

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC36

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(2.36 \pm 0.10) \times 10^{-12}$	295	Atkinson et al., 1984	RR-GC (a)
$(2.38 \pm 0.05) \times 10^{-12}$	296	Atkinson et al., 1988	RR-GC (b)
$(1.1 \pm 0.4) \times 10^{-12}$	298*	Kotzias et al., 1989	RR-FTIR (c)
$(2.81 \pm 0.47) \times 10^{-12}$	298	Barnes et al., 1990	RR-GC (d)

β -pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane.

Comments

- 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 . β -pinene and 2-methyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(\text{NO}_3 + \beta\text{-pinene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.252 \pm 0.011$ is placed on an absolute basis using $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003).
- 6400 L Teflon chamber at 296 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5 . β -pinene and trans-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(\text{NO}_3 + \beta\text{-pinene}) / k(\text{NO}_3 + \text{trans-2-butene}) = 6.10 \pm 0.14$ is placed on an absolute basis using $k(\text{NO}_3 + \text{trans-2-butene}) = 3.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC 2016, datasheet $\text{NO}_3\text{-VOC30}$).
- 450 L Teflon-coated glass reactor, with β -pinene, N_2O_5 and NO_2 monitored by FTIR. NO_3 , NO_2 and N_2O_5 were assumed to be in equilibrium and the NO_3 concentration was calculated from the equilibrium constant ($1.9 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3$) and used to derive the rate constant from the β -pinene decay constant. The authors did not quote the temperature of these experiments, making re-assessment of their data via e.g. use of a more recently measured equilibrium constant difficult.
- 420 L glass chamber at 298 K and 1bar of air. NO_3 was generated by the thermal decomposition of N_2O_5 . β -pinene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(\text{NO}_3 + \beta\text{-pinene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.30 \pm 0.05$ is placed on an absolute basis using $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.5×10^{-12}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The relative rate studies of this reaction which employed either 2-methyl-2-butene or trans-2-butene as reference reactants are in broad agreement, though there is no obvious reason why Atkinson et al. (1984) and Barnes et al. (1990), who used the same reference reactant should derive rate coefficients which diverge by ~20 %. These studies are preferred over that of Kotzias et al. (1989), as there are greater uncertainties related to using the strongly temperature dependent equilibrium constant for the $\text{NO}_2 + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_5$ reaction, which are compounded by the fact that authors did not cite their experimental temperature. The preferred value of the 298 K rate coefficient is thus an unweighted average of the results derived by Atkinson et al. (1984, 1988) and Barnes et al. (1990).

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. Hallquist et al. (1999) identified the end products nopinone (molar yields of 1-2 %), carbonyls (estimated molar yield of 12-14 %) and organic nitrates (estimated molar yield of 61-74 %) which were also observed using FTIR and MS by Kotzias et al. (1989), but not quantified. Using thermal dissociation of alkyl nitrates and peroxy nitrates coupled to LIF detection of NO_2 , Fry et al., (2009) derived a molar organic nitrate yield of ~40 %. Hydroxynitrates ($m/z = 215$), hydroxycarbonyl nitrates ($m/z = 229$) and dihydroxynitrates / hydroperoxides and cyclic ether hydroxynitrates ($m/z = 231$) have been observed as gas-phase products (Boyd et al., 2015), with altogether more than forty $\text{C}_7\text{-C}_{10}$ organic nitrates (in both gas and particle phase) possessing between 4 and 9 oxygen atoms detected (Boyd et al. 2015, Nah et al., 2016). Formation of peroxy radical that may perform intramolecular H-abstraction (auto-oxidation) has been proposed as a potential explanation for the high O-to-N ratios observed.

Secondary organic aerosol formation has been observed in the smog-chamber studies of $\text{NO}_3 + \beta$ -pinene (Hallquist et al., 1999; Griffin et al. 1999; Fry et al., 2009, 2014; Boyd et al., 2015; Nah et al., 2016) with mass-based yields of up to 100 % depending on the amount of β -pinene reacted. The aerosol yield is not strongly influenced by relative humidity, seed-aerosol acidity or whether the fate of RO_2 is reaction with NO_3 or HO_2 (Boyd et al., 2015). Organonitrates were found to comprise $\approx 45\text{-}75$ % of the aerosol mass (Fry et al., 2014, Boyd et al., 2015; Nah et al., 2016) with evidence for particle-phase hydrolysis of tertiary nitrates (Boyd et al., 2015).

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