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

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NO_3 + (*d*-limonene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(9.4 \pm 0.9) \times 10^{-12}$	298	Martínez et al., 1999	DF-LIF (a)
$(5.8 \pm 0.7) \times 10^{-12}$	433		
Relative Rate Coefficients			
$(1.31 \pm 0.04) \times 10^{-11}$	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

(a) NO_3 radicals (6-30 × 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. 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.

(b) 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, $k(NO_3$ + limonene) / $k(NO_3$ + 2-methyl-2-butene) = 1.40 ± 0.04 is placed on an absolute basis by $k(NO_3$ + 2-methyl-2-butene) = 9.37 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(c) 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, $k(NO_3$ + limonene) / $k(NO_3$ + 2-methyl-2-butene) = 1.20 ± 0.18 is placed on an absolute basis by $k(NO_3$ + 2-methyl-2-butene) = 9.37 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

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Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2 x 10^{-11}	298
Reliability		
$\Delta \log k$	± 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 temeperature dependence (Martínez et al., 1999).

The reaction mechanism involves the initial addition of NO_3 across a double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Product studies suggest that attack of NO_3 at the exocyclic double bond of limonene is insignificant (Spittler et al 2006), which is supported by theoretical calculations (Jiang et al., 2009).

The final stable 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 peroxynitrates coupled to LIF detection of NO_2, 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 at high yield in the smog-chamber studies of NO_3 + limonene. Hallquist et al. (1999) quote a mass-based aerosol yield of 17 %, Fry et al (2011) ~ 30 %. Spittler et al. (2006) suggest that much of the organic aerosol is formed from further reactions of endolim.

References

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