Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.
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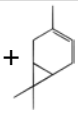
NO_3 +  (3-carene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.01 \pm 0.02) \times 10^{-11}$	295	Atkinson et al., 1984	RR (a)
$(8.2 \pm 1.2) \times 10^{-12}$	298	Barnes et al., 1990	RR (b)

3-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene.

Comments

(a) 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. 3-carene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{3-carene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.08 \pm 0.02$ 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, 2003).

(b) 420 L glass chamber at 298 K and 1 bar of air. NO_3 was generated by the thermal decomposition of N_2O_5. 3-carene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{3-carene}) / k(NO_3 + \text{2-methyl-2-butene}) = 0.87 \pm 0.13$ 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, 2003).

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Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.1×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The two relative rate studies of this reaction are at room temperature only. Atkinson et al. (1984) and Barnes et al. (1990) used the same reference reactant but derived rate coefficients which diverge by ~20 %. There is no obvious reason to favour either study and the preferred value of the 298 K rate coefficient is an unweighted average.

The reaction mechanism involves the addition of NO_3 across the double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Unstable nitrooxy peroxynitrates (from nitrooxyalkyl peroxy radical + NO_2) were observed at early reaction times (Hallquist et al. 1999). These authors also identified the end products caronaldehyde (molar yields of 2-3 %), carbonyls (estimated molar yield of 20-30 %) and nitrates (66-74 %). The atmospheric fate of caronaldehyde is expected to be reaction with OH and photolysis (Hallquist et al., 1997).

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 0.77 with 50 % being located in the aerosol phase. Organonitrates comprised 56 % of the aerosol mass.

Secondary organic aerosol has been observed in the smog-chamber studies of NO_3 + 3-carene (Hallquist et al., 1999; Griffin et al. 1999; Fry et al., 2014) with mass-based yields of up to 72 % depending on the amount of 3-carene reacted. Hallquist et al. (1999) provide evidence for the presence of condensable organics containing the -ONO_2 entity, and organo nitrates were found to be 56 % of the aerosol mass (Fry et al., 2014). A detailed mechanism of the potential routes to aerosol formation is presented by Colville et al. (2004).

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