

*Supporting Information for:*

**Secondary Organic Aerosol Formation via the Isolation of Individual Reactive**

**Intermediates: Role of Alkoxy Radical Structure**

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The relative abundances of each first-generation product (Figure 8) were estimated from the relative rates of reactions available to each alkoxy radical. Alkoxy radicals were assumed to either fragment ( $k_{\text{frag}}$ ) into smaller products, or isomerize “forward” ( $k_{\text{isom-forward}}$ ) to form an alkylperoxy species or “backwards” ( $k_{\text{isom-back}}$ ) to form the hydroxycarbonyl (Figure S1). Reactions of alkoxy radicals with  $\text{O}_2$  to form carbonyls were negligible for the straight-chain species and are not shown in Figure S1; however, they were significant particularly for the alpha-substituted branched species and were considered there. Reactions of peroxy radicals with NO were assumed to produce either alkoxy radicals or organonitrates in a fixed ratio of 80:20, based on measurements and model predictions of alkyl nitrate yields from alkane + OH experiments in the presence of  $\text{NO}_x$ .<sup>1</sup>

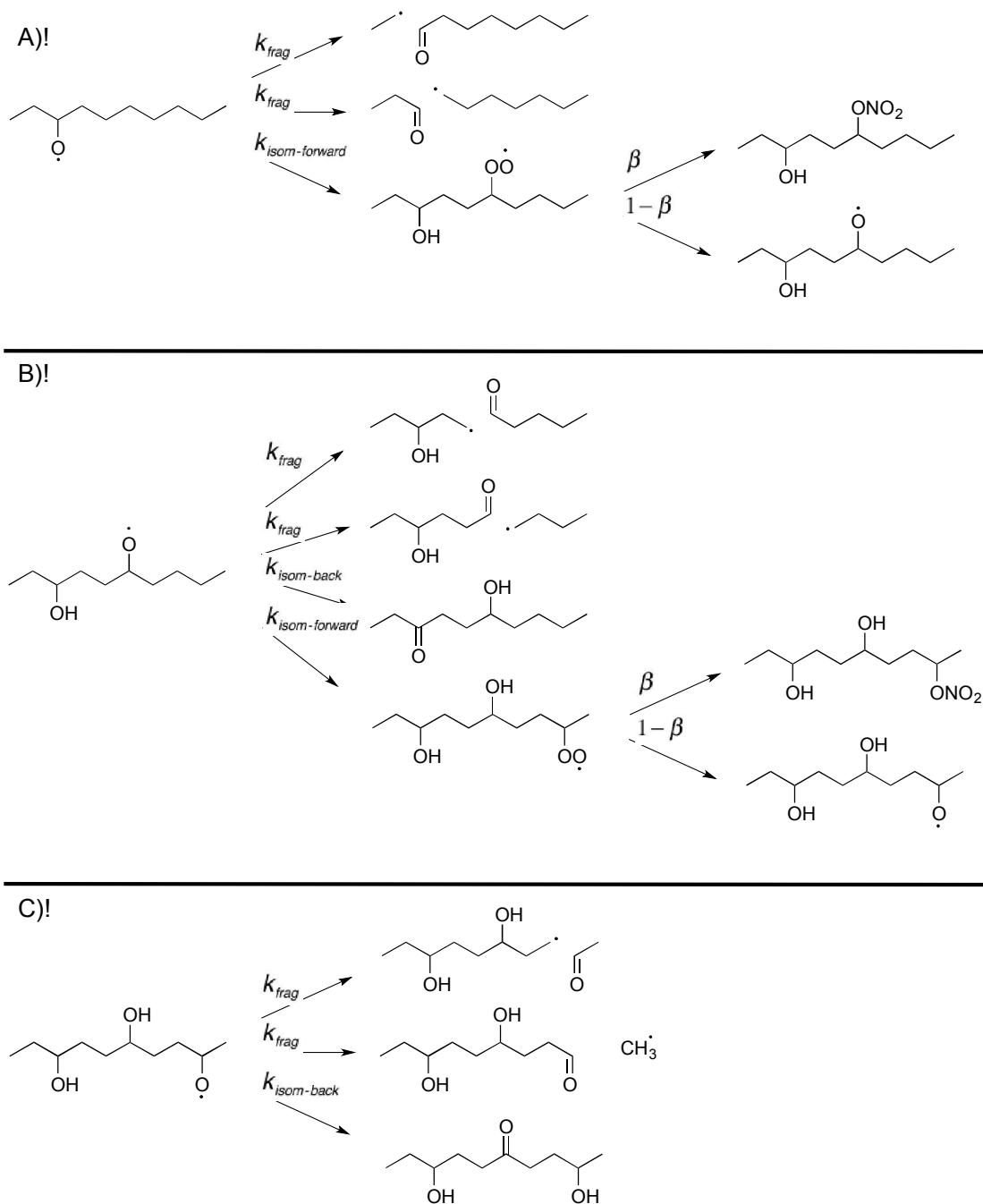


Figure S1. Branching of (A) alkoxy, (B) hydroxyalkoxy, and (C) dihydroxyalkoxy radicals for a representative alkoxy radical system (decyl-3-oxy). Each alkoxy radical pathway is denoted by its absolute rate constant ( $k_{\text{frag}}$  for fragmentation,  $k_{\text{isom-forward}}$  for “forward isomerization”, and  $k_{\text{isom-back}}$  for “backward isomerization”); peroxy radical + NO reactions give the organic nitrate with a yield of  $\beta$ , taken to be 0.2 in all cases.

Estimates for  $k_{\text{isom}}$  are from Atkinson<sup>2</sup> (Table S1); all isomerization reactions involve H atoms at the  $\delta$ -position. Values of  $k_{\text{frag}}$  were estimated using the enthalpy-based parameterization developed by Atkinson<sup>1</sup> (Table S2). This approach provides an estimate of reaction activation energies,  $E_d$  from:

$$E_d = a + \Delta_{\text{frag}}H^*b \quad (\text{S1})$$

where  $a$  is a parameter based on the structure of the leaving radical species,  $b$  is a constant (0.4), and  $\Delta_{\text{frag}}H$  is the reaction enthalpy which was estimated from smaller structurally similar species (Table S2).<sup>1</sup> These  $E_d$  values are then used to calculate  $k_{\text{frag}}$  values using the Arrhenius equation:

$$k_{\text{frag}} = A \cdot \exp(-E_d/RT) \quad (\text{S2})$$

where the recommended<sup>2</sup> pre-exponential factor  $A$  is  $5.0 \times 10^{11} \text{ s}^{-1}$ ,  $R$  is the ideal gas constant ( $1.987 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is the absolute temperature, 298 K. Finally, branching ratios were calculated from the rates of each channel available to all the alkoxy radicals within a given reaction sequence.

Fragmentation rates were also estimated using an alternative SAR, based upon the degree of  $\alpha$ - and  $\beta$ -substitution of the alkoxy radical.<sup>3</sup> In that case,  $E_d$  is calculated from the following formula:

$$E_d = 17.5 - 2.1 \cdot N_\alpha - 3.1 \cdot N_\beta \quad (\text{S3})$$

where  $N_\alpha$  and  $N_\beta$  are the number of alkyl substituents located on the carbon atom  $\alpha$  and  $\beta$  to the alkoxy radical center, respectively.<sup>3</sup> The product distributions predicted using this alternative SAR are shown in Figure S2.

**Table S1. Isomerization rate constants (from Atkinson<sup>2</sup>).**

$\delta$ -Carbon Identity	$k_{\text{isom}} (\text{s}^{-1})$
$\text{RCH}_3$	$3.2 \times 10^5$
$\text{R}_1\text{CH}_2\text{R}_2$	$3.3 \times 10^6$
$\text{R}_1\text{CH}(\text{R}_2)\text{R}_3$	$1.1 \times 10^7$
$\text{R}_1\text{CH}(\text{OH})\text{R}_2$	$2.4 \times 10^7$

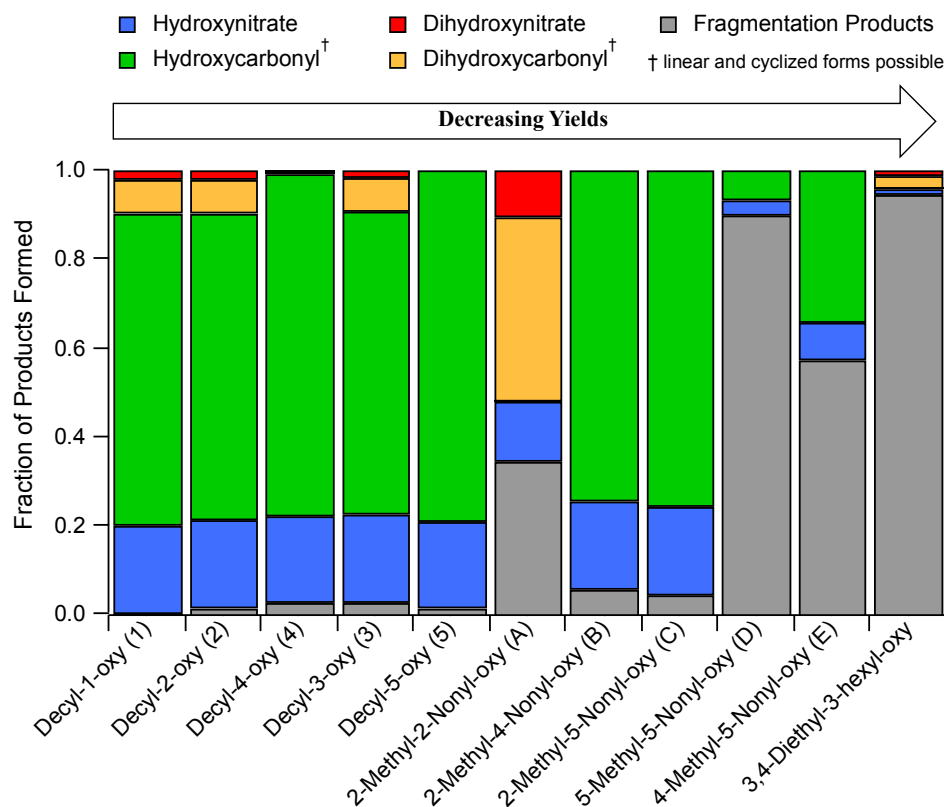
**Table S2. Fragmentation rate constants (based on Atkinson<sup>1</sup>).**

Fragment	a	$\Delta_{\text{frag}}H$ (kcal/mole K)	$E_d$ (kcal/mole)	$k_{\text{frag}} (\text{s}^{-1})$
$\text{R} + \bullet\text{CH}_3$ <i>Methyl radical</i>	12.9 <sup>a</sup>	5.30 <sup>a</sup>	15.00	$4.69 \times 10^2$
$\text{R} + \bullet\text{CH}_2\text{CH}_3$ <i>Ethyl Radical</i>	9.8 <sup>a</sup>	7.60 <sup>a</sup>	12.80	$1.87 \times 10^4$
$\text{R} + \bullet\text{R}'\text{CH}_2\text{CH}_3$ <i>Propyl, Butyl, Pentyl, Hexyl Radical</i>	9.5 <sup>a</sup>	8.73 <sup>b</sup>	13.00	$1.45 \times 10^4$
$\text{R} + \text{R}'(\bullet)\text{R}''\text{CH}_2\text{CH}_3$ <i>Secondary Radical</i>	8.2 <sup>a</sup>	7.95 <sup>b</sup>	11.40	$2.21 \times 10^5$

a. Atkinson<sup>2</sup>b. Calvert<sup>4</sup>**Table S3. Fragmentation rate constants (based on Peeters<sup>3</sup>).**

Fragment <sup>a</sup>	$E_d$ (kcal/mole)	$k (\text{s}^{-1})$
<b>Primary</b>		
$\bullet\text{RCH}_3$	14.10	$1.3 \times 10^3$
<b>Secondary</b>		
$\bullet\text{CH}_3$	10.20	$2.5 \times 10^2$
$\bullet\text{RCH}_2\text{CH}_3$	13.30	$4.7 \times 10^4$
$\text{R}'(\bullet)\text{R}''\text{CH}_2\text{CH}_3$	9.20	$8.8 \times 10^6$
<b>Tertiary</b>		
$\bullet\text{RCH}_3$	10.20	$1.6 \times 10^6$
$\bullet\text{CH}_3$	13.30	$8.6 \times 10^3$

a. Primary, Secondary, and Tertiary headings refer to the substitution at the radical center (at the  $\alpha$ -carbon)



**Figure S2.** Distribution of major first-generation products from each alkoxy radical isomer using the substituent-based parameterization for fragmentation rates. Isomers are listed in order of decreasing yields; the identifiers in parentheses correspond to those used in Figure 4.

## References

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