Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC33

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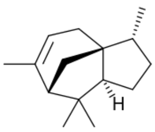
O_3 +  **(α-cedrene[a]) → products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.3) \times 10^{-16}$	295 ± 2	Richters et al., 2015	S-IR/UVA (b)
Relative Rate Coefficients			
$(2.87 \pm 0.85) \times 10^{-17}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (c),(d)
$(2.80 \pm 0.14) \times 10^{-17}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (c),(e)
$(1.5 \pm 0.9) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (f)
$(1.22 \pm 0.19) \times 10^{-16}$	295 ± 2	Richters et al., 2015	RR-MS (g),(d)
$(1.37 \pm 0.37) \times 10^{-16}$	295 ± 2	Richters et al., 2015	RR-MS (g),(e)

Comments

(a) 2,6,6,8-tetramethyl-tricyclo[5.3.1.0^{1,5}]undec-8-ene.

(b) 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 α-cedrene (measured by FTIR), in stopped-flow experiments at a total pressure of ~1 bar, with sufficient propane to scavenge >99 % of HO radicals.

(c) The concentrations of α-cedrene and 2-methyl-but-2-ene or *cis*-but-2-ene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400−6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3. The measured rate coefficient ratios, $k(O_3$ + α-cedrene)/$k(O_3$ + 2-methyl-but-2-ene) = (0.0725 ± 0.0215) and $k(O_3$ + α-cedrene)/$k(O_3$ + *cis*-but-2-ene) = (0.228 ± 0.011), are placed on an absolute basis using $k(O_3$ + 2-methyl-but-2-ene) = 3.96×10^{-16} (Atkinson and Arey, 2003) and $k(O_3$ + *cis*-but-2-ene) = 1.23×10^{-16} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) at 296 K.

(d) Relative to 2-methyl-but-2-ene.

(e) Relative to *cis*-but-2-ene.

(f) The concentrations of α-cedrene 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, $k(O_3$ + α-cedrene)/$k(O_3$ + 2,3-dimethyl-but-2-ene) = 1.08, is placed on an absolute basis using $k(O_3$ + 2,3-dimethyl-but-2-ene) = 1.36×10^{-15} cm^3 molecule^{-1} s^{-1} at 366 K (Atkinson and Arey, 2003). It is noted that the authors used a much lower value of $k(O_3$ + 2,3-dimethyl-but-2-ene) =

2.89 x 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 $k = (3.1 \pm 1.9) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1} at 366 K.

(g) The concentrations of α-cedrene and 2-methyl-but-2-ene or *cis*-but-2-ene (the reference compounds), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratios, $k(O_3$ + α-cedrene)/$k(O_3$ + 2-methyl-but-2-ene) = (0.310 ± 0.006) and $k(O_3$ + α-cedrene)/$k(O_3$ + *cis*-but-2-ene) = (1.13 ± 0.01), are placed on an absolute basis using $k(O_3$ + 2-methyl-but-2-ene) = 3.92 x 10^{-16} (Atkinson and Arey, 2003) and $k(O_3$ + *cis*-but-2-ene) = 1.21 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, current recommendation) at 295 K.

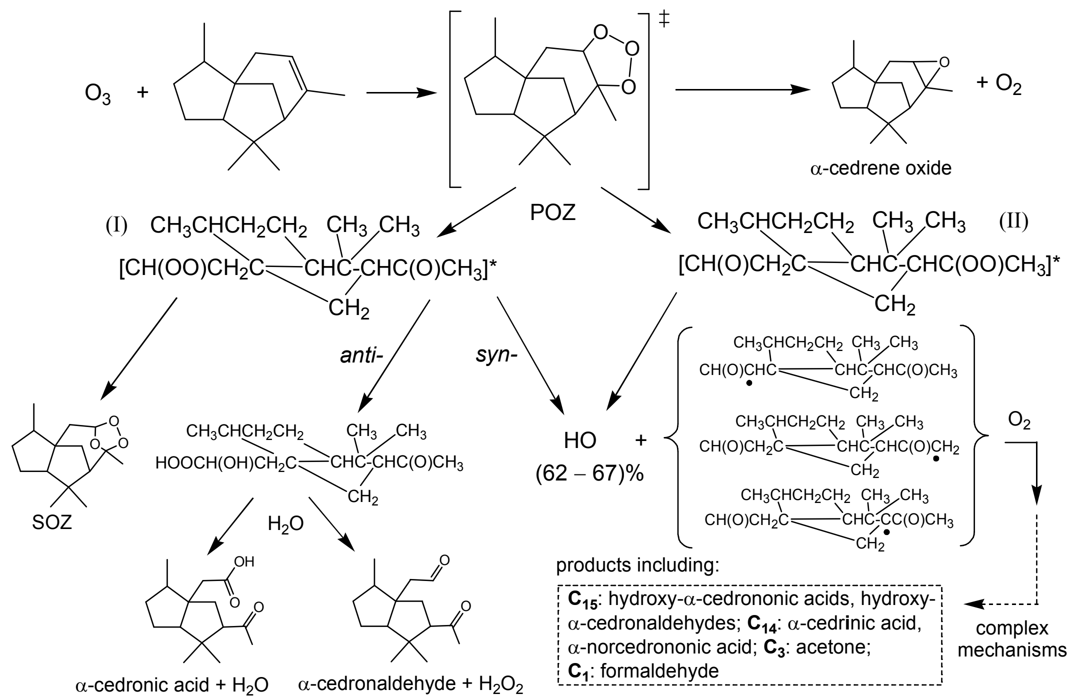
Preferred Values

No recommendation

Comments on Preferred Values

The studies tabulated above provide evidence that the reaction of O_3 with α-cedrene occurs, and that k is sufficiently high that the reaction will contribute to α-cedrene removal under atmospheric conditions. However, the level of disagreement in the reported values of k precludes recommendation of a preferred value. Further kinetics studies are required to allow the current discrepancies to be explained or reconciled.

The addition of O_3 to the C=C bond in α-cedrene forms a "primary ozonide (POZ)". Although minor (~0.1 %) formation of α-cedrene oxide has been reported (Jaoui et al., 2004), it is likely that POZ mainly decomposes to form the two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the schematic below.



The Criegee intermediates can decompose to form HO radicals, which are expected to be formed in conjunction with a number of β-oxo alkyl radicals. HO radical yields of (67^{+34}_{-22}) % and (62.4 ± 4.9) % have been reported Shu and Atkinson (1994) and Yao et al. (2014), with the latter study reporting a large decrease to (9.0 ± 1.6) % when either $CH_3C(O)OH$ or SO_2 were added to scavenge stabilised Criegee intermediates. The further chemistry of the β-oxo alkyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (e.g., Jaoui et al., 2004; Yao et al., 2014), and also acetone and formaldehyde which have been reported to be formed by Jaoui et al. (2004).

Products likely to be produced from alternative reactions of the Criegee intermediates (I) and (II) have also been detected. The formation of α-cedronaldehyde has been positively identified by Jaoui et al. (2004) and Yao et al. (2014), potentially formed from the reaction of (I) with H_2O. Jaoui et al. (2004) also detected α-cedronic acid as a possible alternative product of this reaction, although this was not confirmed by Yao et al. (2014). A thermally-stable secondary ozonide (SOZ), which can be formed by ring-closure of either of the Criegee intermediates (I) and (II), was reported as the major gas phase product of α-cedrene ozonolysis by Yao et al. (2014).

References

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