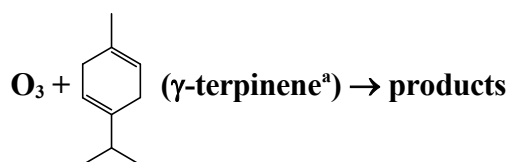


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC30

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This datasheet last evaluated: September 2013; last change in preferred values: September 2013



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
2.8×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(1.52 \pm 0.17) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (b)

Comments

- (a) 1-isopropyl-4-methyl-cyclohexa-1,4-diene.
- (b) The concentrations of a series of alkenes (including γ -terpinene and α -pinene, 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 $k(O_3 + \gamma\text{-terpinene})/k(O_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(O_3 + \alpha\text{-pinene}) = 9.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.5×10^{-16}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.30	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Atkinson et al. (1990). The absolute rate coefficient determination reported by Grimsrud et al. (1975) is about a factor of two higher, but within the upper uncertainty bound assigned to the preferred value. The Atkinson et al. (1990) value is preferred, because those reported by Grimsrud et al.

(1975) for a series of terpenes appear to be systematically high.

There has been only limited product and mechanistic information reported in the literature. Aschmann et al. (2002) reported a yield of HO radicals of $(81 \pm 11) \%$; and Reissell et al. (1999) a yield of acetone of $(11 \pm 2) \%$. The reaction is likely to proceed by initial addition of O_3 to each of the endocyclic C=C bonds, 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 all 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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