

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC33

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The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>)

This datasheet last evaluated: June 2015; last change in preferred values: June 2013



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

- 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 F_2/He) with HNO_3 . Flow tube was operated at ~ 1.33 mbar (1 Torr) He. Limonene 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.
- 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_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. NO_3 was generated by the thermal decomposition of N_2O_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).

Preferred Values		
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.2×10^{-11}	298
<i>Reliability</i>		
$\Delta \log k$	± 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 NO₃ across a double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Product studies suggest that attack of NO₃ 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 NO₂, 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.

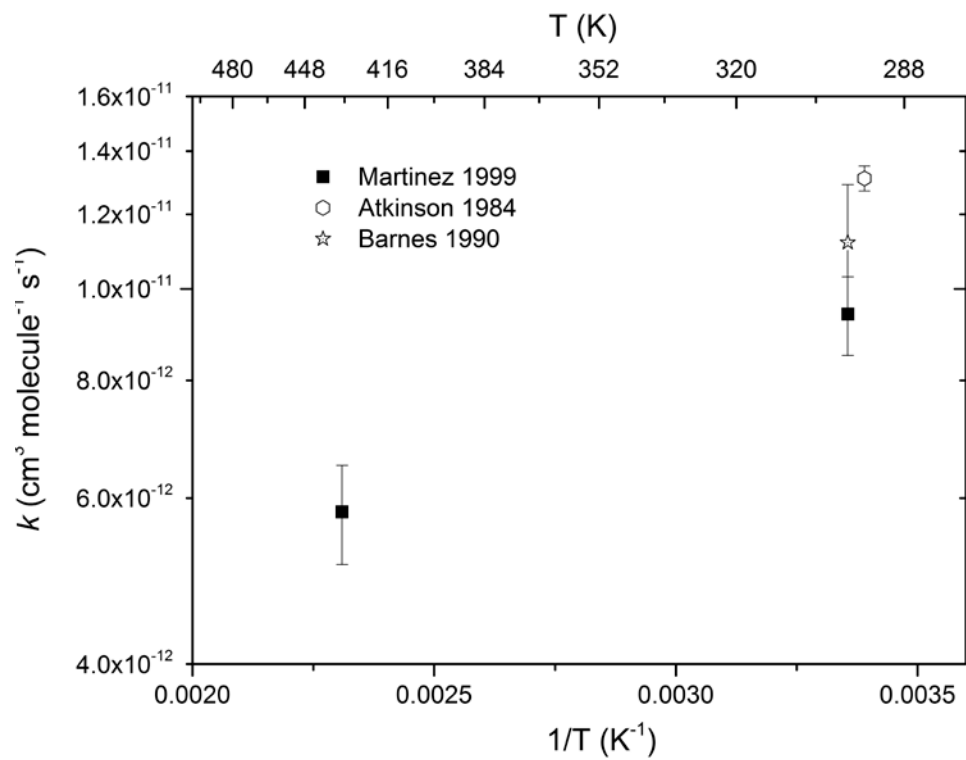
Secondary organic aerosol is formed efficiently in smog-chamber studies of the reaction between NO₃ and limonene with mass-based yields of between 17 and 57% reported (Hallquist et al., 1999; Fry et al., 2011; Fry et al., 2014). Spittler et al. (2006) suggest that much of the organic aerosol is formed from further reactions of endolim.

References

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