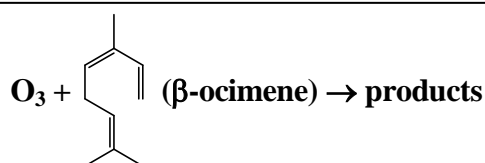


Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC25

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Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|-------------|-----------------------|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| 2.0×10^{-15} | 295 ± 1 | Grimsrud et al., 1975 | F-CL |
| <i>Relative Rate Coefficients</i> | | | |
| $(5.75 \pm 0.88) \times 10^{-16}$ | 296 ± 2 | Atkinson et al., 1990 | RR-GC (a) |
| $(5.29 \pm 0.77) \times 10^{-16}$ | 296 ± 2 | Witter et al., 2002 | RR-GC (b) |
| $3.32 \times 10^{-15} \exp[-(627 \pm 110/T)]$ | 298-318 | Kim et al., 2011 | RR-MS (c) |
| $(4.05^{+0.32}_{-0.30}) \times 10^{-16}$ | 298 | | |

ocimene is 3,7-dimethyl-octa-1,3,6-triene

Comments

- The concentrations of a series of alkenes (including *trans*- β -ocimene and limonene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-ocimene})/k(\text{O}_3 + \textit{limonene})$ is placed on an absolute basis using $k(\text{O}_3 + \textit{limonene}) = 2.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- The concentrations of *trans*- β -ocimene and 2-methyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - *trans*- β -ocimene - 2-methyl-but-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-ocimene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 1.35 \pm 0.08$ is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- The concentrations of β -ocimene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O_3 - β -ocimene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm^3 volume quartz vessel at ~ 1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The measured rate coefficient ratios $k(\text{O}_3 + \beta\text{-ocimene})/k(\text{O}_3 + \textit{trans}\text{-but-2-ene})$ are placed on an absolute basis using $k(\text{O}_3 + \textit{trans}\text{-but-2-ene}) = 7.0 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

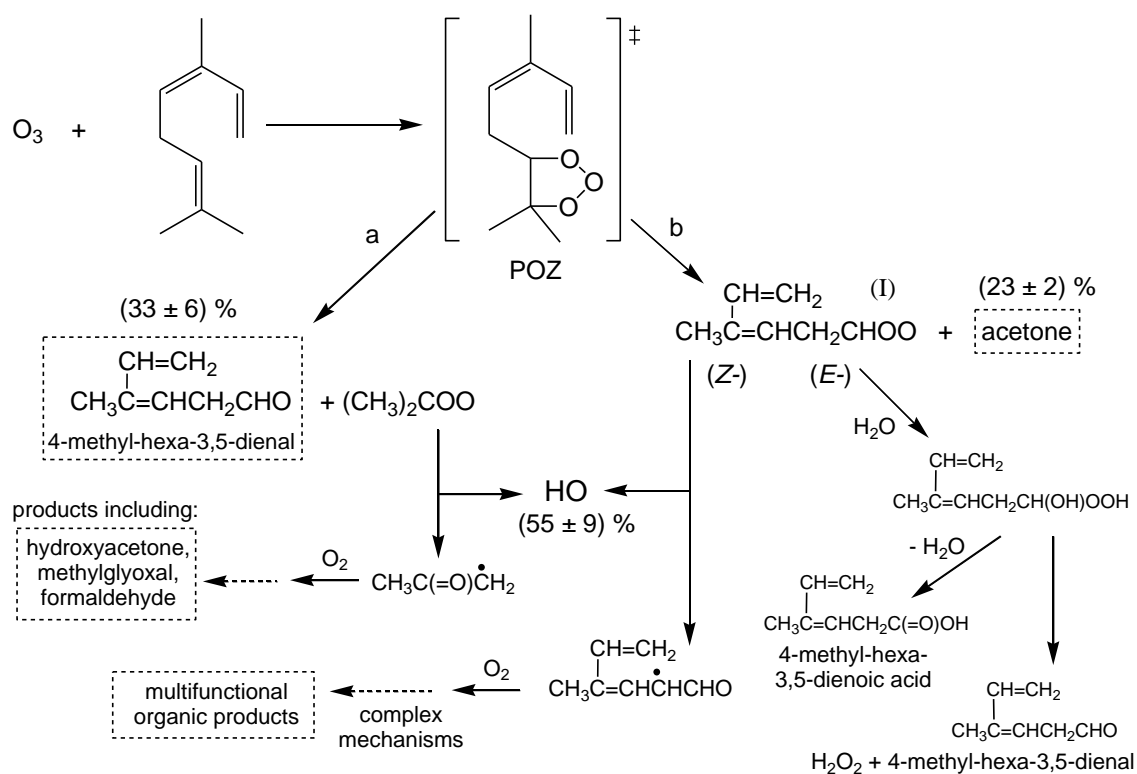
| Parameter | Value | T/K |
|--|-------------------------------------|---------|
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | 5.1×10^{-16} | 298 |
| $k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | $4.15 \times 10^{-15} \exp(-625/T)$ | 290-320 |
| <i>Reliability</i> | | |
| $\Delta \log k$ | ± 0.2 | 298 |
| $\Delta E/R$ | ± 300 | 290-320 |

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Kim et al. (2011). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1990), Witter et al. (2002) and Kim et al. (2011), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value. The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for β -ocimene, and also for several other terpenes, appear to be systematically high

The reaction may proceed by initial addition of O_3 to any of the three C=C bonds in β -ocimene. Comparison of k for the reaction of O_3 with β -ocimene with that reported for the reaction of O_3 with the β -ocimene oxidation product 4-methyl-hexa-3,5-dienal, which retains the conjugated diene structure (Baker et al., 2004), suggests that the reaction of O_3 with β -ocimene occurs predominantly ($\approx 90\%$) at the isolated C=C bond.

The addition of O_3 to the isolated C=C bond in β -ocimene forms a "primary ozonide (POZ)" which rapidly decomposes to form two sets of "primary" carbonyl product plus Criegee intermediate, as shown in the following schematic:



Acetone has been reported to be formed with a yield of (23 ± 2) % (Reissell et al., 1999; 2002), and 4-methyl-hexa-3,5-dienal with a yield of (33 ± 6) % (Reissell et al., 2002). This suggests important contributions from both decomposition channels, (a) and (b), as shown in the schematic, but with other unidentified pathways also contributing. These are partly accounted for by the products potentially formed from addition of O_3 to the C=C bonds in the conjugated diene system, which are not represented in the schematic (and for which there are no reported yields).

The dimethyl-substituted Criegee intermediate $(CH_3)_2COO$ decomposes almost exclusively to form HO radicals and the acetyl radical (see discussion in data sheet Ox_VOC41), the further chemistry of which potentially leads to the formation of a number of products, e.g. hydroxyacetone, methylglyoxal and formaldehyde. HO radicals have been reported to be formed with a yield of (55 ± 9) % from the reaction of O_3 with β -ocimene (Aschmann et al., 2002).

The *Z*- conformer of Criegee intermediate (I), formed in channel (b), may also decompose to form HO radicals and the β -oxo-dienyl radical shown in the schematic. HO formation via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is unavailable for the *E*- conformer, which is likely to react predominantly with H_2O under atmospheric conditions, potentially forming additional 4-methyl-hexa-3,5-dienal and H_2O_2 , or 4-methyl-hexa-3,5-dienoic acid.

References

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