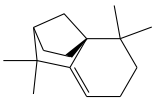
Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC38

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (http://iupac.pole-ether.fr)
This datasheet last evaluated: August 2018; last change in preferred values: June 2015

O_3 +  **(isolongifolene) → products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(8.8 \pm 0.8) \times 10^{-18}$	295 ± 2	Richters et al., 2015	S-IR/UVA (a)
Relative Rate Coefficients			
$(1.1 \pm 0.5) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (b)
$(1.57 \pm 0.29) \times 10^{-17}$	295 ± 2	Richters et al., 2015	RR-MS (c)
$(7.56 \pm 0.21) \times 10^{-18}$	295 ± 2	Richters et al., 2015	RR-MS (d)

isolongifolene is (1R)-2,2,7,7-tetramethyltricyclo[6.2.1.0^{1,6}]undec-5-ene

Comments

(a) k determined from the observed pseudo-first order rate of ozone decay (measured by UVA at 254 nm) in the presence of known excess concentrations of isolongifolene (measured by FTIR), in stopped-flow experiments at a total pressure of ~1 bar, with sufficient propane to scavenge >99 % of HO radicals.

(b) The concentrations of isolongifolene and 2,3-dimethyl-but-2-ene (the reference compound), with excess cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 123 L Teflon-coated chamber at 780 Torr (1040 mbar) pressure of N_2, with repeated injections of O_3/O_2. The measured rate coefficient ratio, $k(O_3 + \text{isolongifolene})/k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 0.87$, is placed on an absolute basis using $k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 1.32 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 2.89 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (2.5 \pm 1.1) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 366 K.

(c) The concentrations of isolongifolene and 2-methyl-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(O_3 + \text{isolongifolene})/k(O_3 + \text{2-methyl-but-2-ene}) = (0.040 \pm 0.004)$, is placed on an absolute basis using $k(O_3 + \text{2-methyl-but-2-ene}) = 3.92 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson and Arey, 2003).

(d) The concentrations of isolongifolene and *cis*-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The

measured rate coefficient ratio, $k(O_3$ + isolongifolene$)/k(O_3$ + *cis*-but-2-ene) = (0.060 ± 0.004), is placed on an absolute basis using $k(O_3$ + *cis*-but-2-ene) = 1.26×10^{-16} cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-17}	298
Reliability		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on a rounded average of the absolute and relative rate determinations of Richters et al. (2015), with an uncertainty that encompasses the range of values. Although Ghalaieny et al. (2012) report a comparable value of *k* at 366 K (see comment (c)), this was apparently based on use of an anomalously low value of the rate coefficient for the reference reaction of O_3 with 2,3-dimethyl-but-2-ene. The value tabulated above is based on the current IUPAC recommendation (see comment (c)), leading to a value of *k* (at 366 K) that is two orders of magnitude higher than the preferred value.

The reaction is expected to proceed via addition of O_3 to the C=C bond, with the subsequent mechanism following the general framework outlined in the datasheets for other mono- and sesquiterpenes possessing endocyclic C=C bonds (e.g. α-cedrene). However, there have apparently been no product or mechanistic studies to confirm this.

References

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

Ghalaieny, M., Bacak, A., McGillen, M., Martin, D., Knights, A. V., O'Doherty, S., Shallcross, D. E. and Percival, C. J.: Phys. Chem. Chem. Phys., 14, 6596, 2012.

Richters, S., Herrmann, H. and Berndt, T.: Phys. Chem. Chem. Phys., 17, 11658, 2015.