In section 3.1, we choose to discuss the effect of photolysis on SOA formation yields as typically done in chamber experiments because we are using idealized box model simulations to quantify the effect of a given process on SOA formation. Talking about concentrations is not appropriate in this case as concentrations depend on e.g. dilution, boundary layer mixing and deposition which are not included in these idealized box model simulations.

R1.8) In section 3.2 for the first approach, it seems to me that there is another assumption which is that radiation at actinic wavelengths penetrates through the particle and can induce photolysis in the whole volume of the particle. I think this is a different thing than the "caging" effects mentioned by the authors. This may not be a bad assumption for small accumulation mode particles, but may not be correct for the larger particles and the smaller wavelengths. I must say I am not sure of this though but it would be good to discuss it!

Response R1.8) We interpret this question as asking whether it is realistic to assume that light can penetrate the whole volume of the particle without being attenuated by the absorbers. This could be a problem for species having a large MAC >> 1 m^2/g such as soot but it is a reasonable assumption for organic species and for MAC values considered in our calculations.

For instance, in the manuscript we consider a typical organic particle with MAC = 0.1 m^2/g and 200 nm diameter particles, density 1.5 g/cm^3. Its optical cross section is MAC x mass of particle = 0.1 x 6.3e-15 m^2, whereas its geometric cross section is (pi)R^2 = 3.1 e-14 m^2. So the ratio between optical/geometric cross section ~ 0.02. This is a rough calculation and should be done fully with Mie theory if the opt/geom ratio were closer to unity, but when it is so small it is just not necessary. For comparison, for soot MAC = 10 m^2/g and the ratio optical/geometric = 2, suggesting that the attenuation is expected to occur within the particle.

The following sentence was added to the manuscript:

"We note that for the chosen MAC value the light can penetrate the whole volume of the particle without being significantly attenuated by the absorbers (light attenuation was estimated to be less than 2-3%, see discussion SI Annex IV)."

And the following Supplementary Information was included:

Annex IV: Estimate of the light attenuation by an absorbing particle

<u>1) Method 1:</u>

The light attenuation can be roughly estimated as a ratio between the absorption cross section of the particle and its physical cross section. Here we assume a typical organic particle with MAC = 0.1 m^2/g, 200 nm diameter and 1.5 g/cm^3 density. Its optical cross section is MAC x mass of particle = 0.1 x 6.3 x 10^{-15} m^2, whereas its geometric cross section is πr^2 = 3.1 x 10^{-14} m^2. Thus, the ratio between optical and geometric cross section is ~ 0.02, meaning that about 2% of photons are absorbed by the particle, and that the rest will go through the particle. A more accurate estimate could be derived from the Mie theory, but the corrections due to the full theory are typically within a factor of 2 (Ray and Bhanti, 1997; Mayer and Madronich, 2004), and thus that is not required in this case. For comparison, for soot MAC = 10 m^2/g and the ratio optical/geometric = 2, suggesting that substantial attenuation is expected to occur within the particle.

Ray A.K., and Bhanti D.D., Effect of optical resonances on photochemical reactions in microdroplets. Applied Optics, Vol. 36, No. 12, 1997.

Mayer B., and Madronich, S. Actinic flux and photolysis in water droplets: Mie calculations and geometrical optics limit. Atmos. Chem. Phys. 4, 2241–2250, 2004.

2) Method 2:

According to the Beer Lamber's law the transmitted light can be written as:

$$I/I_0 = \exp(-MAC \times \rho \times L) \qquad (1)$$

Where MAC represents the mass absorption coefficient ($m^2\ kg^{-1}$), ρ density of the particle ($g\ cm^{-3}$), and L the particle diameter (m). If we consider a particle with $MAC = 0.1\ m^2/g$, $\rho = 1.5\ g\ cm^{-3}$, and $L = 2\times10^{-5}$ cm, we can calculate $I/I_0 = 0.9704$, which means that ~97% of the initial signal was transmitted.

The attenuation by the particle is ~3%. In other words, the optical depth of the considered particle is 0.03, which suggests that the attenuation of light (in the continuous model) is small.

R1.9) line 25, page 8124: do the authors mean "urban scale" or "urban conditions" here? Or is it the time the air mass passes over an urban area that is relevant?

Response R1.9) Urban scale is the correct wording here as we refer to the lifetime of SOA with regards to photolysis compared to its typical lifetime with respect to other removal processes and transport/mixing timescales.

R1.10) A mass absorption coefficient of 10 m2/g is not credible for SOA, and even less so if all the absorption occurs between the 300–400 nm wavelength range. Values of 10m2/g are typical for black carbon with absorption throughout the solar spectrum.

Response R1.10) In this study we use the value of 0.1 m^2/g for SOA. However, according to ambient measurements reported by Barnard et al., 2008, values as high as 10.5 m^2/g were observed at 300nm in Mexico City which is dominated by organic aerosols. They estimated that the light absorption by the "brown" (organic) carbonaceous aerosol can add about 40% to the light absorption of black carbon in Mexico City. We note that absorption coefficients are wavelength specific, and do not need to apply to the whole solar spectral range.

This study is referenced in the manuscript: *"Recently measured MAC values range from 0.03 to 0.5 m^2g^{-1} for laboratory data (Lambe et al., 2013) or from 0.1 to 10 m^2g^{-1} for ambient urban measurements (e.g. Barnard et al., 2008) in the 300-400 nm wavelength interval."*

R1.11) I am not sure Eqn. 1 and 2 are consistent, the first one depends on JNO2, the second not. Or is one of the JNO2 for normalized conditions in Eqn 1 but not the other one? What is the unit of the 0.4 value in Eqn 2?

Response R1.11) Eqs 1 and 2 are consistent, and are written as:

$$J\_SOA = [AF/J\_NO2] \times [mc] \times J\_NO2 \times [MAC] \times [QY] \qquad (1)$$

$$J\_SOA = 0.4 \times J\_NO2 \times [MAC] \times [QY] \qquad (2)$$

where AF is the actinic flux (photons m^{-2} s^{-1}), MAC is the SOA mass absorption coefficient (m^{2} g^{-1}), mc is the mass of one carbon atom (g) and QY is the quantum yield. Using the photolysis model TUV we estimated estimate AF/jNO2 = 2e22 photons m^{-2} over 280-400 nm at 1 km altitude and overhead sun, which combined with mc gives: (2e22 photons m^{-2})(12 g mol^{-1})/(6e23 mol^{-1})= 0.4 photons g m^{-2}.

We have clarified this in the revised manuscript:

"We represent the photolytic SOA loss as a first order reaction, with effective reaction rate coefficient J_{SOA}:

$$J_{SOA} = [AF] \times [MAC] \times [mc] \times [QY] \qquad (1)$$

where AF is the actinic flux (photons m^{-2} s^{-1}), MAC is the SOA mass absorption coefficient (m^{2} g^{-1}), mc is the mass of one carbon atom (g) and QY is the quantum yield or the probability that absorbed photons will lead to bond cleavage and the loss of some mass from the particle. We assume that if each absorbed photon leads to the loss of one C atom, the quantum yield is equal to one.

We scaled (1) to known NO_2 photolysis:

$$J_{SOA} = J_{NO2} \times [AF/J_{NO2}] \times [MAC] \times [mc] \times [QY] \qquad (2)$$

The photolysis model TUV (v5.1, (Madronich et al. 1993)) was used to estimate the UV actinic flux (= 2×10^{20} photons m^{-2} s^{-1}) and NO_2 photolysis (= 9.7×10^{-3} s^{-1}) over 280-400 nm at 1 km altitude and overhead sun, which combined with [mc] gives $[AF/J_{NO2}] \times [mc] = 0.4$ photons g m^{-2}."

R1.12) Line 13 on page 8127: 1.2 must be 1.2% or what?

Response R1.12) 1.2 is the average effective photolysis quantum yield that was reported by Wong et al., 2014 as 1.2 +/- 0.2 for a-pinene photolysis. Effective quantum yields can be larger than unity, depending on further reactions after the initial photodissociation. This is already explained in the manuscript:

"..whereas Wong et al. (2014) estimated an effective quantum yield of 1.2+/-0.2 for the loss of organics in the case of α-pinene SOA photolysis."

R1.13) Line 14 on page 8128: is the lifetime of 20 days a summer equivalent one? or for continuous daylight conditions?

Response R1.13) Those are equivalent days. This is now clarified in the manuscript:

"except for high-NOX toluene SOA with a lifetime of 20 equivalent summer days for which the effect of photolysis is likely underestimated in our simulations as discussed above."

R1.14) Table 1: the JNO2 exposure in 1 day is a complicated term accompanied by a complicated footnote to say that it is the same quantity as in the previous column but in unit of day -1 instead of s-1. Or am I missing something?

Response R1.14) We agree with the reviewer that this probably added more confusion than clarity. Thus we have removed the JNO2 exposure in 1 day columns from Table 1. This term wasn't used in the text and can be easily calculated from the JNO2 value itself as mentioned by the reviewer.

R1.15) Figure 2: the sums of the C atom ratios in each plot is far from 1. Where is the rest of the C mass? How many SOA constituents in total?

Response R1.15) On these plots we only show the fraction that has partitioned to the particle-phase, the rest of the C mass is in the gas-phase. The number of SOA constituents varies for various precursors e.g. 22,600 species for C12 n-alkane, 32,315 for C16 n-alkane, 126,587 for alpha-pinene, and 2,305 for toluene. We have added the following sentence to the caption of Figure 2 for clarity:

"The carbon atom ratio indicates the ratio of the carbon atoms in the condensed phase to the initial carbon load included in the parent backbone. The sum of the shown particle-phase constituents is lower than one as the rest of the carbon mass is in the gas-phase."

R1.16) Figure 4 is particularly unclear and the caption and the associated text calling Figure 4 did not help me at all. What is C*? Why is volatility expressed in mass concentrations of SOA?

Response R1.16) The volatility is expressed in terms of the effective saturation concentration (C*; which is the inverse of a Pankow-type partitioning coefficient, Donahue et al., 2006). The C* notation is very commonly used in the SOA literature at present. This was clarified in the caption of the figure:

"Distribution of products of OH oxidation of 1 ppt of α-pinene, toluene, C12 and C16 n-alkanes at low (0.01 ppb) and high (10 ppb) NOx levels according to their volatility. The volatility is expressed in terms of the effective saturation concentration (C*)."

R1.17) The caption of Figure 5 does not describe what is represented on the figure. The figure represents SOA concentration, not SOA formation, as a function of time, although I agree it tells something on SOA formation.

Response R1.17) We agree with the reviewer and have corrected the corresponding caption to read:

"Predicted effect of photolysis on SOA concentrations from the oxidation of 1 ppt of α-pinene, toluene, C12 and C16 n-alkanes at low (0.01 ppb) and high (10 ppb) NO_X levels."

R1.18) On Figure 7, bottom panels, it should be d[SOA]/[SOA] rather than just d[SOA]. The figures are far too small and I had to zoom many times to be able to read them. I also noted that figures are not called in order in the text.

Response R1.18) We thank the reviewer for catching this error, we have fixed the labels of the Figure 8 to read d[SOA]/[SOA]. We will make sure that the figures are big enough and easy to read on the ACP final pages during the proofreading stage.