

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_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)

α -phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

Comments

- NO_3 radicals ($6\text{-}30 \times 10^{11} \text{ molecule cm}^{-3}$) 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. α -phellandrene was present at similar concentrations (1-3 fold) to NO_3 . So that absolute NO_3 concentrations (derived by titration with tetramethylethane) were necessary to derive the rate coefficient.
- 4000 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5 . Correction made to the α -phellandrene loss rate due to reaction with NO_2 was 29 – 46 %. α -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 using $k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003).
- Flow tube at 15 mbar N_2 . NO_3 was generated by the thermal decomposition of N_2O_5 , 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 using $k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	7.3×10^{-11}	298
<i>Reliability</i>		
$\Delta \log k$	± 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 α -phellandrene by reaction with 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 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 ~ 20 % at pressures above 150 mbar N_2 or air (Berndt et al., 1996). Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in N_2/O_2 bath gas.

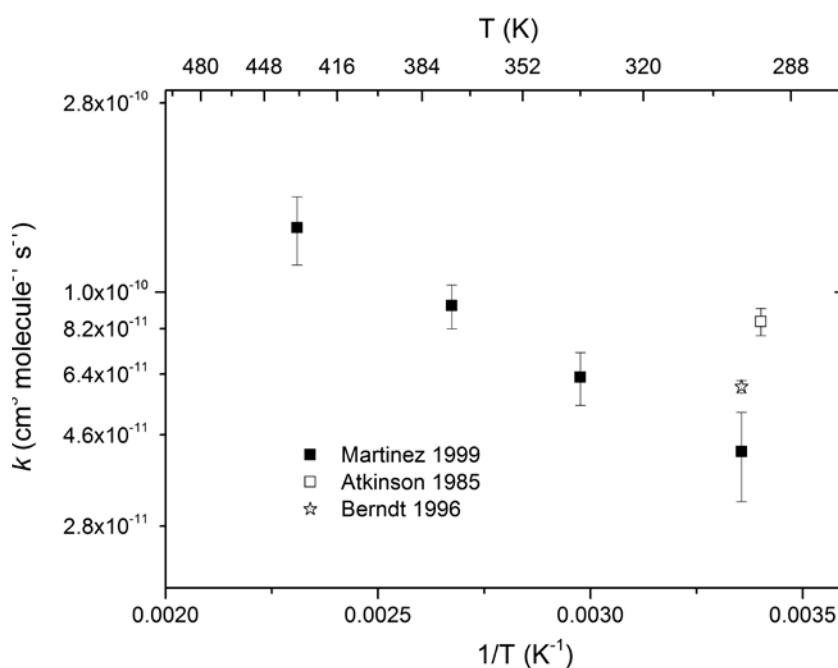
References

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Rate coefficients for $\text{NO}_3 + \gamma$ -phellandrene