IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC9

This data sheet last evaluated: June 2016; last change in preferred values: 2007.

$$NO_3 + \text{(α-Pinene)} \rightarrow products$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.19 \times 10^{-12} \exp[(490 \pm 70)/T]$	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		
Relative Rate Coefficients			
$(5.82 \pm 0.16) \times 10^{-12}$	295 ± 1	Atkinson et al., 1984	RR (c)
$(6.56 \pm 0.94) \times 10^{-12}$	298 ± 2	Barnes et al., 1990	RR (d)
$(4.88 \pm 0.46) \times 10^{-12}$	298	Stewart et al., 2013	RR (e)

α-Pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene.

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at ~400 K. Experiments were carried out in a low-pressure flow tube at ~1.3-1.4 mbar of He diluent. The NO_2 yield at 1.3 mbar He and 298 K was 67%.

(b) NO_3 radicals ($6-30 \times 10^{11}$ molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He. α-pinene was present at similar concentrations (1-3 fold) to NO_3. So that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of α-pinene and 2-methyl-2-butene (the reference compound) were monitored by GC in reacting N_2O_5 - NO_2 - α-pinene - 2-methyl-2-butene - air mixtures at 980 mbar pressure in a ~6400 L Teflon chamber. The measured rate coefficient ratio $k(NO_3 + \text{α-pinene})/k(NO_3 + \text{2-methyl-2-butene}) = 0.621 \pm 0.017$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson and Arey, 2003a).

(d) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of α-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 $k(NO_3 + \text{α-pinene})/k(NO_3 + \text{2-methyl-2-butene}) = 0.70 \pm 0.10$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003a).

(e) 1 L glass vessel at 1013 mbar (760 Torr) of air. Relative changes in concentration of α-pinene and cycloheptene (reference reactant) were monitored by GC. The rate constant ratio $k(NO_3 + \text{α-pinene}) / (k(NO_3 + \text{cycloheptene}) = 9.58 \pm 1.10$ is placed on an absolute basis using $k(NO_3 + \text{cycloheptene}) = 5.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey,

2003a).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.2×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-12} exp(490/T)	260-390
Reliability		
$\Delta \log k$	± 0.10	298
Δ E/R	± 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 Dlugokency 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 NO_3 to the C=C bond. At low pressures or in the absence of O_2, the initially formed nitrooxyalkyl radicals eliminate NO_2 and form α-pinene oxide (Dlugokencky and Howard, 1989; Atkinson, 1991; Berndt and Böge, 1997). At atmospheric pressure of air, O_2 addition to the nitrooxyalkyl radicals forms two nitrooxyalkyl peroxy radicals, although some α-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 HO_2 radicals, organic peroxy radicals, NO, NO_2, and 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, $\approx 60 \pm 12$ % (Wängberg et al., 1997. Hallquist et al., 1999, Spittler et al., 2006); 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 α-pinene oxide, $3 \pm 0.5\%$ (Wängberg et al., 1997), with a total organic nitrate yield of $\approx$ 14-20% (Wängberg et al., 1997; Hallquist et al., 1999: Spittler et al., 2006). Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of NO_2, Fry et al., (2014) derived a molar organic nitrate yield of 0.10, which was entirely in the gas phase. Perraud et al (2010) and Nah et al. (2016) identified C_9-C_{10} organic nitrates (both gas and particle phase) with 5, 6 or 9 oxygen atoms including 3-oxopinane-2-nitrate, 2-hydroxypinane-3-nitrate, pinonaldehyde-PAN, norpinonaldehyde-PAN, and (3-acetyl-2,2-dimethyl-3-nitrooxycyclobutyl) acetaldehyde and a carbonyl hydroxynitrate. The low yield of organic nitrates (compared to e.g. β-pinene) is attributed to the rapid dissociation (to pinonaldehyde and NO_2) of the tertiary alkoxy radical formed from the initial tertiary peroxy radical (Spittler et al. 2006; Perraud et al. (2010).

The formation of secondary organic aerosol has been documented in the studies of NO_3 + α-pinene, though, compared to other terpenes (e.g. β-pinene) the mass yields are low with values of generally less than 10 % reported (Hallquist et. al., 1999; Moldanova and Ljungstrom, 2000; Bonn and Moortgat, 2002; Spittler et al., 2006; Perraud et al., 2010; Fry et al 2014; Nah et al., 2016). The low secondary organic aerosol yield is related to the high yield of formation of

pinonaldehyde and NO_2 and resultant low yield of condensable organic nitrate.

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 HO_2, RO_2 and NO_3 radicals and NO and NO_2.

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Rate coefficients for NO_3 + α-pinene