

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC46

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(6.2 \pm 2.1) \times 10^{-13}$	298	Martínez et al., 1998	DF-LIF (a)
$3.1 \times 10^{-12} \exp[(-481 \pm 55)/T]$	298-433		
<i>Relative Rate Coefficients</i>			
$(6.59 \pm 0.16) \times 10^{-13}$	296	Atkinson et al., 1990	RR (b)

Camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane.

Comments

- (a) NO₃ radicals ($\approx 3\text{-}6 \times 10^{12} \text{ molecule cm}^{-3}$) generated from reaction of F atoms (made in a microwave discharge through F₂/He) with HNO₃. Flow tube was operated at ~ 1.33 mbar (1 Torr) He at 4 temperatures between 298 and 393 K. Camphene was present at similar concentrations ($\approx 3\text{-}20 \times 10^{12} \text{ molecule cm}^{-3}$) to NO₃. So that absolute NO₃ concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.
- (c) Relative rate of loss of camphene and trans-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air was monitored by GC. NO₃ was generated by the thermal decomposition of N₂O₅. The rate constant ratio, $k(\text{NO}_3 + \text{camphene}) / k(\text{NO}_3 + \text{trans-2-butene}) = 1.69 \pm 0.04$ required correction for an impurity in the camphene sample and 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 NO₃_VOC30).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	6.6×10^{-13}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.10	298

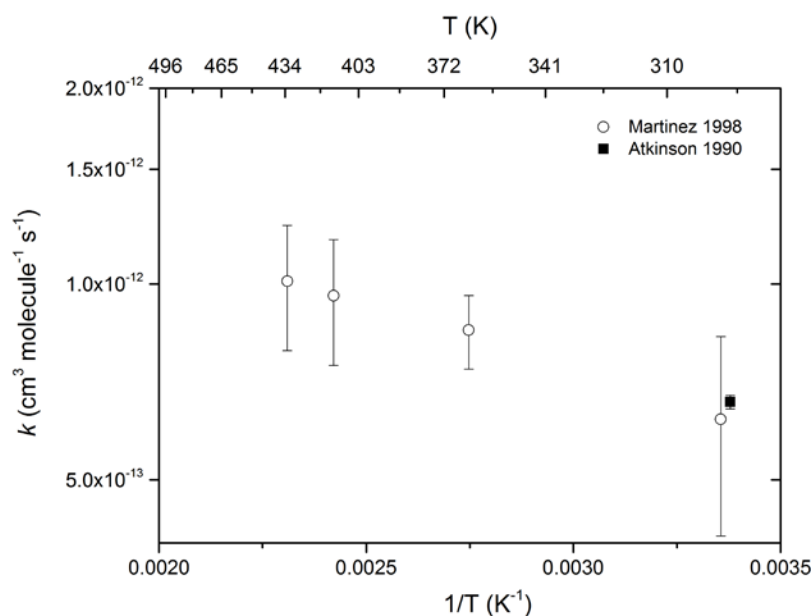
Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Atkinson et al. 1990, which agrees with the absolute study of Martínez et al. (1999). The significant, positive dependence of k on temperature observed by Martínez et al. (1999) requires validation.

There are no product studies of this reaction, though by analogy to other $\text{NO}_3 +$ terpene reactions, the reaction will proceed 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.

References

- Atkinson, R., Aschmann, S. M., and Arey, J., *Atmos. Env. A*, 24, 2647-2654, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.) <http://iupac.pole-ether.fr/index.html>, <http://iupac.pole-ether.fr/index.html>, 2016.
Martínez, E., Cabañas, B., Aranda, A. and Martín, P., *Env. Sci. Tech.*, 32, 3730-3734, 1998.



Rate coefficients for the reaction $\text{NO}_3 +$ camphene