IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC37

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

NO_3 +  **(myrcene) → products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.28 \pm 0.11) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$2.2 \times 10^{-12} \exp[(523 \pm 35)/T]$	298-433		
Relative Rate Coefficients			
$(1.06 \pm 0.02) \times 10^{-11}$	294	Atkinson et al., 1985	RR (b)

Myrcene is 7-methyl-3-methylene-1,6-octadiene.

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. γ-terpinene was present at similar concentrations (1-3 fold) to NO_3. So that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Correction made to the myrcene loss rate due to reaction with NO_2 was < 18 %. Myrcene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3$ + myrcene) / $k(NO_3$ + 2-methyl-2-butene) = 1.13 ± 0.02 is placed on an absolute basis using $k(NO_3$ + 2-methyl-2-butene) = 9.37 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.1 x 10^{-11}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) 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 myrcene by reaction with NO_2 and the ≈ 20 % difference to the absolute rate measurement (Martínez et al., 1999). The temperature dependence observed by Martínez et al. (1999) requires validation before a recommendation can be made.

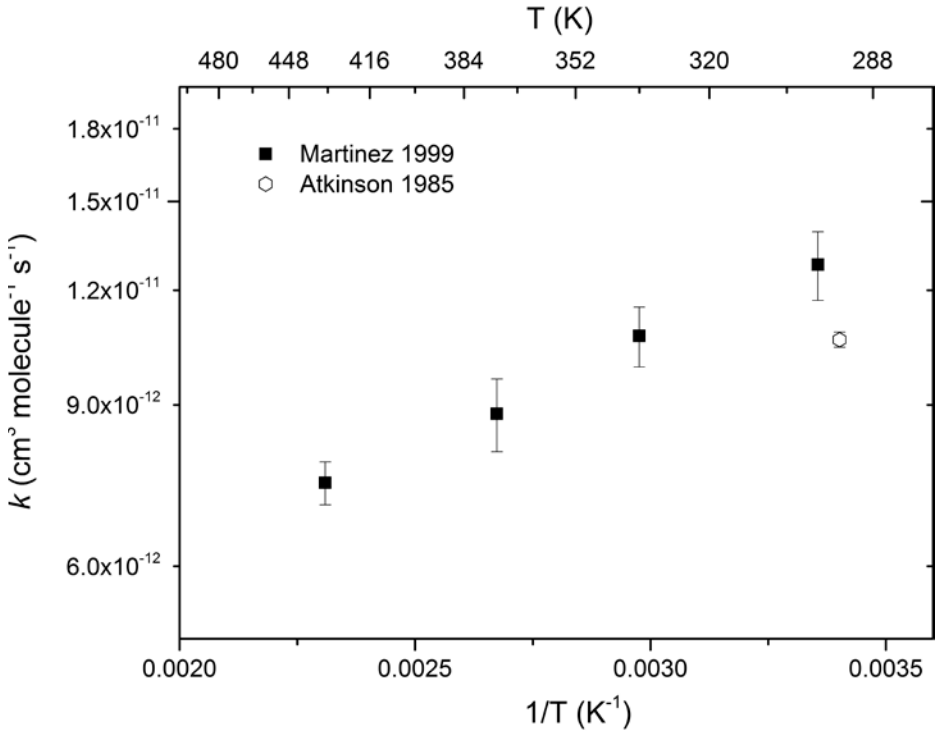
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization 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., 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.

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



Rate coefficient for NO_3 + myrcene