

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>3</sub>\_VOC42

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



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.2 \pm 1.0) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$1.9 \times 10^{-9} \exp[-(1158 \pm 270)/T]$	298-433		
<i>Relative Rate Coefficients</i>			
$(8.52 \pm 0.63) \times 10^{-11}$	294	Atkinson et al., 1985	RR (b)
$(5.98 \pm 0.20) \times 10^{-11}$	298	Berndt et al., 1996	RR (c)

$\alpha$ -phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

### Comments

- (a) NO<sub>3</sub> radicals ( $6\text{--}30 \times 10^{11} \text{ molecule cm}^{-3}$ ) generated from reaction of F atoms (made in a microwave discharge through F<sub>2</sub>/He) with HNO<sub>3</sub>. Flow tube was operated at  $\sim 1.33$  mbar (1 Torr) He.  $\alpha$ -phellandrene was present at similar concentrations (1-3 fold) to NO<sub>3</sub>. So that absolute NO<sub>3</sub> concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.
- (b) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. NO<sub>3</sub> was generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>. Correction made to the  $\alpha$ -phellandrene loss rate due to reaction with NO<sub>2</sub> was 29 – 46 %.  $\alpha$ -phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio,  $k(\text{NO}_3 + \alpha\text{-phellandrene}) / k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 1.49 \pm 0.11$  is placed on an absolute basis by  $k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).
- (c) Flow tube at 15 mbar N<sub>2</sub>. NO<sub>3</sub> was generated by the thermal decomposition of N<sub>2</sub>O<sub>5</sub>, 2,3-dimethyl-2-butene was used as reference reactant. Various detection schemes (electron impact MS, FTIR and GC-MS/FID) were available though it is not stated which was used for the relative rate analysis. The rate constant ratio obtained,  $k(\text{NO}_3 + \alpha\text{-phellandrene}) / k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 1.046 \pm 0.035$  is placed on an absolute basis by  $k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson and Arey, 2003).

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.3 \times 10^{-11}$	298
<i>Reliability</i> $\Delta \log k$	$\pm 0.15$	298

#### *Comments on Preferred Values*

The preferred value of the room temperature rate coefficient is an average of the two relative rate studies in which accurate determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of  $\alpha$ -phellandrene by reaction with  $\text{NO}_2$  and the poor agreement between the three studies. The significant, positive dependence of  $k$  on temperature observed by Martínez et al. (1999) requires validation.

The large rate constant indicates that addition of  $\text{NO}_3$  across a double bond to form a nitrooxyalkyl radical is the initial step. This can decompose to *c*-cymene, with a yield of  $\sim 20\%$  at pressures above 150 mbar  $\text{N}_2$  or air (Berndt et al., 1996). Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in  $\text{N}_2/\text{O}_2$  bath gas.

### References

- Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., *Env. Sci. Tech.*, 19, 159-163, 1985.
- Atkinson, R., and Arey, J., *Chem. Rev.*, 103, 4605-4638, 2003.
- Berndt, T., Böge, O., Kind, I., and Rolle, W., *Ber. Bunsen-Ges. Phys. Chem.* 100, 462-469, 1996.
- Martínez, E., Cabañas, B., Aranda, A., Martín, P., and Salgado, S., *J. Atmos. Chem.*, 33, 265-282, 1999.