Supplementary Information for "Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol"

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1 OH Reaction Rate Coefficients

1.1 Structure-Reactivity Relationship

As discussed in Kwok and Atkinson (1995), the rate coefficients for abstraction of a hydrogen atom from primary ($-CH_3$), secondary ($-CH_2-$) and tertiary ($>CH-$) groups depends on the nature of the substituents attached to the carbon atom. They give generalized rate coefficients for these different carbon groups as:

$$k(CH_3 - X) = k_{prim}f_x \tag{S1.}$$

$$k(X - CH_2 - Y) = k_{sec}f_xf_y \tag{S2.}$$

$$k(X - CH < XZ) = k_{tert}f_xf_yf_z \tag{S3.}$$

1   where X, Y and Z represent different substituent groups, k_{prim}, k_{sec} and k_{tert} are the "group" rate

2   coefficients for the primary, secondary and tertiary groups and the f_x, f_y and f_z are substituent-

3   dependent modification factors for the rate coefficients. Kwok and Atkinson (1995) give values

4   of the modification factors for a variety of functional group substituents, with $f_{CH3} = 1$, $f_{CH2} = f_{CH}$

5    $= 1.23$, $f_{>CO} = 0.75$, $f_{OH} = 3.5$ and $f_{CH2C(O)} = 3.9$, where $f_{>CO}$ indicates an adjacent ketone, $f_{CH2C(O)}$

6   indicates a ketone that is two carbons away and f_{OH} is for an alcohol.

7   For a given molecule, the total rate coefficient is the sum over the (substituent-specific) group

8   rate coefficients for each carbon atom in the molecule, or

9    $$k_{OH} = k(CH_3) + k(CH_2) + k(CH) = \sum_h k(CH_3)_h + \sum_i k(CH_2)_i + \sum_j k(CH)_j \qquad \text{(S4.)}$$

10   and h, i and j are the number of primary, secondary and tertiary carbon atoms in the molecule,

11   respectively. Thus, for a straight-chain hydrocarbon with N_C carbon atoms, k_{OH} can be simply

12   written as

13    $$k_{OH} = 2k_{prim}f_{CH2} + 2k_{sec}f_{CH3}f_{CH2} + (N_C - 4)k_{sec}(f_{CH2})^2 \qquad \text{(S5.)}$$

14   where f_{CH3} and f_{CH2} are the modification factor for CH_3 and CH_2 substituent groups, respectively,

15   and where $k_{prim} = 1.36 \times 10^{-13}$ cm^3 molecules^{-1} s^{-1}, $k_{sec} = 9.34 \times 10^{-13}$ cm^3 molecules^{-1} s^{-1}, $k_{tert} =$

16   1.94×10^{-12} cm^3 molecules^{-1} s^{-1} (Kwok and Atkinson, 1995).

17   **1.2   SOM-Reactivity Relationship**

18   Upon reaction with OH, oxygen-containing functional groups will be added. The types of

19   functional groups that can be added include alcohols, ketones, aldehydes, carboxylic acids,

20   organic nitrates and peroxides, among others. The SOM, does not track explicitly the type of

1 functional group added, only the number of oxygen atoms added (with an assumption of some

2 relationship between volatility and the nature of the functional group added). It is therefore not

3 possible to make direct use of the structure-reactivity relationships of Kwok and Atkinson (1995)

4 within the SOM framework, and therefore a new, approximate parameterization must be

5 developed.

6 To develop a "structure"-reactivity relationship that is appropriate for the SOM we make the

7 simplifying assumption that only ketone and alcohol functionalities are added. Also, we make

8 the assumption that oxygen is added to all CH_2 groups before it is added to CH_3 groups and that

9 all carbon atoms (i.e. CH_2 and CH_3 groups) add at least one oxygen-containing functional group

10 before a second functional group is added to any specific carbon atom. In very general terms, the

11 addition of an alcohol group increases the reactivity of a molecule by increasing the reactivity of

12 the carbon atom to which the alcohol group is attached. The addition of a ketone group decreases

13 slightly the reactivity of the carbon atom adjacent to the ketone group but increases the reactivity

14 of the carbon atom that is two carbons away, as is clear from comparison of the $f_{>CO}$ and $f_{CH2(CO)}$

15 modification factors.

16 Equation S5 gives the reactivity for the parent hydrocarbon. The SOM requires that we specify

17 the reactivity of all product species. First, consider a limiting case of only alcohol addition, but

18 where $N_C - N_O \geq 2$. In this case, the reactivity of the molecule after alcohol addition is

19 approximately:

20 $$k_{OH} \sim 2k_{prim}f_{CH2} + (N_C - 2 - N_O)k_{sec}f_{CH2}^2 + N_O k_{tert}f_{OH}f_{CH2}f_{CH2} \qquad \text{(S6.)}$$

1   where we have made use of the relationship $f_{CH2} = f_{CH}$ and have treated all CH_2 groups the same

2   for simplicity. The result is that alcohol addition leads to an increase in the overall reactivity of a

3   molecule.

4   What happens instead if only ketone groups are added? Ketone groups affect not only the

5   reactivity of the adjacent carbon atoms, but also those atoms that are two carbons away. As the

6   number of ketone groups increases, the number of possible isomers increases, making it

7   impossible to come up with a general solution (note that the same is true for alcohol addition, but

8   since alcohol groups only influence the reactivity of the carbon to which the alcohol is added and

9   the adjacent carbon, the challenge is not quite so acute). Nonetheless, some generalizations can

10   nonetheless be made: (1) the number of CH's with adjacent CH_2 groups decreases approximately

11   linearly with ketone addition, (2) the number of CH's with adjacent ketone groups increases

12   approximately linearly with ketone addition, and (3) the number of CH's with ketone groups two

13   carbons away and without an adjacent ketone group decreases once the number of ketones is

14   ~half the number of carbon atoms. To account for these different situations, we introduce two

15   parameters, a and b, where:

16      $$a = \frac{N_O}{N_C - 2} \tag{S7.}$$

17   and

18      $$b = 1 - \frac{\left|\frac{N_C - 2}{2} - N_O\right|}{\frac{N_C - 2}{2}} \; if \, N_O > \frac{N_C - 2}{2}, else \; b = 1 \tag{S8.}$$

1   Here, $N_C - 2$ is used as the reference case (instead of N_C) because only the case where $N_O \leq N_C -$

2   2 is currently being considered. The parameter a increases linearly with oxygen addition whereas

3   the parameter b is unity until $0.5(N_C\text{-}2) = N_O$, after which it decreases towards zero. The total

4   reactivity then evolves approximately as:

5    $k_{OH} \sim 2k_{prim}\left[(1-a)f_{CH2} + a\left(\frac{f_{>CO}+f_{CH2C(O)}}{2}\right)\right]$

6    $+(N_C - 2 - N_O)k_{sec}\left[(1-a)f_{CH2}f_{CH2} + a\left(\frac{bf_{>CO}f_{CH2(CO)}+f_{>CO}f_{CH2}+bf_{CH2}f_{CH2C(O)}}{2b+1}\right)\right]$ (S9.)

7

8   The above alcohol-only and ketone-only cases provide some understanding of how the reactivity

9   of the hydrocarbon evolves as oxygen is added. However, as our base case we make the

10   simplifying assumption that equal numbers of ketone and alcohol groups are added. Combining

11   the alcohol-only and ketone-only expressions, the following is obtained for the *approximate*

12   variation of k_{OH} with oxygen addition:

13    $k_{OH} \sim 2k_{prim}\left[(1-a)f_{CH2} + a\left(\frac{f_{>CO}+f_{CH2C(O)}+f_{OH}}{3}\right)\right]$

14    $+(N_C - 2 - N_O)k_{sec}\left[(1-a)f_{CH2}f_{CH2} + a\left(\frac{bf_{>CO}f_{CH2C(O)}+f_{>CO}f_{CH2}+bf_{CH2}f_{CH2C(O)}}{2b+1}\right)\right]$

15    $+0.5N_Ok_{tert}\left[(1-a)f_{OH}f_{CH2}^2 + af_{OH}\left(\frac{f_{>CO}+bf_{CH2C(O)}+f_{CH}}{b+2}\right)^2\right]$ (S10.)

16

17   Equation 10 is the general expression that is used in the SOM to calculate the reactivity of all

18   species when $N_O \leq N_C - 2$. As an example, consider the predicted k_{OH} values for C_6 species

19   relative to observations. The measured k_{OH} for hexane (C_6H_{14}), 2-hexanol ($C_6H_{14}O$) and

20   hexanone ($C_6H_{12}O$) are 5.2×10^{-12}, 1.21×10^{-11} and 8.06×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively, and

21   where the hexanone value is the average of 2-hexanone and 3-hexanone (Atkinson et al.,

1   1982;Wallington et al., 1988;Atkinson, 2003). The average of the ketone and alcohol-containing

2   species k_{OH} values is 9.14×10^{-2} cm^3 molecules^{-1} s^{-1}. The Atkinson structure-reactivity relationship

3   predicts values of k_{OH} for hexane, 2-hexanol, 2-hexanone and 3-hexanone of 5.46×10^{-12},

4   1.27×10^{-11}, 8.17×10^{-12} and 7.89×10^{-12} cm^3 molecules^{-1} s^{-1}, giving an average k_{OH} for molecules

5   with one oxygen (either ketone or alcohol) of 1.04×10^{-11} cm^3 molecules^{-1} s^{-1}. For comparison, the

6   SOM k_{OH} values for C_6 and for C_6O are 5.45×10^{-12} and 1.17×10^{-11} cm^{-3} molecule^{-1} s^{-1}, which

7   differ from the measured values by 5% and 28%, respectively and are in very good agreement

8   with the values derived using the Atkinson structure-reactivity relationship. A few further

9   examples are shown in Section 1.2 to illustrate that Eq. S8 provides reasonable k_{OH} values (at

10   least under the assumption that equal numbers of ketones and alcohol groups are added).

11   Equation S12 was developed for the case $N_C - N_O \geq 2$. As more oxygen atoms are added (again

12   assuming equal addition of alcohols and ketones), a modified expression is required. Since we

13   have made the simplifying assume that all carbon atoms add one oxygen before any carbon can

14   add two oxygens, when $N_C - N_O > 2$ there are no longer any secondary carbon atoms to react

15   (since we also assumed the oxygen is preferentially added to CH_2 groups over CH_3 groups).

16   Thus, when $N_C - 1 = N_O$:

17   $k_{OH} \sim k_{prim} \left[\frac{f_{>CO} + f_{CH2C(O)} + f_{OH}}{3} \right]$

18   $\qquad + 0.5 k_{sec} \left[f_{OH} \frac{(f_{>CO} + f_{CH2C(O)} + f_{CH})}{3} \right] + 0.5 N_O k_{tert} \left[f_{OH} \left(\frac{f_{>CO} + f_{CH}}{2} \right)^2 \right]$ (S11.)

19

20   And when $N_C = N_O$

6

1 $$k_{OH} \sim k_{sec}\left[f_{OH}\frac{(f_{>CO}+f_{CH2C(O)}+f_{CH})}{3}\right] + 0.5N_O k_{tert}\left[f_{OH}\left(\frac{f_{>CO}+f_{CH}}{2}\right)^2\right] \qquad\text{(S12.)}$$

2

3 As even more oxygen atoms are added, such that each carbon atom can now have multiple

4 oxygen atoms, the reactivity will decrease because the number of hydrogen atoms available for

5 abstraction will decrease (where we are neglecting the abstraction of hydrogen atoms from

6 alcohol groups). With these assumptions, when $2N_C = N_O$ the reactivity will drop to zero and it

7 will decrease linearly with N_O from the reactivity at $N_C = N_O$. Thus, when $N_O > N_C$:

8 $$k_{OH} \sim 0.5N_O k_{tert}\left[f_{OH}\left(\frac{f_{>CO}+f_{CH}}{2}\right)^2\right]\left(1 - \frac{N_O}{2N_C}\right) \qquad\text{(S13.)}$$

9

10 Equations S10-S13 define a "structure"-reactivity relationship that is appropriate for use in the

11 SOM, termed the SOM-reactivity relationship. The rate coefficients determined from the SOM-

12 reactivity relationship are shown in Figure S1 and explicitly illustrate how the calculated rate

13 coefficients vary with the number of carbon atoms in the parent atom, the absolute number of

14 oxygen atoms and the O:C ratio. For larger N_C compounds, the variations of k_{OH} with O:C are

15 similar. However, as N_C decreases the calculated k_{OH} values increase more steeply with O:C.

16 Similarly, the increase in k_{OH} per oxygen atom added is greater for smaller N_C compounds.

17 Noting that the y-axis in Figure S1 is logarithmic, this is in large part the reason for the relatively

18 flat aerosol yield with N_C when $N_C < \sim 12$ for the case when fragmentation is not included in the

19 SOM (c.f. Figure 2c in the main text).

1   Not considered in the SOM-reactivity formulation is the influence of nitrogen containing groups

2   on reactivity. In general, the presence of $-NO_2$ or $-ONO_2$ groups leads to a substantial decrease

3   in the reactivity of a molecule, affecting both the reactivity of the CH to which the nitrogen

4   group is bonded as well as the reactivity of the adjacent CH's. Thus, when organic nitrates are

5   formed (which can occur during reactions under high NO_x conditions), the SOM-reactivity

6   relationship may over-estimate the reactivity of the product molecules. If the k_{OH} values for the

7   product species are over-estimated, the best-fit ΔLVP may be somewhat lower or the

8   fragmentation probability somewhat higher than if a more appropriate k_{OH} matrix were used.

9   However, this is unlikely to affect the ability of the SOM to be fit to laboratory observations of

10 SOA growth.

11 **1.3   Structure-Reactivity vs. SOM-Reactivity Example: Dodecane + 4 oxygens**

12 Here, k_{OH} values for five different isomers of a C_{12} compound (i.e. dodecane, $CH_3(CH_2)_{10}CH_3$)

13 that all contain 4 oxygen functional groups are calculated using the Atkinson structure-reactivity

14 relationship and compared with the SOM-reactivity k_{OH} values. In all cases, we consider only

15 isomers in which equal numbers of ketones and alcohols have been added, consistent with the

16 SOM-reactivity relationship derivation. Since the SOM provides an average representation of the

17 reactivity, it is most appropriate to compare the *average* k_{OH} derived from the k_{OH} values of the

18 individual isomers with the SOM k_{OH}, as will be done in Section 1.3.6.

19 **1.3.1   Case 1**

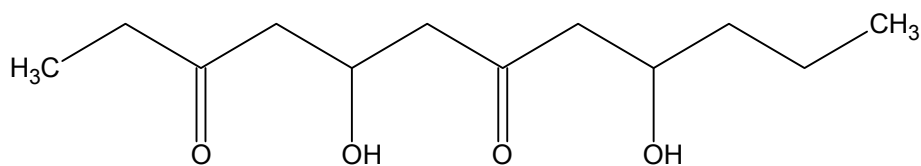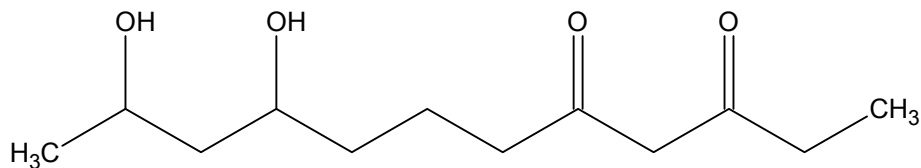20 One possible $C_{12}O_4$ isomer is:
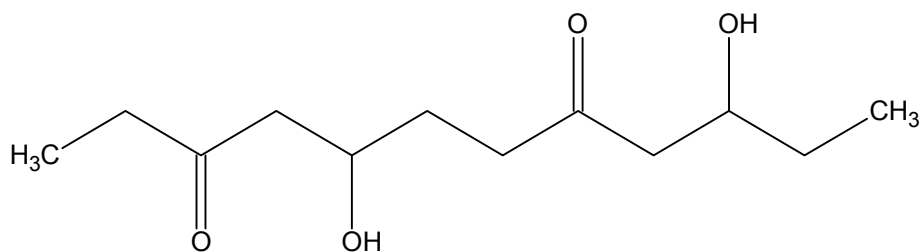
1

2   The k_{OH}, using the explicit Atkinson structure-reactivity relationships for this molecule, is:

$$k_{OH} = k_{prim}f_{CH2C(O)} + k_{sec}f_{CH3}f_{>CO} + k_{sec}f_{>CO}f_{CH} + k_{tert}f_{CH2C(O)}f_{OH}f_{CH2} + k_{sec}f_{CH}f_{CH2C(O)}$$

$$+ k_{sec}f_{>CO}f_{CH} + k_{sec}f_{<CO}f_{CH} + k_{tert}f_{CH2C(O)}f_{OH}f_{CH2} + k_{sec}f_{CH2}f_{CH3}$$

$$+ k_{prim}f_{CH2}$$

3   which gives k_{OH} = 7.46×10^{-11} cm^3 molecule^{-1} s^{-1}. This can be compared to the k_{OH} from the

4   SOM-reactivity relationship developed above, which for $C_{12}O_4$ gives 4.38×10^{-11} cm^3 molecule^{-1}

5   s^{-1}.

6   **1.3.2   Case 2**

7   Another $C_{12}O_4$ isomer is considered:

8

9   The k_{OH} using the explicit Atkinson structure-reactivity relationships for this molecule is:

$$k_{OH} = k_{prim}f_{CH2C(O)} + k_{sec}f_{CH3}f_{>CO} + k_{sec}f_{>CO}f_{CH} + k_{tert}f_{CH2C(O)}f_{OH}f_{CH2C(O)}$$

$$+ k_{sec}f_{CH}f_{>CO} + k_{sec}f_{>CO}f_{CH} + k_{tert}f_{CH2C(O)}f_{OH}f_{CH2} + k_{sec}f_{CH}f_{CH2}$$

$$+ k_{sec}f_{CH2}f_{CH3} + k_{prim}f_{CH2}$$

1   which gives $k_{OH} = 1.42 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, compared to the SOM-reactivity value of

2   4.38×10^{-11} cm^3 molecule^{-1} s^{-1} for a generic $C_{12}O_4$ species.

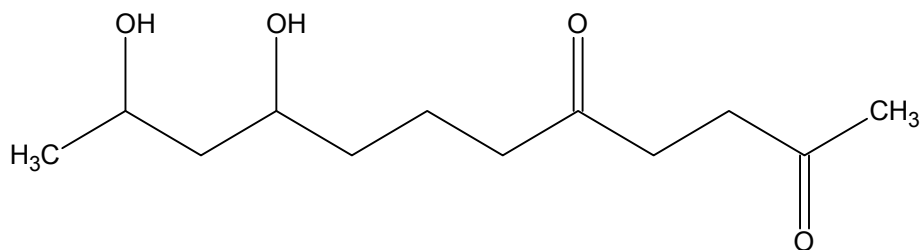3   **1.3.3 Case 3:**

4   Another $C_{12}O_4$ isomer is considered:

5

6   The k_{OH} using the explicit structure-reactivity relationships for this molecule would be:

$$k_{OH} = k_{prim}f_{CH} + k_{tert}f_{CH3}f_{CH2}f_{OH} + k_{sec}f_{CH}f_{CH} + k_{tert}f_{CH2}f_{CH2}f_{OH} + k_{sec}f_{CH}f_{CH2}$$

$$+ k_{sec}f_{CH2C(O)}f_{CH2} + k_{sec}f_{CH}f_{>CO} + k_{sec}f_{>CO}f_{>CO} + k_{sec}f_{>CO}f_{CH3}$$

$$+ k_{prim}f_{CH2C(O)}$$

7   which gives $k_{OH} = 2.87 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, compared to the SOM-reactivity value of

8   4.38×10^{-11} cm^3 molecule^{-1} s^{-1} for a generic $C_{12}O_4$ species.

9   **1.3.4 Case 4:**

10   Another $C_{12}O_4$ species is considered:

1
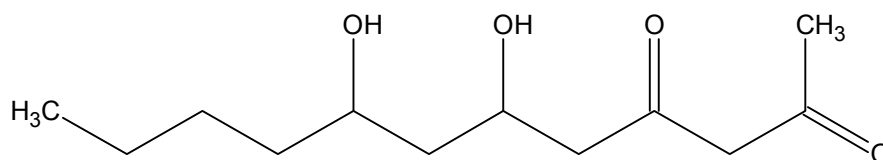
2   The k_{OH} using the explicit structure-reactivity relationships for this molecule would be:

$$k_{OH} = k_{prim}f_{CH} + k_{tert}f_{CH3}f_{CH2}f_{OH} + k_{sec}f_{CH}f_{CH} + k_{tert}f_{CH2}f_{CH2}f_{OH} + k_{sec}f_{CH}f_{CH2}$$

$$+ k_{sec}f_{CH2C(O)}f_{CH2} + k_{sec}f_{CH2}f_{>CO} + k_{sec}f_{>CO}f_{CH2C(O)} + k_{sec}f_{>CO}f_{CH2C(O)}$$

$$+ k_{prim}f_{>CO}$$

3   which gives $k_{OH} = 3.25 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, compared to the SOM-reactivity value of

4   4.38×10^{-11} cm^3 molecule^{-1} s^{-1} for a generic $C_{12}O_4$ species.

5   **1.3.5   Case 5:**

6   Another $C_{12}O_4$ species is considered:

7

8   The k_{OH} using the explicit structure-reactivity relationships for this molecule would be:

$$k_{OH} = k_{prim}f_{CH} + k_{sec}f_{CH3}f_{CH2} + k_{sec}f_{CH2}f_{CH2} + k_{sec}f_{CH2}f_{CH2} + k_{tert}f_{CH2}f_{CH2}f_{OH}$$

$$+ k_{sec}f_{CH}f_{CH} + k_{tert}f_{CH2}f_{OH}f_{CH2C(O)} + k_{sec}f_{>CO}f_{CH} + k_{sec}f_{>CO}f_{>CO}$$

$$+ k_{prim}f_{>CO}$$

11

1   which gives k_{OH} = 4.99x10^{-11} cm^3 molecule^{-1} s^{-1}, compared to the SOM-reactivity value of

2   4.38x10^{-11} cm^3 molecule^{-1} s^{-1} for a generic $C_{12}O_4$ species.

3   **1.3.6   Average Results**

4   Comparing cases 1-5, the extent to which the SOM-reactivity relationship yields a k_{OH} that

5   agrees with the explicit calculation depends on the structure of the molecule under consideration.

6   The calculated SOM k_{OH} can either over-predict or under-predict the k_{OH} for the individual

7   isomers, as would be expected since the SOM-reactivity parameterization assumes mean

8   properties for all CH groups. Overall, the SOM-reactivity relationship does a reasonable job in

9   estimating the reactivity of the *average* species, with the average k_{OH} for these five species

10   6.56x10^{-11} cm^3 molecules^{-1} s^{-1} compared with the SOM k_{OH} = 4.38x10^{-11} cm^3 molecules^{-1} s^{-1},

11   giving a ratio between the SOM k_{OH} and the average k_{OH} of 0.67. Note that for the C_6 species

12   considered above, the SOM actually slightly over-predicted compared to the measured and the

13   values derived from the Atkinson structure-reactivity relationship. This suggests that, within the

14   constraints imposed by the fundamental assumptions underpinning the SOM-reactivity

15   relationship, the k_{OH} for the oxygenated species will be within a factor of 2 of the average from

16   the Atkinson relationship.

17
18   **References**

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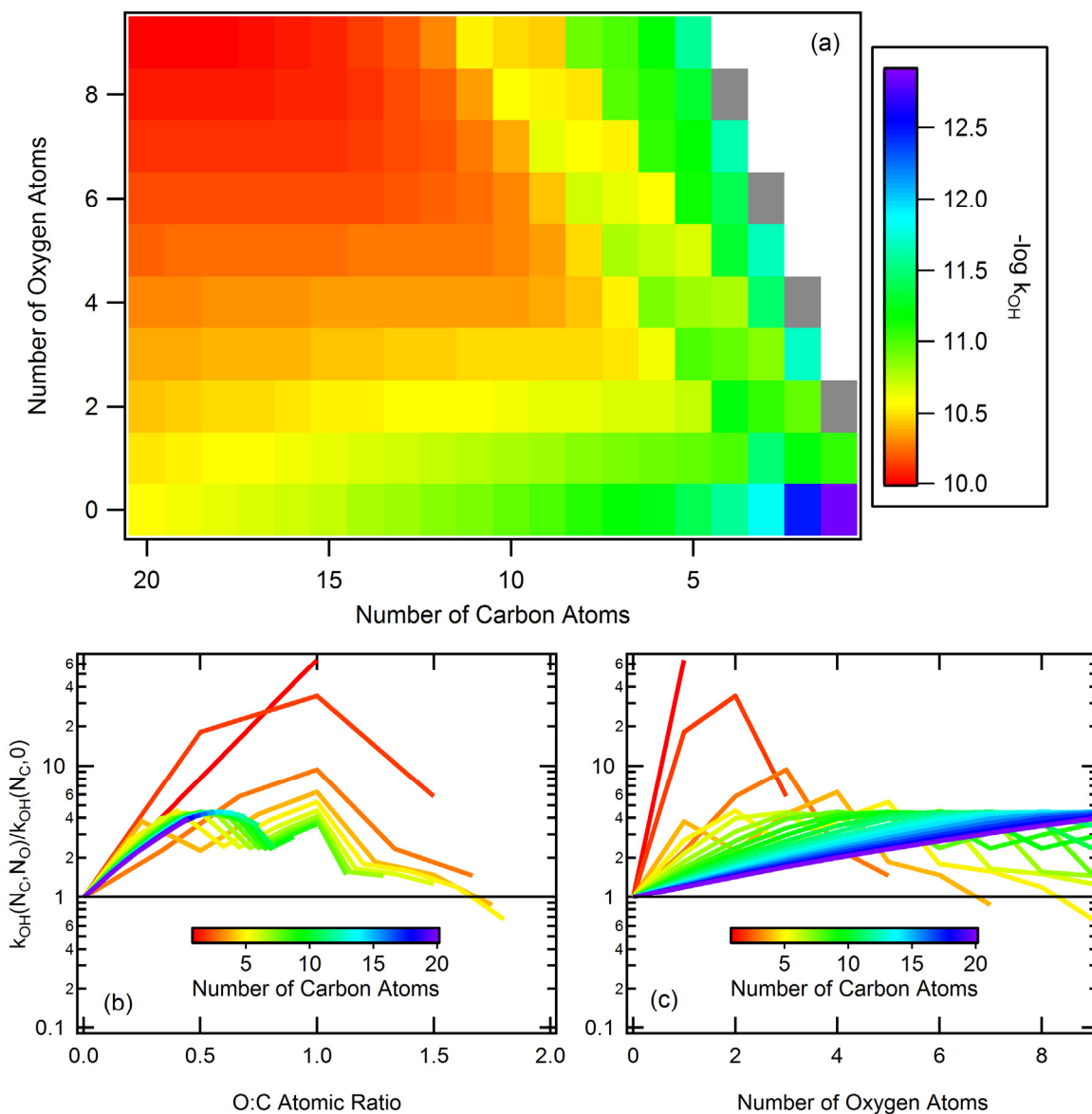
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Figure S1: (a) The rate coefficients for reaction with OH from the SOM-reactivity relationship. Colors correspond to $-\log k_{OH}$, where k_{OH} is in cm^3 molecules^{-1} s^{-1}. Gray boxes indicate species with O:C = 2, which are assumed to be non-reactive. White regions indicate species with O:C > 2, which are assumed to not exist. (b) k_{OH} values for each N_C vs. O:C, normalized by the k_{OH} when $N_O = 0$. (c) k_{OH} values for each N_C vs. N_O, normalized by the k_{OH} when $N_O = 0$.