

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC31

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Rate coefficient data

$k/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(7.3 \pm 2.2) \times 10^{-16}$	298	Japar et al., 1974	S-CL
1.0×10^{-14}	295 ± 1	Grimsrud et al., 1975	F-CL
<i>Relative Rate Coefficients</i>			
$(1.46 \pm 0.26) \times 10^{-15}$	296 ± 2	Atkinson et al., 1990	RR-GC (a)
$(1.83 \pm 0.04) \times 10^{-15}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b)
$(1.74 \pm 0.46) \times 10^{-15}$	295 ± 0.5	Witter et al., 2002	RR-GC (c)
$(1.41 \pm 0.40) \times 10^{-15}$	298 ± 2	Stewart et al., 2013	RR-GC (d)

terpinolene is 4-isopropylidene-1-methyl-cyclohexene

Comments

- The concentrations of a series of alkenes (including terpinolene 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 $k(O_3 + \text{terpinolene})/k(O_3 + \text{limonene})$ is placed on an absolute basis using $k(O_3 + \text{limonene}) = 2.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- The concentrations of terpinolene and 2,3-dimethyl-but-2-ene (the reference compound), 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 ratio $k(O_3 + \text{terpinolene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene})$ is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- The concentrations of terpinolene and 2,3-dimethyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - terpinolene - 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 of $k(O_3 + \text{terpinolene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.60 \pm 0.06$ is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- The concentrations of terpinolene and limonene (the reference compound) were monitored by GC-FID in flowing mixtures of O_3 , terpinolene, limonene, cyclohexane (the HO radical scavenger) and air

at 760 Torr (1.013 bar) pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \text{terpinolene})/k(\text{O}_3 + \text{limonene}) = 6.41 \pm 0.08$ is placed on an absolute basis using $k(\text{O}_3 + \text{limonene}) = 2.2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

Preferred Values

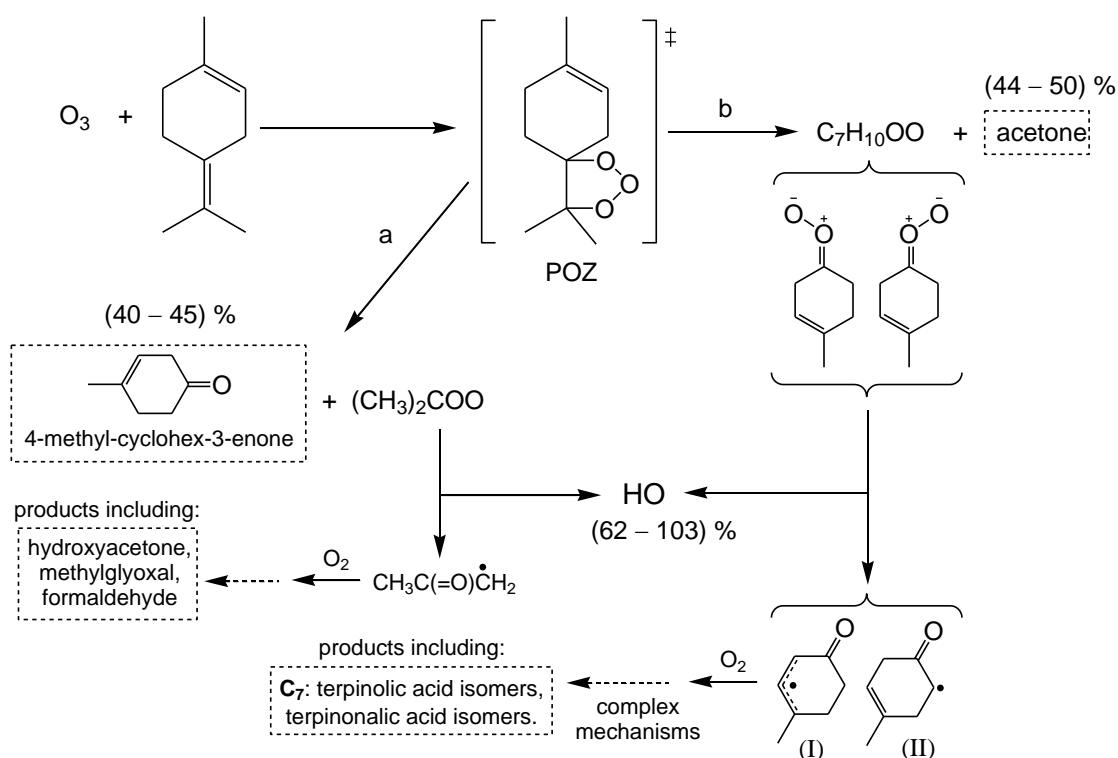
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.6×10^{-15}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is an average of the relative rate coefficient determinations of Atkinson et al. (1990), Shu and Atkinson (1994), Witter et al. (2002) and Stewart et al. (2013), which are in good agreement.

The reaction may proceed by initial addition of O_3 to either of the endocyclic or exocyclic $\text{C}=\text{C}$ bonds in terpinolene. Comparison of k for the reaction of ozone with terpinolene with that reported for the reaction of ozone with the terpinolene oxidation product, 4-methylcyclohex-3-en-1-one, which retains the endocyclic $\text{C}=\text{C}$ bond (Baker et al., 2004), suggests that the reaction of O_3 with terpinolene occurs predominantly ($\approx 95\%$) at the exocyclic bond. Support for this comes from the distribution of products reported in a number of studies.

The addition of O_3 to the exocyclic $\text{C}=\text{C}$ bond in terpinolene 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 (44 – 50) % (Reissell et al., 1999; Orlando et al., 2000; Lee et al., 2006), and 4-methylcyclohex-3-en-1-one with a yield of (40 – 45) % (Hakola et al., 1994; Reissell et al., 1999; Ma and Marston, 2009). This suggests approximately equal contributions from each of the decomposition channels, (a) and (b), as shown in the schematic.

The dialkyl-substituted Criegee intermediates ((CH₃)₂COO and both conformers of C₇H₁₀OO) are expected to decompose mainly to form HO radicals and a number of organic co-radicals, as shown in the schematic. Accordingly, high HO radical yields in the range (62 – 103) % have been reported from the reaction of O₃ with terpinolene (Atkinson et al., 1992; Aschmann et al., 2002; Herrmann et al., 2010), preferred value 70 ± 8 %. The decomposition of (CH₃)₂COO is expected to form HO in conjunction with 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, including formaldehyde, which has been reported to be formed with a yield of (29 ± 3) % from the ozonolysis of terpinolene (Lee et al., 2006). Decomposition of the two conformers of the more complex Criegee intermediate, C₇H₁₀OO, by the accepted HO-forming mechanism (involving abstraction of a β-hydrogen via a vinyl hydroperoxide intermediate), produces a resonant β-/δ-oxo-alkenyl radical (I) and a β-oxo-alkenyl radical (II), the further chemistry of which may form a number of multifunctional organic products containing hydroxy, carbonyl and acid functionalities, including the terpinolic and terpinonic acids reported and discussed by Ma and Marston (2009).

References

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