

## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3\_VOC33

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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.4 \pm 0.9) \times 10^{-12}$	298	Martínez et al., 1999	DF-LIF (a)
$(5.8 \pm 0.7) \times 10^{-12}$	433		
<i>Relative Rate Coefficients</i>			
$(1.31 \pm 0.04) \times 10^{-11}$	295	Atkinson et al., 1984	RR (b)
$(1.12 \pm 0.17) \times 10^{-11}$	298	Barnes et al., 1990	RR (c)

Limonene is 4-isopropenyl-1-methyl-cyclohexene.

### Comments

- $\text{NO}_3$  radicals ( $6\text{-}30 \times 10^{11} \text{ molecule cm}^{-3}$ ) generated from reaction of F atoms (made in a microwave discharge through  $\text{F}_2/\text{He}$ ) with  $\text{HNO}_3$ . Flow tube was operated at  $\sim 1.33$  mbar (1 Torr) He. Limonene was present at similar concentrations (1-3 fold) to  $\text{NO}_3$ . So that absolute  $\text{NO}_3$  concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.
- 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air.  $\text{NO}_3$  was generated by the thermal decomposition of  $\text{N}_2\text{O}_5$ . Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \text{limonene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 1.40 \pm 0.04$  is placed on an absolute basis by  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).
- 420 L glass chamber at 298 K and 980 mbar (735 Torr) of air.  $\text{NO}_3$  was generated by the thermal decomposition of  $\text{N}_2\text{O}_5$ . Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \text{limonene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 1.20 \pm 0.18$  is placed on an absolute basis by  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).

<b>Preferred Values</b>		
<b>Parameter</b>	<b>Value</b>	<b>T/K</b>
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.2 \times 10^{-11}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.12$	298

#### *Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is based on the relative rate studies, which indicate a larger rate coefficient than observed in the single absolute study. The difference between the rate coefficients obtained at 298 and 433 K (factor 1.6) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

The reaction mechanism involves the initial addition of NO<sub>3</sub> across a double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Product studies suggest that attack of NO<sub>3</sub> at the exocyclic double bond of limonene is insignificant (Spittler et al 2006), which is supported by theoretical calculations (Jiang et al., 2009).

The reaction products in air include endolim (yield of 29 %, Spittler et al., 2006) and organic nitrates (expected to include both mono- and dinitrates) with yields (per limonene reacted) between 30 and 67 % (Spittler et al. 2006; Hallquist et al., 1999; Fry et al 2011; Fry et al., 2014). Using thermal dissociation of alkyl nitrates and peroxy nitrates coupled to LIF detection of NO<sub>2</sub>, Fry et al., (2014) derived a molar organic nitrate yield (gas- and aerosol) of 0.54 with 83 % being located in the aerosol phase. Organonitrates comprised 82 % of the aerosol mass.

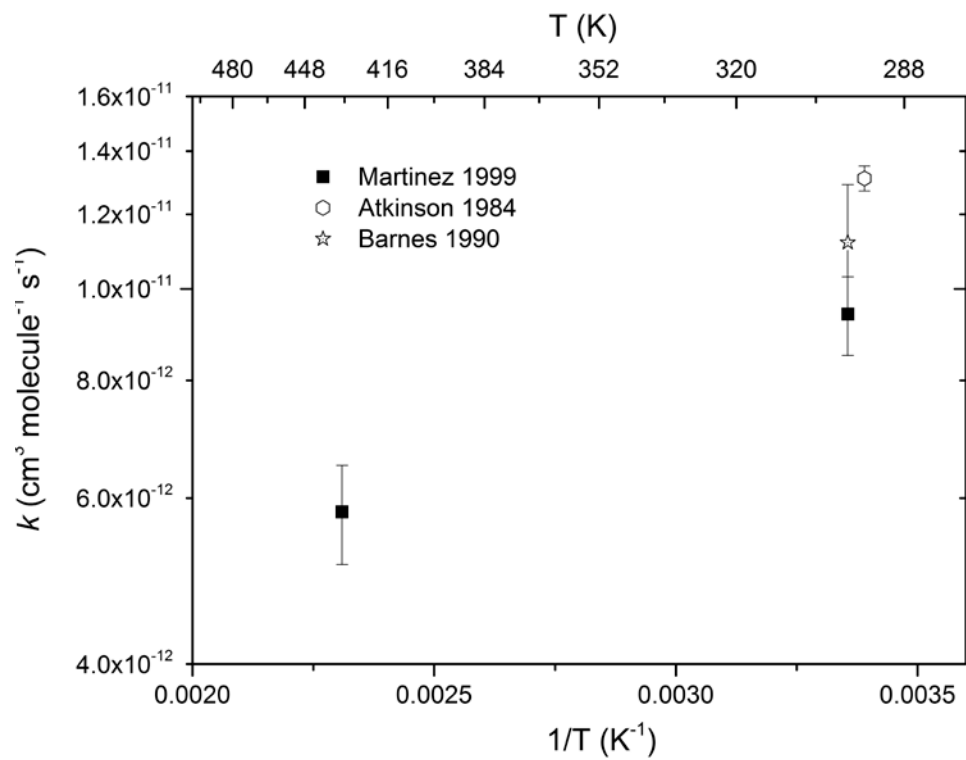
Secondary organic aerosol is formed efficiently in smog-chamber studies of the reaction between NO<sub>3</sub> and limonene with mass-based yields of between 17 and 57% reported (Hallquist et al., 1999; Fry et al., 2011; Fry et al., 2014). Spittler et al. (2006) suggest that much of the organic aerosol is formed from further reactions of endolim.

#### **References**

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Rate coefficients for  $\text{NO}_3 + \text{limonene}$