Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC29

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O_3 + (α-terpinene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
8.8×10^{-14}	295 ± 1	Grimsrud et al., 1975	F-CL
Relative Rate Coefficients			
$(9.82 \pm 2.64) \times 10^{-15}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)
$(2.62 \pm 0.88) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(c)
$(2.18 \pm 0.23) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(d)
$(1.60 \pm 0.43) \times 10^{-14}$	296 ± 2	Witter et al., 2002	RR-GC (e)

α-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene

Comments

(a) The concentrations of a series of alkenes (including α-terpinene and terpinolene, 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, $k(O_3 + \alpha\text{-terpinene})/k(O_3 + \text{terpinolene}) = (6.14 \pm 1.24)$, is placed on an absolute basis using $k(O_3 + \text{terpinolene}) = 1.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) The concentrations of α-terpinene and 2,3-dimethyl-but-2-ene or β-caryophyllene (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, $k(O_3 + \alpha\text{-terpinene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = (24.0 \pm 8.0)$ and $k(O_3 + \alpha\text{-terpinene})/k(O_3 + \beta\text{-caryophyllene}) = (1.82 \pm 0.06)$, are placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} and $k(O_3 + \beta\text{-caryophyllene}) = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendations). The final value of k quoted by the authors was based on the more precise measurement relative to β-caryophyllene.

(c) Relative to 2,3-dimethyl-but-2-ene.

(d) Relative to β-caryophyllene.

(e) The concentrations of α-terpinene and 2,3-dimethyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - α-terpinene - 2,3-dimethyl-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(O$_3$ + α-terpinene)/k(O$_3$ + 2,3-dimethyl-but-2-ene) = (14.7 ± 0.7), is placed on an absolute basis using k(O$_3$ + 2,3-dimethyl-but-2-ene) = 1.09 × 10^{-15} 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}	1.9 × 10^{-14}	298
Reliability		
Δ log k	± 0.20	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is the average of the more precise determination of Shu and Atkinson (1994), as favoured by the authors (see comment (c)), and the determination of Witter et al. (2002). The more approximate determination of Atkinson et al. (1990) is superseded by the study of Shu and Atkinson (1994). The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for α-terpinene, and also for several other terpenes, appear to be systematically high. The assigned uncertainty in k reflects the range of values reported in the relative rate studies.

There has been only limited product and mechanistic information reported in the literature. Aschmann et al. (2002) and Herrmann et al. (2010) reported respective HO radical yields of (38 ± 5) % and (24 – 28) %; and Reissell et al. (1999) a yield of acetone of (3 ± 1) %. The reaction is likely to proceed by initial addition of O$_3$ to each of the C=C bonds in the cyclic conjugated diene system, to form a pair of "primary ozonides" which rapidly decompose to form four carbonyl-substituted Criegee intermediates. HO radicals may be formed (in conjunction with a number of β-oxo-alkenyl radicals) from decomposition of the Criegee intermediates, via the accepted mechanism involving abstraction of a β-hydrogen via a vinyl hydroperoxide intermediate (e.g. see Johnson and Marston, 2008). Acetone is most likely to be formed as a first-generation product from the further reactions of one of the β-oxo-alkenyl radicals.

References

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