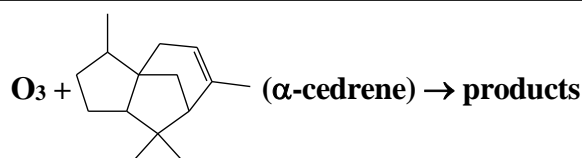


## Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox\_VOC33

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### Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K     | Reference              | Technique/<br>Comments |
|--|-------------|------------------------|------------------------|
| <i>Absolute Rate Coefficients</i>                    |             |                        |                        |
| $(2.2 \pm 0.3) \times 10^{-16}$                      | $295 \pm 2$ | Richters et al., 2015  | S-IR/UVA (a)           |
| <i>Relative Rate Coefficients</i>                    |             |                        |                        |
| $(2.87 \pm 0.85) \times 10^{-17}$                    | $296 \pm 2$ | Shu and Atkinson, 1994 | RR-GC (b),(c)          |
| $(2.90 \pm 0.14) \times 10^{-17}$                    | $296 \pm 2$ | Shu and Atkinson, 1994 | RR-GC (b),(d)          |
| $(1.4 \pm 0.9) \times 10^{-15}$                      | $366 \pm 2$ | Ghalaieny et al., 2012 | RR-GC (e)              |
| $(1.22 \pm 0.19) \times 10^{-16}$                    | $295 \pm 2$ | Richters et al., 2015  | RR-MS (f),(c)          |
| $(1.42 \pm 0.38) \times 10^{-16}$                    | $295 \pm 2$ | Richters et al., 2015  | RR-MS (f),(d)          |

$\alpha$ -cedrene is 2,6,6,8-tetramethyl-tricyclo[5.3.1.0<sup>1,5</sup>]undec-8-ene

### Comments

- $k$  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  $\alpha$ -cedrene (measured by FTIR), in stopped-flow experiments at a total pressure of  $\sim 1$  bar, with sufficient propane to scavenge  $>99\%$  of HO radicals.
- The concentrations of  $\alpha$ -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  $\text{O}_3$ . The measured rate coefficient ratios,  $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = (0.0725 \pm 0.0215)$  and  $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + \textit{cis-but-2-ene}) = (0.228 \pm 0.011)$ , are placed on an absolute basis using  $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.96 \times 10^{-16}$  (Atkinson and Arey, 2003) and  $k(\text{O}_3 + \textit{cis-but-2-ene}) = 1.27 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) at 296 K.
- Relative to 2-methyl-but-2-ene.
- Relative to *cis*-but-2-ene.
- The concentrations of  $\alpha$ -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  $\text{N}_2$ , with repeated injections of  $\text{O}_3/\text{O}_2$ . The measured rate coefficient ratio,  $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.08$ , is placed on an absolute basis using  $k(\text{O}_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.32 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of  $k(\text{O}_3 + 2,3\text{-dimethyl-}$

but-2-ene) =  $2.89 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , based on a relative rate measurement reported in the same study, leading to a reported value of  $k = (3.1 \pm 1.9) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 366 K.

- (f) The concentrations of  $\alpha$ -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,  $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = (0.310 \pm 0.006)$  and  $k(\text{O}_3 + \alpha\text{-cedrene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = (1.13 \pm 0.01)$ , are placed on an absolute basis using  $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.92 \times 10^{-16}$  (Atkinson and Arey, 2003) and  $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.26 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation) at 295 K.

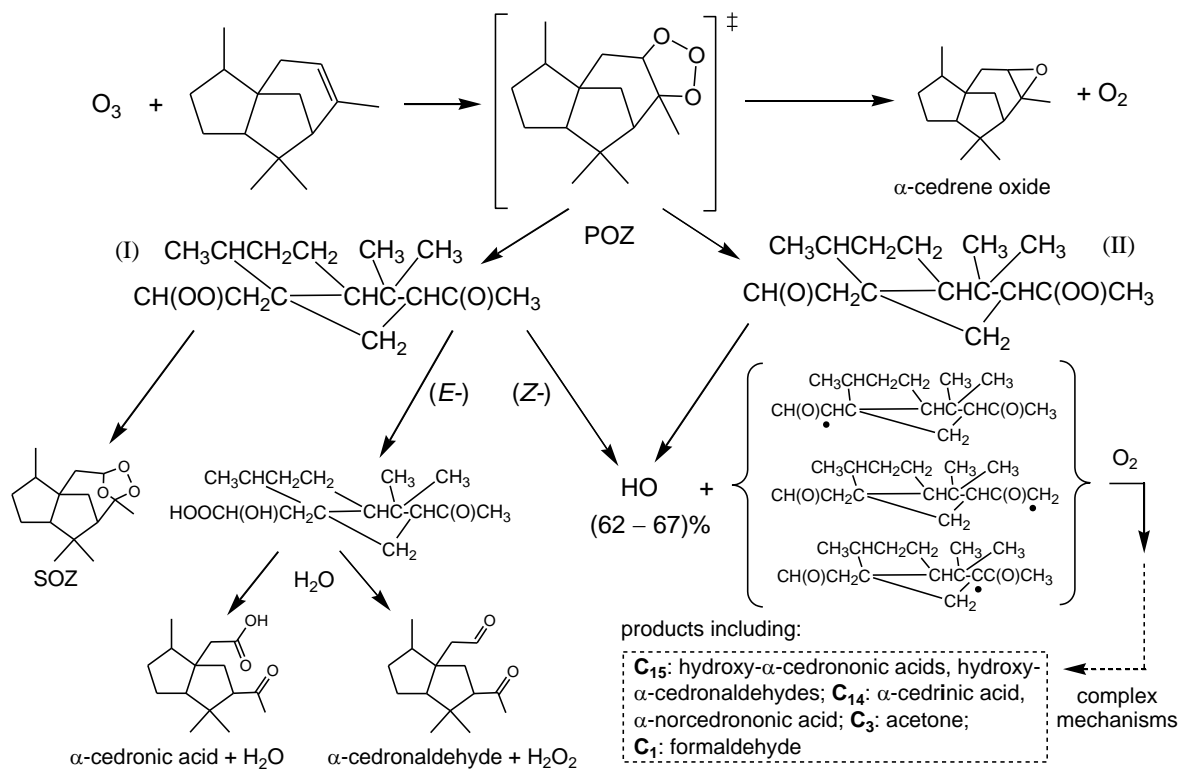
## Preferred Values

No recommendation

### Comments on Preferred Values

The studies tabulated above provide evidence that the reaction of  $\text{O}_3$  with  $\alpha$ -cedrene occurs, and that  $k$  is sufficiently high that the reaction will contribute to  $\alpha$ -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  $\text{O}_3$  to the C=C bond in  $\alpha$ -cedrene forms a “primary ozonide (POZ)”. Although minor ( $\sim 0.1\%$ ) formation of  $\alpha$ -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.



Criegee intermediates (II) and the *Z*-conformer of (I) can decompose to form HO radicals, which are expected to be formed in conjunction with a number of  $\beta$ -oxo alkyl radicals, as shown in the schematic. HO radical yields of  $67^{+34}_{-22}\%$  and  $62.4 \pm 4.9\%$  have been reported Shu and Atkinson (1994) and Yao et al. (2014), preferred value  $65 \pm 5\%$ . The latter study reported a large decrease to  $(9.0 \pm 1.6)\%$  when either

CH<sub>3</sub>C(O)OH or SO<sub>2</sub> were added to scavenge stabilized 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<sub>2</sub>O. 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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