Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC38

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NO_3 +  (sabinene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.07 \pm 0.16) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$2.3 \times 10^{-10} \exp[-(940 \pm 200)/T]$	298-393		
Relative Rate Coefficients			
$(1.01 \pm 0.03) \times 10^{-11}$	296	Atkinson et al., 1990	RR (b)

Sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.

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 at 4 temperatures between 298 and 393 K. Sabinene 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) Relative rate of loss of sabinene and 2-methyl-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air was monitored by GC. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, k(NO_3 + sabinene) / k(NO_3 + 2-methyl-2-butene) = 1.08 ± 0.03 is placed on an absolute basis using k(NO_3 + 2-methyl-2-butene) = 9.37 × 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}	1.0×10^{-11}	298
Reliability		
$\Delta \log k$	± 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). 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 the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitro-oxyalkyl 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.

Secondary organic aerosol has been observed in the smog-chamber studies of NO_3 + sabinene (Fry et al., 2014) with mass-based yields of up to 45 % (at 10 μg m^{-3} aerosol loading).

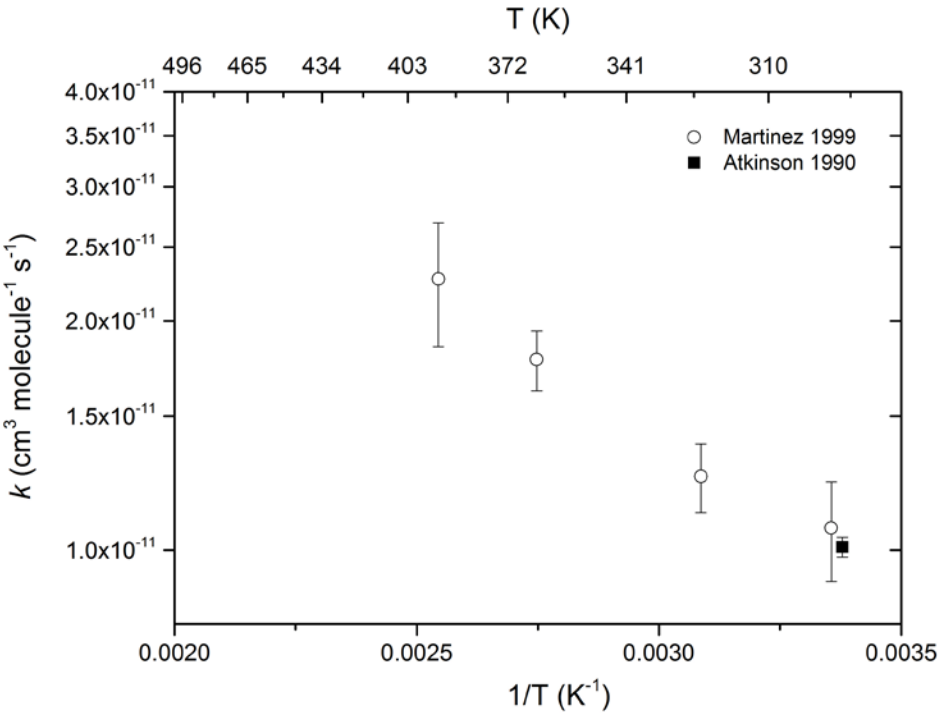
References

Atkinson, R., Aschmann, S. M., and Arey, J., Atmos. Env. A, 24, 2647-2654, 1990.

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

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.

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



Rate coefficients for NO_3 + sabinene