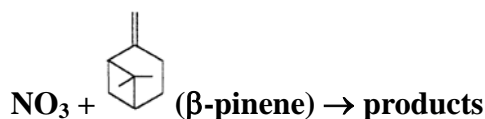


## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC36

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### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(2.36 \pm 0.10) \times 10^{-12}$	295	Atkinson et al., 1984	RR (a)
$(2.38 \pm 0.05) \times 10^{-12}$	296	Atkinson et al., 1988	RR (b)
$(1.1 \pm 0.4) \times 10^{-12}$	298*	Kotzias et al., 1989	RR (c)
$(2.81 \pm 0.47) \times 10^{-12}$	298	Barnes et al., 1990	RR (d)

$\beta$ -pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane.

### Comments

- 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO<sub>3</sub> was generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>.  $\beta$ -pinene and 2-methyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \beta\text{-pinene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.252 \pm 0.011$  is placed on an absolute basis using  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).
- 6400 L Teflon chamber at 296 K and 980 mbar (735 Torr) of air. NO<sub>3</sub> was generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>.  $\beta$ -pinene and trans-2-butene (reference reactant) were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \beta\text{-pinene}) / k(\text{NO}_3 + \text{trans-2-butene}) = 6.10 \pm 0.14$  is placed on an absolute basis using  $k(\text{NO}_3 + \text{trans-2-butene}) = 3.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC 2013, datasheet NO<sub>3</sub>\_VOC30).
- 450 L Teflon-coated glass reactor, with  $\beta$ -pinene, N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub> monitored by FTIR. NO<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> were assumed to be in equilibrium and the NO<sub>3</sub> concentration was calculated from the equilibrium constant ( $1.9 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3$ ) and used to derive the rate constant from the  $\beta$ -pinene decay constant. The authors did not quote the temperature of these experiments, making re-assessment of their data via e.g. use of a more recently measured equilibrium constant difficult.
- 420 L glass chamber at 298 K and 1bar of air. NO<sub>3</sub> was generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>.  $\beta$ -pinene and 2-methyl-2-butene were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \beta\text{-pinene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.30 \pm 0.05$  is placed on an absolute basis using  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.5 \times 10^{-12}$	298
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.12$	298

### Comments on Preferred Values

The relative rate studies of this reaction which employed either 2-methyl-2-butene or trans-2-butene as reference reactants are in broad agreement, though there is no obvious reason why Atkinson et al. (1984) and Barnes et al. (1990), who used the same reference reactant should derive rate coefficients which diverge by ~20 %. These studies are preferred over that of Kotzias et al., as there are greater uncertainties related to using the strongly temperature dependent equilibrium constant for the  $\text{NO}_2 + \text{NO}_3 = \text{N}_2\text{O}_5$  reaction, which are compounded by the fact that authors did not cite their experimental temperature. The preferred value of the 298 K rate coefficient is thus an unweighted average of the results derived by Atkinson et al. (1984, 1988) and Barnes et al. (1990).

The reaction mechanism involves the addition of  $\text{NO}_3$  across the double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Hallquist et al. (1999) identified the end products nopinone (molar yields of 1-2 %), carbonyls (estimated molar yield of 12-14 %) and organic nitrates (estimated molar yield of 61-74 %) which were also observed using FTIR and MS by Kotzias et al. (1989), but not quantified.

Using thermal dissociation of alkyl nitrates and peroxy nitrates coupled to LIF detection of  $\text{NO}_2$ , Fry et al., (2009) derived a molar organic nitrate yield of ~40 %. Later, similar experiment using the same method (Fry et al. 2014) resulted in a total (gas- and aerosol) yield of 0.22 with 76 % being located in the aerosol phase. Organonitrates were found to comprise 56 % of the aerosol mass.

Secondary organic aerosol formation was also observed in the smog-chamber studies of  $\text{NO}_3 + \beta$ -pinene (Hallquist et al., 1999; Griffin et al. 1999), with mass-based yields of up to 90 % depending on the amount of  $\beta$ -pinene reacted.

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