Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC47

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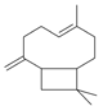
NO_3 +  **(β-caryophyllene) → products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.92 \pm 0.35) \times 10^{-11}$	296	Atkinson et al., 1990	RR (a)

β-caryophyllene is: *trans*-(1*R*,9*S*)-8-Methylene-4,11,11-trimethylbicyclo[7.2.0]undec-4-ene.

Comments

(a) Relative rate of loss of β-caryophyllene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air was monitored by GC-FID. NO_3 was generated by the thermal decomposition of N_2O_5. A correction was applied to take into account loss of β-caryophyllene by reaction with NO_2. The rate constant ratio, k(NO_3 + β-caryophyllene) / k(NO_3 + 2-methyl-2-butene) = 2.05 ± 0.37 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}	1.9×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents around them (Atkinson 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across a double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

Secondary aerosol is formed efficiently in chamber studies of this reaction, with yields (defined as the mass of aerosol formed per mass of β-caryophyllene reacted) of close to 100 % (Jaoui et al., 2013; Fry et al., 2014) with compounds of molecular weight up to *m/z* 375 identified. Product organic nitrates have low vapour pressures and have been found to partition entirely to the aerosol phase (Fry et al., 2014).

References

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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.

Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H., Environmental Chemistry, 10, 178-193, 2013.

Shu, Y. H., and Atkinson, R., J. Geophys. Res. -Atmos., 100, 7275-7281, 1995.