

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC19

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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>			
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 (b)
$(1.48 \pm 0.17) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (c)
$(1.22 \pm 0.13) \times 10^{-17}$	295 ± 1	Grosjean et al., 1993	S-UVA (d)
<i>Relative Rate Coefficients</i>			
$(1.34 \pm 0.19) \times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR-GC (e)
$(1.79 \pm 0.22) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	RR-GC (f)
$(2.29 \pm 0.26) \times 10^{-17}$	298 ± 2	Johnson et al., 2000	RR-GC (g)
$1.63 \times 10^{-15} \exp[-(1273 \pm 84)/T]$	298-363	Khamaganov and Hites, 2001	RR-MS (h,i)
$(2.26 \pm 0.13) \times 10^{-17}$	298		
$(2.16 \pm 0.18) \times 10^{-17}$	298	Khamaganov and Hites, 2001	RR-MS (h,j)

Comments

- (a) 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane.
- (b) 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.
- (c) 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.
- (d) 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.
- (e) 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 $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.25 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation). Details concerning the reactant mixtures and the

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

- (f) 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 O_3 . The measured rate coefficient ratio $k(O_3 + \beta\text{-pinene})/k(O_3 + \alpha\text{-pinene})$ 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).
- (g) 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 O_3 . The measured rate coefficient ratio $k(O_3 + \beta\text{-pinene})/k(O_3 + 2\text{-methylpropene})$ is placed on an absolute basis using $k(O_3 + 2\text{-methylpropene}) = 1.1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (h) The concentrations of β -pinene and *cis*-but-2-ene or but-1-ene (the reference compounds) were monitored by MS in reacting O_3 - β -pinene - *cis*-but-2-ene (or but-1-ene) - acetaldehyde (or ethanol) - He mixtures in a 192 cm^3 volume quartz vessel at ~ 1 bar pressure, with acetaldehyde or ethanol being present to scavenge HO radicals. The measured rate coefficient ratios $k(O_3 + \beta\text{-pinene})/k(O_3 + \textit{cis}\text{-but-2-ene}) = 0.51 \exp[(-308 \pm 84)/T]$ and $k(O_3 + \beta\text{-pinene})/k(O_3 + \textit{but-1-ene}) = (0.18 \pm 0.01)$ at 298 K are placed on an absolute basis using $k(O_3 + \textit{cis}\text{-but-2-ene}) = 3.20 \times 10^{-15} \exp(-965/T)$ and $k(O_3 + \textit{but-1-ene}) = 9.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).
- (i) Relative to $k(O_3 + \textit{cis}\text{-but-2-ene})$. 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.
- (j) Relative to $k(O_3 + \textit{but-1-ene})$, using (+)- β -pinene.

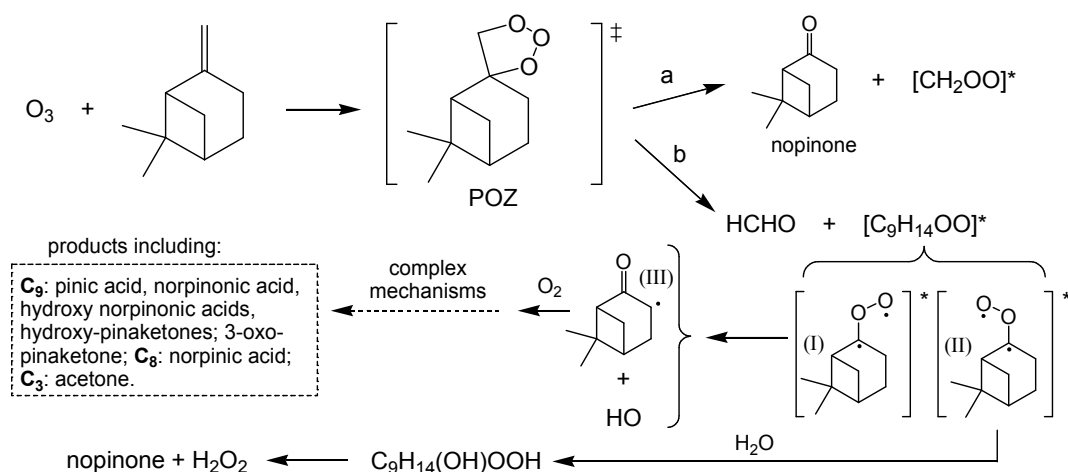
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.9×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.35 \times 10^{-15} \exp(-1270/T)$	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 O_3 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. Reported yields of the carbonyl compounds, nopinone and HCHO, of $(26^{+14}_{-10})\%$ and $(63^{+12}_{-21})\%$, respectively, under dry conditions (Atkinson and Arey, 2003), suggest a relative importance of the two decomposition channels, $k_b/k_a \approx 2$, which is also consistent with that typically observed for primary ozonides formed from alkenes of generic structure $R_1(R_2)C=CH_2$ (Rickard et al., 1999).

In the absence of other information, it is assumed that the reactions of the Criegee intermediate $[\text{CH}_2\text{OO}]^*$ formed in the minor channel (a) are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene (see datasheets Ox_VOC3 and Ox_VOC5). This leads to a relatively small overall yield ($\approx 5\%$) of HO radicals. The majority of the reported HO production from β -pinene ozonolysis ($\approx 30\%$) is therefore expected to result from reactions of the Criegee intermediate $[\text{C}_9\text{H}_{14}\text{OO}]^*$ formed in channel (b), which has the two conformers, (I) and (II). 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); and this would help explain the relatively low HO yield from β -pinene ozonolysis. In the absence of the decomposition route, conformer (II) is likely to react predominantly with H_2O under atmospheric conditions, potentially forming additional nopinone and H_2O_2 , for which evidence was reported by Winterhalter et al. (2000). The generation of HO is accompanied by the formation of 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.

References

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