Modelling organic aerosol concentrations and properties during ChArMEx summer campaigns of 2012 and 2013 in the western Mediterranean region

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Appendix A: Formation of ELVOC

The reactions involved in the formation of ELVOCs are

$$MT + O_2 \xrightarrow{k_1} \gamma_{RO_2}.RO_2 + (1 - \lambda - \gamma_{RO_2}).R'O_2 + OH + 0.001\ HO_2 \tag{A1}$$

$$R'O_2 \xrightarrow{k_{H/O2}} \alpha.R''O_2 \tag{A2}$$

$$R''O_2 \xrightarrow{k_{H/O2}} \alpha.R'''O_2 \tag{A3}$$

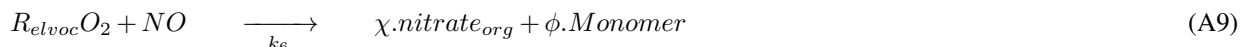
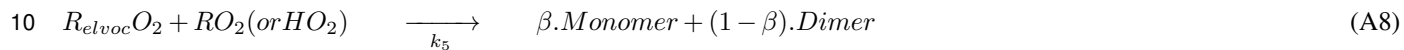
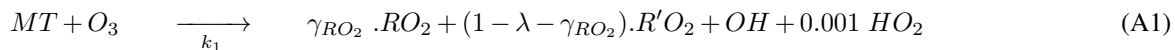
$$R'''O_2 \xrightarrow{k_{H/O2}} \alpha.R_{elvoc}O_2 \tag{A4}$$

$$RO_2 + R'O_2 \xrightarrow{k_2} Products \tag{A5}$$

$$RO_2 + NO \xrightarrow{k_3} \delta.RO_2 \tag{A6}$$

$$RO_2 + HO_2 \xrightarrow{k_4} Products \tag{A7}$$

$$R_{elvoc}O_2 + RO_2(or HO_2) \xrightarrow{k_5} \beta.Monomer + (1 - \beta).Dimer \tag{A8}$$

$$R_{elvoc}O_2 + NO \xrightarrow{k_6} \chi.nitrate_{org} + \phi.Monomer \tag{A9}$$

After numerous combinations, the stoichiometric coefficients of equations [A1] were determined, such as reproducing the observations of Ehn et al. (2014) for both the low-NOx and high-NOx regimes (Table[2]).

Kinetic constant	Value ($cm^3 s^{-1}$ or s^{-1})
k_1	8.4×10^{-17}
k_2	1.0×10^{-12}
k_3	4.7×10^{-12}
k_4	2.7×10^{-11}
k_5	5.0×10^{-11}
k_6	4.7×10^{-12}
k_{H/O_2}	0.5

Table 1. Kinetic constants used in the ELVOC kinetic model

Stoichiometric coefficient	γ_{RO_2}	λ	α	δ	β	χ	ϕ
Value	0.0002	0.0998	1.0	0.995	0.6	0.00012	0.00001

Table 2. Stoichiometric coefficients used in the model

For model validation, comparisons are made to the experiments of Ehn et al. (2014). In the low-NOx regime, the experiments of Ehn et al. (2014) lasted 45 min and the initial ozone concentration was 80 ppb. In the model, we modified the initial concentration of α-pinene from 0 ppb to 11 ppb to reproduce the observations. Figure [1], which shows one-fifth of the ELVOC concentrations as a function of the α-pinene reaction rate, reproduces successfully the extended data Figure 10 of Ehn et al. (2014). According to Figure [1], the increase of peroxy radicals has a square root dependence while ELVOC monomers and dimers evolve nearly linearly. Therefore, the total ELVOC concentration has a near-linear dependence on the amount of α-pinene reacting with O_3 indicative of first-generation oxidation products. These findings are consistent qualitatively and quantitatively with Ehn et al. (2014) measured and modeled results.

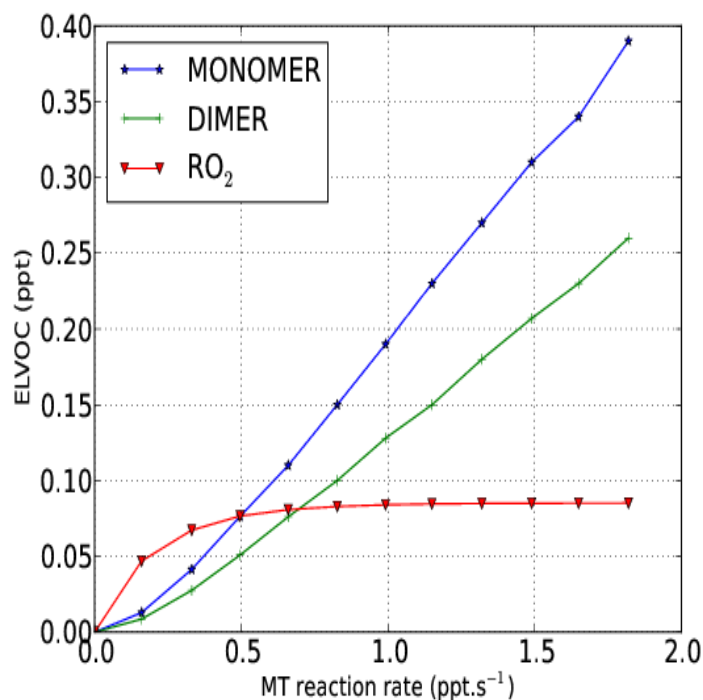



Figure 1. ELVOC concentrations as a function of the α-pinene reaction rate for the low-NO$_x$ experiment

In the high NO$_x$ regime, the experiments of Ehn et al. (2014) also lasted 45 min and the initial ozone and α-pinene concentrations were 80 ppb and 5 ppb respectively. The initial NO concentration was changed gradually from 0.3 ppb to 5 ppb. Figure [2], which shows one-fifth of the ELVOC as a function of the RO$_2$ concentration, reproduces successfully the Extended Data Figure 10 of Ehn et al. (2014). While increasing NO concentration, both monomer and dimer concentrations decrease rapidly as expected because a fraction of peroxy radicals is consumed by the NO reaction. Moreover, the dimer concentration decreases rapidly while the monomer concentration decreases more slowly. Simultaneously, the organic nitrate concentration increases with increasing NO.

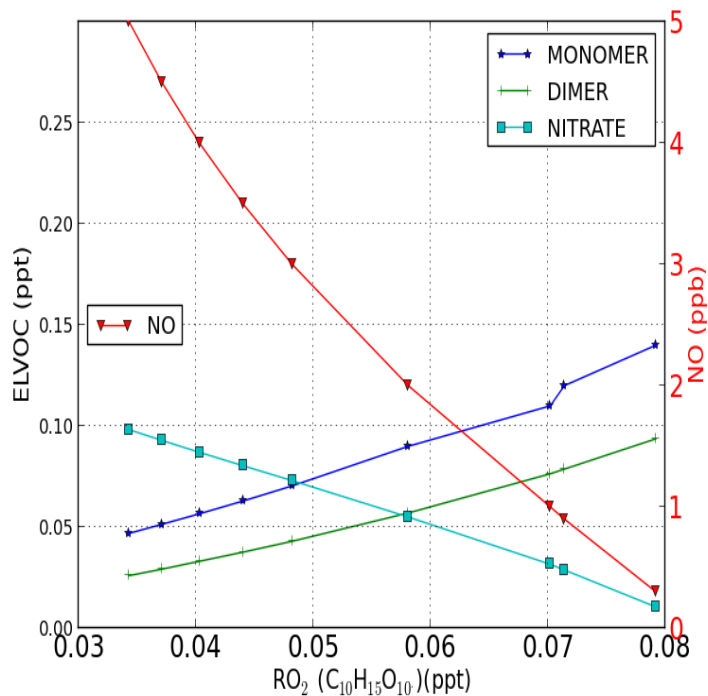



Figure 2. ELVOC concentration as a function of the RO_2 concentration in the high-NO_x regime.

Appendix B: Formation of organic nitrate

The formation of organic nitrate (orgNIT) from monoterpenes (MT) is modeled with the following reactions:

$$Terpene + OH \xrightarrow{k_1'} TERPRO_2 \tag{B1}$$

$$TERPRO_2 + NO \xrightarrow{k_2'} 0.201 orgNIT \tag{B2}$$

$$MT + NO_3 \xrightarrow{k_3'} TERPNRO_2 \tag{B3}$$

$$TERPNRO_2 + NO \xrightarrow{k_4'} 0.688 orgNIT + Products \tag{B4}$$

$$TERPNRO_2 + HO_2 \xrightarrow{k_5'} orgNIT + Products \tag{B5}$$

$$TERPNRO_2 + NO_3 \xrightarrow{k_6'} 0.422 orgNIT + Products \tag{B6}$$

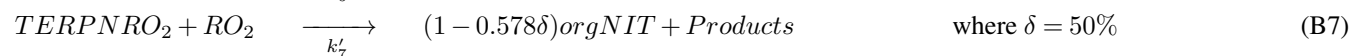
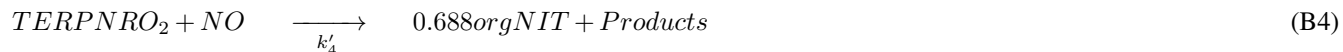
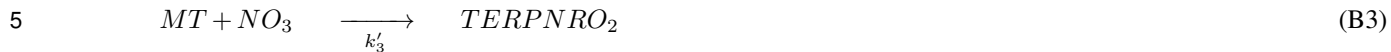
$$TERPNRO_2 + RO_2 \xrightarrow{k_7'} (1 - 0.578\delta) orgNIT + Products \qquad \text{where } \delta = 50\% \tag{B7}$$

Kinetic constant	Value ($cm^3 s^{-1}$ or s^{-1})
k'$_1$	α-pinene ($1.21\ 10^{-11}$ exp(444/T))
	Limonene ($4.20\ 10^{-11}$ exp(401/T))
	β-pinene ($2.38\ 10^{-11}$ exp(357/T))
	Humulene ($2.93\ 10^{-10}$)
k'$_2$	$2.27\ 10^{-11}$ exp(435/T)
k'$_3$	α-pinene ($1.19\ 10^{-12}$ exp(490/T))
	Limonene ($1.22\ 10^{-11}$)
	β-pinene ($2.51\ 10^{-12}$)
	Humulene ($1.33\ 10^{-12}$ exp(490/T))
k'$_4$	$2.6\ 10^{-12}$ exp(380/T)
k'$_5$	$2.65\ 10^{-13}$ exp(1300/T)
k'$_6$	$2.3\ 10^{-12}$
k'$_7$	$3.5\ 10^{-14}$

Table 3. Kinetic constants used in the organic nitrate formation mechanism

Appendix C: Statistic indicators and criteria

The statistic indicators used in this paper are described in Table 4. The performance and goal criteria used in this paper are described in Table 5.

Statistic indicator	Definition
Root mean square error (RMSE)	$\sqrt{\frac{1}{n}\sum_{i=1}^{n}(c_i - o_i)^2}$
Correlation (Corr)	$\frac{\sum_{i=1}^{n}(c_i - \bar{c})(o_i - \bar{o})}{\sqrt{\sum_{i=1}^{n}(c_i - \bar{c})^2}\sqrt{\sum_{i=1}^{n}(o_i - \bar{o})^2}}$
Mean fractional bias (MFB)	$\frac{1}{n}\sum_{i=1}^{n}\frac{c_i - o_i}{(c_i + o_i)/2}$
Mean fractional error (MFE)	$\frac{1}{n}\sum_{i=1}^{n}\frac{\mid c_i - o_i \mid}{(c_i + o_i)/2}$

Table 4. Definitions of the statistics used in this work. $(o_i)_i$ and $(c_i)_i$ are the observed and the simulated concentrations at time and location i, respectively. n is the number of data

Criteria	Performance criterion	Goal criterion
MFB	$\leq 60\%$	$\leq 30\%$
MFE	$\leq 75\%$	$\leq 50\%$

Table 5. Boylan and Russel criteria

References

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