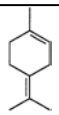
IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC43

This data sheet last evaluated: June 2013; last change in preferred values: June 2013.

NO_3 +  (terpinolene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.9) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$(7.5 \pm 1.0) \times 10^{-11}$	433		
Relative Rate Coefficients			
$(9.67 \pm 0.51) \times 10^{-11}$	295	Corchnoy and Atkinson, 1990	RR (b)
$(6.12 \pm 0.52) \times 10^{-11}$	298	Stewart et al., 2013	RR (c)

Terpinolene is 4-isopropylidene-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. Terpinolene was present at similar concentrations (1-3 fold) to NO_3 and absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Terpinolene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio $k(NO_3$ + terpinolene) / ($k(NO_3$ + 2,3-dimethyl-2-butene) = 1.69 ± 0.09 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72 × 10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(c) 1 L glass vessel at 1013 mbar (760 Torr) of air. Relative changes in concentration of terpinolene and limonene (reference reactant) were monitored by GC. The rate constant ratio $k(NO_3$ + terpinolene) / ($k(NO_3$ + limonene) = 5.10 ± 0.43 is placed on an absolute basis using $k(NO_3$ + limonene) = 1.2 × 10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2016, datasheet NO3_VOC33).

Preferred Values

Parameter	Value	T/K

k /cm^3 molecule^{-1} s^{-1}	9.7 x 10^{-11}	298

Reliability

$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate study of Corchnoy and Atkinson (1990) in which accurate determination of the reactant concentrations was not required. The error limits are expanded to reflect the poor agreement with the absolute rate measurement at the same temperature (Martínez et al., 1999) and the relative rate study of Stewart et al (2013). The difference between the rate coefficients obtained at 298 and 433 K (factor 1.44) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

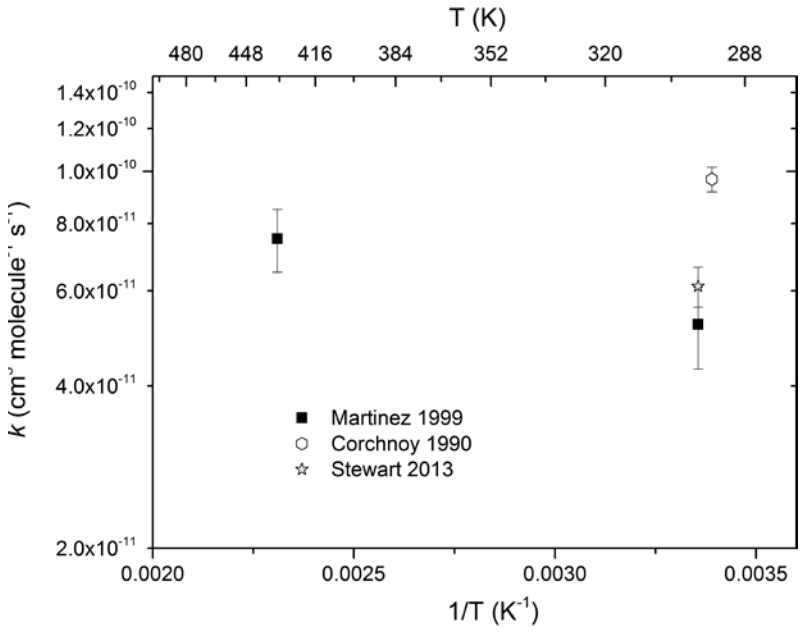
Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Corchnoy, S. B., and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.

IUPAC, Task Group on Atmospheric Chemical kinetic data evaluation. (Ammann, M., Atkinson, R., Cox, R.A., Crowley, J.N., Hynes, R. G., Jenkin, M.E., Mellouki, W., Rossi, M. J., Troe, J. and Wallington, T. J.) Evaluated kinetic data: http://iupac.pole-ether.fr, 2016.

Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.

Stewart, D. J., Almabrok, S. H., Lockhart, J. P., Mohamed, O. M., Nutt, D. R., Pfrang, C., and Marston, G., Atmos. Env., 70, 227-235, 2013.



Rate coefficients for NO_3 + terpinolene