

Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC8

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This datasheet last evaluated: August 2020; last change in preferred values: August 2018



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.6×10^{-16}	294	Ripperton et al., 1972	S-CL
$(3.3 \pm 0.3) \times 10^{-16}$	298	Japar et al., 1974	S-CL
1.45×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
$9.4 \times 10^{-16} \exp[-(731 \pm 173)/T]$	276-324	Atkinson et al., 1982	S-CL/GC (a)
$(8.4 \pm 1.9) \times 10^{-17}$	296 ± 2		
$(9.71 \pm 1.06) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (b)
$1.4 \times 10^{-15} \exp[-(833 \pm 86)/T]$	243.1-303.2	Tillmann et al., 2009	S-UVA/MS (c)
$(9.0 \pm 0.6) \times 10^{-17}$	303.2		
$(1.1 \pm 0.1) \times 10^{-16}$	296 ± 1	Bernard et al., 2012	F-CL (d)
<i>Relative Rate Coefficients</i>			
$(8.54 \pm 1.29) \times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR-GC (e)
$6.0 \times 10^{-16} \exp[-(560 \pm 87)/T]$	288-363	Khamaganov and Hites, 2001	RR-MS (f,g)
$(9.39 \pm 0.46) \times 10^{-17}$	298		
$3.8 \times 10^{-16} \exp[-(447 \pm 303)/T]$	288-343	Khamaganov and Hites, 2001	RR-MS (f,h)
$(8.26 \pm 0.34) \times 10^{-17}$	298		
$(1.06 \pm 0.09) \times 10^{-16}$	295 ± 0.5	Witter et al., 2002	RR-GC (i)
$(9.26 \pm 0.84) \times 10^{-17}$	302 ± 1	Bernard et al., 2012	RR-IR (j,k)
$(1.03 \pm 0.04) \times 10^{-16}$	302 ± 1		RR-IR (j,l)
$(1.13 \pm 0.14) \times 10^{-16}$	298 ± 2	Stewart et al., 2013	RR-GC (m)

α -pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene

Comments

- (a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of α -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.
- (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 α -pinene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber. From measurements of the absolute rate coefficient for the reaction of O₃ with sabinene and the ratio $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \text{sabinene})$, a rate

coefficient of $k(\text{O}_3 + \alpha\text{-pinene}) = (7.99 \pm 1.20) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was also derived.

- (c) k determined from the observed first-order rate of ozone decay (measured with a UV absorption monitor) in the presence of known excess concentrations of α -pinene (measured by PTR-MS) and cyclohexane to scavenge HO radicals. Experiments were carried out at atmospheric pressure in a thermostatically-controlled 84.3 m³ aluminium chamber.
- (d) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of α -pinene, in a flow reactor at a total pressure of ~ 1 bar.
- (e) The concentrations of a series of alkenes (including α -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 $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$ is placed on an absolute basis using a rate coefficient at 297 K of $k(\text{O}_3 + \textit{cis}\text{-but-2-ene}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (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 α -pinene and but-1-ene or 2-methylpropene (the reference compounds) were monitored by MS in reacting O₃ - α -pinene - but-1-ene (or 2-methylpropene) - acetaldehyde (or ethanol) [HO radical scavengers] - He mixtures in a 192 cm³ volume quartz vessel at ~ 1 bar pressure. The measured rate coefficient ratios $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{but-1-ene}) = 0.17 \exp[(1190 \pm 87)/T]$ and $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{2-methylpropene}) = 0.13 \exp[(1203 \pm 303)/T]$ are placed on an absolute basis using $k(\text{O}_3 + \textit{but-1-ene}) = 3.55 \times 10^{-15} \exp(-1750/T)$ and $k(\text{O}_3 + \textit{2-methylpropene}) = 2.92 \times 10^{-15} \exp(-1650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendations). Khamaganov and Hites (2001) also report the Arrhenius expression, $k(\text{O}_3 + \alpha\text{-pinene}) = 4.8 \times 10^{-16} \exp[-(530 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 288-363 K and $k(\text{O}_3 + \alpha\text{-pinene}) = (8.41 \pm 0.74) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, based on the combined data.
- (g) Relative to $k(\text{O}_3 + \textit{but-1-ene})$.
- (h) Relative to $k(\text{O}_3 + \textit{2-methylpropene})$.
- (i) The concentrations of α -pinene and 2-methylbut-2-ene (the reference compound) were monitored by GC in reacting O₃ - α -pinene - 2-methylbut-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{2-methylbut-2-ene}) = 0.270 \pm 0.022$ is placed on an absolute basis using a rate coefficient at 295 K of $k(\text{O}_3 + \textit{2-methylbut-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
- (j) The concentrations of α -pinene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O₃ - α -pinene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~ 1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{cyclohexene}) = 1.09 \pm 0.10$ and $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{cis-cyclooctene}) = 0.27 \pm 0.01$, are placed on an absolute basis using $k(\text{O}_3 + \textit{cyclohexene}) = 8.50 \times 10^{-17}$ and $k(\text{O}_3 + \textit{cis-cyclooctene}) = 3.80 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 302 K (Atkinson and Arey, 2003a).
- (k) Relative to $k(\text{O}_3 + \textit{cyclohexene})$.
- (l) Relative to $k(\text{O}_3 + \textit{cis-cyclooctene})$.
- (m) The concentrations of α -pinene and cycloheptene (the reference compound) were monitored by GC-FID in flowing mixtures of O₃, α -pinene, cycloheptene, cyclohexane (the HO radical scavenger) and air at 760 Torr (1.013 bar) pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + \textit{cycloheptene}) = 0.453 \pm 0.036$ is placed on an absolute basis using a rate coefficient at 298 K of $k(\text{O}_3 + \textit{cycloheptene}) = 2.50 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).

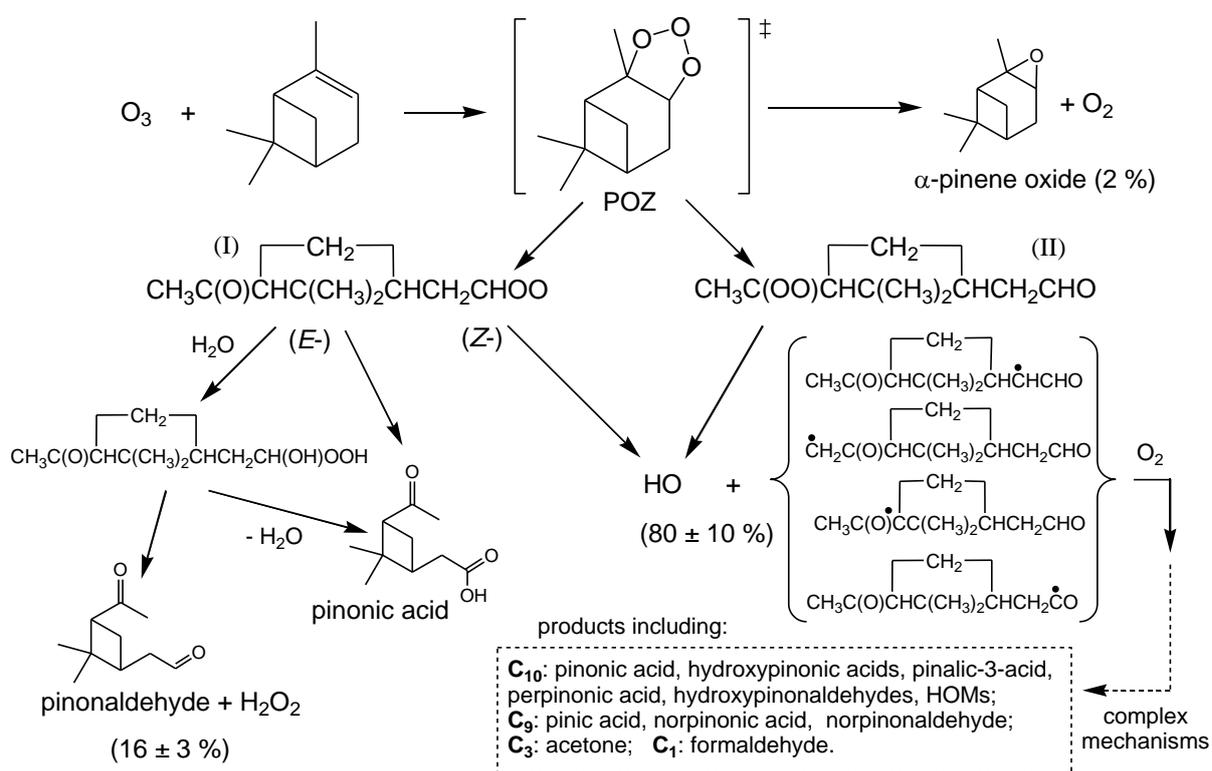
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	9.6×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$8.22 \times 10^{-16} \exp(-640/T)$	240-370
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta E/R$	± 300	240-370

Comments on Preferred Values

The room temperature rate coefficients reported by Ripperton et al. (1972), Japar et al. (1974) and Grimsrud et al. (1975) are significantly higher than the more recent measurements of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001), Witter et al. (2002), Tillmann et al. (2009), Bernard et al. (2012) and Stewart et al. (2013); 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 obtained from a simple average of the temperature dependences obtained by Atkinson et al. (1982), Khamaganov and Hites (2001) and Tillmann et al. (2009). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001), Witter et al. (2002), Tillmann et al. (2009), Bernard et al. (2012) and Stewart et al. (2013), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

Product yields and mechanistic information have been reported in a number of studies, as summarized in the reviews of Atkinson and Arey (2003b) and Johnson and Marston (2008). The reaction proceeds by initial addition of O₃ to the C=C bond in α -pinene to form a "primary ozonide (POZ)" which rapidly decomposes, mainly to form two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the following schematic:



The stabilization of the Criegee intermediates is reported to be limited, with a preferred stabilized Criegee intermediate (sCI) yield of 0.18 ± 0.05 recommended at atmospheric pressure, based on the determinations of Sipilä et al. (2014) (adjusted using the preferred value of k) and Newland et al. (2018), and also consistent with Drozd and Donahue (2011). Whether excited or stabilized, the *Z*- conformer of Criegee intermediate (I) and Criegee intermediate (II) mainly decompose to form HO radicals and a number of β -oxo alkyl radicals, as shown in the schematic. The further chemistry of the β -oxo alkyl radicals may form a number of reported multifunctional organic products containing hydroxy, hydroperoxy, carbonyl and acid functionalities (e.g. Johnson 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). Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (Atkinson et al., 1992; Chew and Atkinson, 1996; Paulson et al., 1998; Rickard et al., 1999; Siese et al., 2001; Aschmann et al., 2002; Berndt et al., 2003; Presto and Donahue, 2004; Forester and Wells, 2011), with yields in the range 0.68-0.91 (preferred value, 0.80 ± 0.10). Formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is not possible for the *E*- conformer of Criegee Intermediate (I) (e.g. see Johnson and Marston, 2008). If stabilized, this is expected to react predominantly with H₂O under atmospheric conditions, leading to the formation of pinonaldehyde and H₂O₂, or pinonic acid. Consensus yields are shown for α -pinene oxide and pinonaldehyde.

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