

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC19

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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>			
6.5×10^{-17}	294	Ripperton et al., 1972	S-CL
3.6×10^{-17}	295 ± 1	Grimsrud et al., 1975	F-CL
$(2.1 \pm 0.5) \times 10^{-17}$	296 ± 2	Atkinson et al., 1982	S-CL/GC (a)
$(1.48 \pm 0.17) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (b)
$(1.22 \pm 0.13) \times 10^{-17}$	295 ± 1	Grosjean et al., 1993	S-UVA (c)
<i>Relative Rate Coefficients</i>			
$(1.39 \pm 0.20) \times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR-GC (d)
$(1.82 \pm 0.22) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	RR-GC (e)
$(2.39 \pm 0.27) \times 10^{-17}$	298 ± 2	Johnson et al., 2000	RR-GC (f)
$1.72 \times 10^{-15} \exp[-(1278 \pm 84)/T]$	298-363	Khamaganov and Hites, 2001	RR-MS (g,h)
$(2.34 \pm 0.13) \times 10^{-17}$	298		
$(2.25 \pm 0.19) \times 10^{-17}$	298	Khamaganov and Hites, 2001	RR-MS (g,i)

β -pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane

Comments

- k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of β -pinene (measured by GC-FID). Experiments were carried out either in a 175 L Teflon bag or in the SAPRC 5800 L Teflon-coated environmental chamber.
- k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of β -pinene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber.
- k determined from the observed first-order rate of ozone decay (measured by UV photometry) in the presence of excess concentrations of β -pinene, with cyclohexane to scavenge HO radicals. Experiments were carried out in a 3.5 m³ Teflon chamber.
- The concentrations of a series of alkenes (including β -pinene and *cis*-but-2-ene, the reference compound) were monitored by GC in a 520 L Pyrex chamber at ~1 bar pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$ is placed on an absolute basis using a rate coefficient of $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation). Details concerning the reactant mixtures and the

presence or absence of an HO radical scavenger were not reported.

- (e) The concentrations of a series of alkenes (including β -pinene 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 O₃. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (f) The concentrations of β -pinene and 2-methylpropene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 50 L collapsible Teflon chamber at 760 Torr (1013 mbar) pressure of purified air in the presence of O₃. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + 2\text{-methylpropene})$ is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methylpropene}) = 1.15 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (g) The concentrations of β -pinene and *cis*-but-2-ene or but-1-ene (the reference compounds) were monitored by MS in reacting O₃ - β -pinene - *cis*-but-2-ene (or but-1-ene) - acetaldehyde (or ethanol) - He mixtures in a 192 cm³ volume quartz vessel at ~1 bar pressure, with acetaldehyde or ethanol being present to scavenge HO radicals. The measured rate coefficient ratios $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 0.51 \exp[(-308 \pm 84)/T]$ and $k(\text{O}_3 + \beta\text{-pinene})/k(\text{O}_3 + \textit{but-1-ene}) = (2.25 \pm 0.19)$ at 298 K are placed on an absolute basis using $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 3.37 \times 10^{-15} \exp(-970/T)$ and $k(\text{O}_3 + \textit{but-1-ene}) = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).
- (h) Relative to $k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$. Identical rate coefficients obtained at 298 K for two enantiomers of β -pinene, (+)- β -pinene and (-)- β -pinene, indicating no associated steric effects on the reaction. Measurements at other temperatures obtained using (+)- β -pinene.
- (i) Relative to $k(\text{O}_3 + \textit{but-1-ene})$, using (+)- β -pinene.

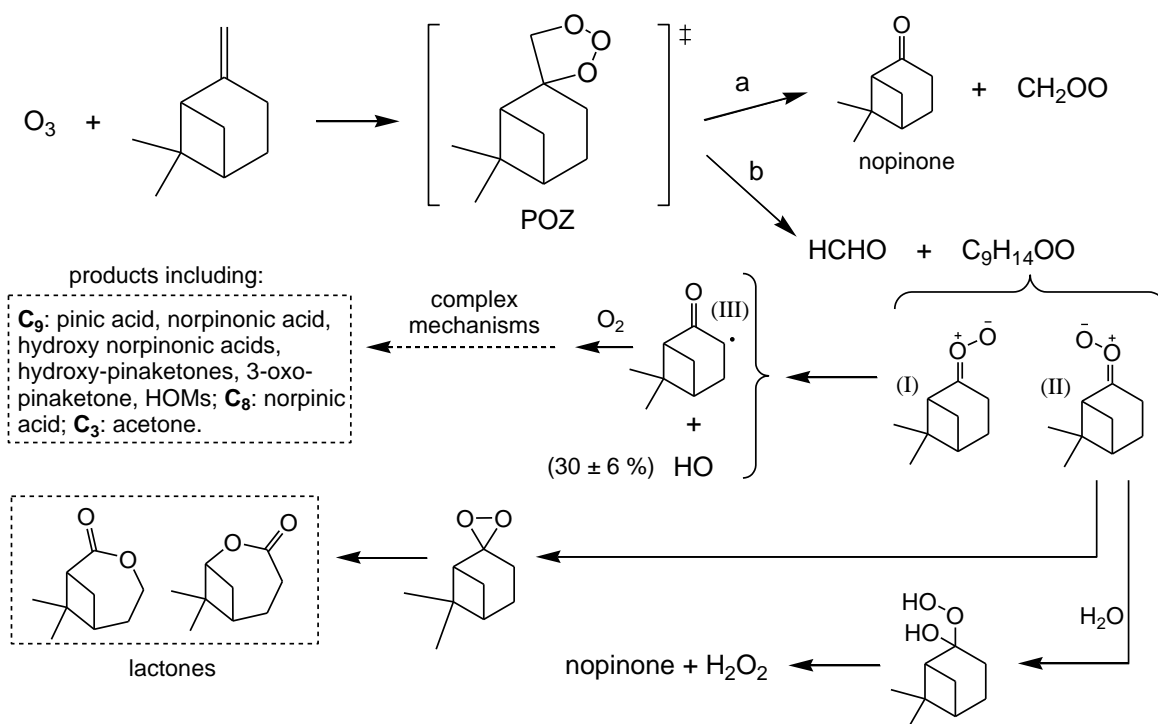
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.9×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.39 \times 10^{-15} \exp(-1280/T)$	290-370
<i>Reliability</i>		
$\Delta \log k$	± 0.25	298
$\Delta E/R$	± 300	290-370

Comments on Preferred Values

The room temperature rate coefficients reported by Ripperton et al. (1972) and Grimsrud et al. (1975) are significantly higher than the more recent measurements of Atkinson et al. (1982, 1990), Nolting et al. (1988), Grosjean et al. (1993), Johnson et al. (2000) and Khamaganov and Hites (2001); although there is still a significant amount of scatter between the room temperature rate coefficients of these more recent measurements. The preferred temperature dependence is based on that reported by Khamaganov and Hites (2001). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1982, 1990), Nolting et al. (1988), Grosjean et al. (1993), Johnson et al. (2000) and Khamaganov and Hites (2001), 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 reaction proceeds by initial addition of O₃ to the C=C bond to form a “primary ozonide (POZ)” which rapidly decomposes to form two sets of “primary” carbonyl product plus Criegee intermediate, as shown in the following schematic:



Product yields have been reported in a number of studies (e.g. see the review of Atkinson and Arey, 2003), allowing some possible features of the subsequent mechanism to be characterized. The carbonyl compound, nopinone, has been reported to be formed with yields in the range 16 % to 23 % under dry conditions in the presence of an HO radical scavenger (Grosjean et al., 1993; Hakola et al., 1994; Yu et al., 1999; Winterhalter et al., 2000; Ma and Marston, 2008), suggesting a relative importance of the two decomposition channels, $k_b/k_a \approx 4$. The dominance of channel (b) is also supported by the results of theoretical studies (Zhang and Zhang, 2005; Nguyen et al., 2009). Reported yields of HCHO are also consistent with channel (b) being the major decomposition route for POZ (e.g. Atkinson and Arey, 2003), although it is likely partially sequestered in the form of a secondary ozonide following reaction with the C₉ Criegee intermediate, C₉H₁₄OO, under many reported experimental conditions (e.g. see Winterhalter et al., 2000; Carlsson et al., 2012).

The Criegee intermediate, CH₂OO (formed from the minor channel (a)), is expected to be almost fully stabilised at atmospheric pressure (Nguyen et al., 2009). Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH₂OO under tropospheric conditions is expected to be removal via bimolecular reactions, e.g. with (H₂O)₂, NO₂ and SO₂. Substantial stabilisation of the major C₉ Criegee intermediate, C₉H₁₄OO (formed from channel (b)), has also been reported (Winterhalter et al., 2000; Ahrens et al., 2014), based on scavenging with added H₂O or SO₂ and quantification of the additional nopinone formed. A corresponding yield of 0.35 ± 0.05 was reported by Winterhalter et al. (2000), with support from the subsequent theoretical study of Nguyen et al. (2009). Taking account of the additional contribution of CH₂OO, a total stabilized Criegee intermediate (sCI) yield of 0.5 ± 0.1 is currently recommended.

Indirect evidence for the formation of HO radicals from β -pinene ozonolysis has been reported by Atkinson et al. (1992) and Rickard et al. (1999), with respective yields of $0.35^{+0.18}_{-0.12}$ and 0.26 ± 0.06 (preferred value, 0.30 ± 0.06). This is expected to result from reactions of the Criegee intermediate C₉H₁₄OO formed in channel (b), which has the two conformers, (I) and (II), shown in the schematic. In practice, formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) may only be possible for conformer (I), owing to the relevant β -hydrogen in conformer (II) being at the bridgehead of a constrained bicyclic structure (e.g. see Rickard et al., 1999; Nguyen et al., 2009); and this helps to explain the relatively low HO yield from β -

pinene ozonolysis. The alternative decomposition route, via a dioxirane intermediate, is available for conformer (II), and formation of the lactone products has been reported (Griesbaum et al., 1998). However, conformer (II) is likely to react predominantly with H₂O under atmospheric conditions (Vereecken et al., 2017), forming additional nopinone and H₂O₂, for which evidence was reported by Winterhalter et al. (2000) and Ma and Marston (2008). The generation of HO is accompanied by the formation of the β-oxo alkyl radical (III), the further chemistry of which may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (e.g. Winterhalter et al., 2000; Ma and Marston, 2008), including a small yield of highly oxidized multifunctional organic compounds, HOMs, with very high oxygen to carbon ratios (e.g. Ehn et al., 2012)..

References

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- Recommendation
- Nolting et al. (1988)
- Atkinson et al. (1990), relative
- ▲ Johnson et al. (2000)
- Khamaganov and Hites (2001), relative (cis-but-2-ene)

