

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC9

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This data sheet last evaluated: June 2013; last change in preferred values: 2007.



## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.19 \times 10^{-12} \exp[(490 \pm 70)/T]$	261-384	Dlugokencky and Howard, 1989	F-LIF (a)
$(6.18 \pm 0.74) \times 10^{-12}$	298		
$3.5 \times 10^{-13} \exp[(841 \pm 144)/T]$	298-423	Martínez et al., 1998	DF-LIF (b)
$(5.9 \pm 0.8) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(5.82 \pm 0.16) \times 10^{-12}$	$295 \pm 1$	Atkinson et al., 1984	RR (c)
$(6.56 \pm 0.94) \times 10^{-12}$	$298 \pm 2$	Barnes et al., 1990	RR (d)
$(4.88 \pm 0.46) \times 10^{-12}$	298	Stewart et al., 2013	RR (e)

$\alpha$ -Pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene.

## Comments

- (a) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub> at ~400 K. Experiments were carried out in a low-pressure flow tube at ~1.3-1.4 mbar of He diluent. The NO<sub>2</sub> yield at 1.3 mbar He and 298 K was 67%.
- (b) NO<sub>3</sub> radicals ( $6\text{-}30 \times 10^{11} \text{ molecule cm}^{-3}$ ) generated from reaction of F atoms (made in a microwave discharge through F<sub>2</sub>/He) with HNO<sub>3</sub>. Flow tube was operated at ~1.33 mbar (1 Torr) He.  $\alpha$ -pinene was present at similar concentrations (1-3 fold) to NO<sub>3</sub>. So that absolute NO<sub>3</sub> concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.
- (c) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>. The concentrations of  $\alpha$ -pinene and 2-methyl-2-butene (the reference compound) were monitored by GC in reacting N<sub>2</sub>O<sub>5</sub> - NO<sub>2</sub> -  $\alpha$ -pinene - 2-methyl-2-butene - air mixtures at 980 mbar pressure in a ~6400 L Teflon chamber. The measured rate coefficient ratio  $k(\text{NO}_3 + \alpha\text{-pinene})/k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.621 \pm 0.017$  is placed on an absolute basis by use of a rate coefficient at 295 K of  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003a).
- (d) NO<sub>3</sub> radicals were generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>. The concentrations of  $\alpha$ -pinene and 2-methyl-2-butene (the reference compound) were monitored by GC at 1 bar pressure in a 420 L glass reaction vessel. The measured rate coefficient ratio  $k(\text{NO}_3 + \alpha\text{-pinene})/k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.70 \pm 0.10$  is placed on an absolute basis by use of a rate coefficient at 298 K of  $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003a).
- (e) 1 L glass vessel at 1013 mbar (760 Torr) of air. Relative changes in concentration of  $\alpha$ -

pinene and cycloheptene (reference reactant) were monitored by GC. The rate constant ratio  $k(\text{NO}_3 + \alpha\text{-pinene}) / (k(\text{NO}_3 + \text{cycloheptene}) = 9.58 \pm 1.10$  is placed on an absolute basis by  $k(\text{NO}_3 + \text{cycloheptene}) = 5.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003a).

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$6.2 \times 10^{-12}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.2 \times 10^{-12} \exp(490/T)$	260-390
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.10$	298
$\Delta E/R$	$\pm 300$	290-450

### Comments on Preferred Values

The room temperature relative rate coefficients of Atkinson et al. (1984) and Barnes et al. (1990) and the absolute rate coefficients of Dlugokencky and Howard (1989) and Martínez et al. (1998) are in excellent agreement. The somewhat lower value of Stewart et al. (2013) may be related to use of a very slowly reacting reference compound. The temperature dependencies obtained by Dlugokencky and Howard (1989) and Martínez et al. (1998) differ significantly. Because the study of Dlugokencky and Howard (1989) extends to lower temperatures representative of the troposphere, the data from the studies of Atkinson et al. (1984), Dlugokencky and Howard (1989) and Barnes et al. (1990) are used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares fit of the rate coefficients of Atkinson et al. (1984), Dlugokencky and Howard (1989) and Barnes et al. (1990). There is no evidence for a pressure dependence of the rate coefficient over the range ~1-1000 mbar, at least at room temperature.

The reaction proceeds by initial addition of  $\text{NO}_3$  to the  $\text{C}=\text{C}$  bond. At low pressures or in the absence of  $\text{O}_2$ , the initially formed nitrooxyalkyl radicals eliminate  $\text{NO}_2$  and form  $\alpha$ -pinene oxide (Dlugokencky and Howard, 1989; Atkinson, 1991; Berndt and Böge, 1997). At atmospheric pressure of air,  $\text{O}_2$  addition to the nitrooxyalkyl radicals forms two nitrooxyalkyl peroxy radicals, although some  $\alpha$ -pinene oxide ( $3 \pm 0.5\%$ ) is still observed at 1 bar of air (Wängberg et al., 1997). The nitrooxyalkyl peroxy radicals then react with  $\text{HO}_2$  radicals, organic peroxy radicals,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_3$  radicals, leading to the observed products (Atkinson and Arey, 2003a,b). Under laboratory conditions, the observed products and their yields at atmospheric pressure of air are: pinonaldehyde,  $62 \pm 4\%$  (Wängberg et al., 1997) and 69% (Hallquist et al., 1999); 2-hydroxypinan-3-nitrate,  $5 \pm 0.4\%$  (Wängberg et al., 1997); 3-oxopinan-2-nitrate,  $3 \pm 0.2\%$  (Wängberg et al., 1997); and  $\alpha$ -pinene oxide,  $3 \pm 0.5\%$  (Wängberg et al., 1997), with a total organic nitrate yield of 14-19% (Wängberg et al., 1997; Hallquist et al., 1999). Using thermal dissociation of alkyl nitrates and peroxy nitrates coupled to LIF detection of  $\text{NO}_2$ , Fry et al., (2014) derived a molar organic nitrate yield (gas- and aerosol) of 0.10, which was entirely in the gas phase.

Note that the products formed in the atmosphere, and their yields, may be different from those observed in laboratory studies, because of the differing concentrations (both absolute and relative) of  $\text{HO}_2$ ,  $\text{RO}_2$  and  $\text{NO}_3$  radicals and  $\text{NO}$  and  $\text{NO}_2$ .

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