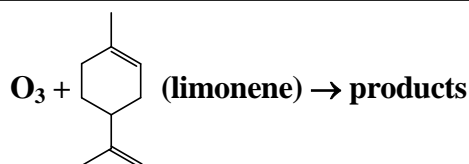


Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC20

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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>			
6.4×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
3.5×10^{-16}	297.3	Zhang et al., 1994	S-CL/GC (a)
$(3.8 \pm 0.3) \times 10^{-16}$	297 ± 1	Bernard et al., 2012	F-CL (b)
<i>Relative Rate Coefficients</i>			
$(2.27 \pm 0.23) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (c)
$(2.10 \pm 0.07) \times 10^{-16}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (d)
$2.97 \times 10^{-15} \exp[-(771 \pm 76)/T]$	298-363	Khamaganov and Hites, 2001	RR-MS (e,f)
$(2.24 \pm 0.16) \times 10^{-16}$	298		
$(2.20 \pm 0.19) \times 10^{-17}$	298	Khamaganov and Hites, 2001	RR-MS (e,g)
$(2.06 \pm 0.21) \times 10^{-17}$	298	Khamaganov and Hites, 2001	RR-MS (e,h)
$(2.44 \pm 0.30) \times 10^{-17}$	295 ± 0.5	Witter et al., 2002	RR-GC (i)
$(1.95 \pm 0.17) \times 10^{-16}$	302 ± 1	Bernard et al., 2012	RR-IR (j,k)
$(2.10 \pm 0.31) \times 10^{-16}$	303 ± 1		RR-IR (j,l)

limonene is 4-isopropenyl-1-methyl-cyclohexene

Comments

- k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in an experiment with a known excess concentration of limonene (measured by GC-FID), in a 4300 L Teflon 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 limonene, in a flow reactor at a total pressure of ~1 bar.
- The concentrations of a series of alkenes (including limonene 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 $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \alpha\text{-pinene})$ 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).
- The concentrations of limonene and *cis*-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 O₃. The measured rate coefficient ratio $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cis-but-2-ene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 1.27 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

- (e) The concentrations of limonene and *cis*-but-2-ene, but-1-ene or 2-methylpropene (the reference compounds) were monitored by MS in reacting O₃ - limonene - reference compound - 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 $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cis-but-2-ene}) = 0.88 \exp[(-199 \pm 76)/T]$; and $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{but-1-ene}) = (22.04 \pm 1.92)$ and $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{2-methylpropene}) = (17.88 \pm 1.84)$ at 298 K are placed on an absolute basis using $k(\text{O}_3 + \text{cis-but-2-ene}) = 3.37 \times 10^{-15} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; and $k(\text{O}_3 + \text{but-1-ene}) = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \text{2-methylpropene}) = 1.15 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).
- (f) Relative to $k(\text{O}_3 + \text{cis-but-2-ene})$.
- (g) Relative to $k(\text{O}_3 + \text{but-1-ene})$.
- (h) Relative to $k(\text{O}_3 + \text{2-methylpropene})$.
- (i) The concentrations of limonene and 2-methylbut-2-ene (the reference compound) were monitored by GC in reacting O₃ - limonene - 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 $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{2-methylbut-2-ene}) = 0.622 \pm 0.024$ is placed on an absolute basis using $k(\text{O}_3 + \text{2-methylbut-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- (j) The concentrations of limonene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O₃ - limonene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cyclohexene}) = 2.3 \pm 0.2$ and $k(\text{O}_3 + \text{limonene})/k(\text{O}_3 + \text{cis-cyclooctene}) = 0.55 \pm 0.08$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.50 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 302 K and $k(\text{O}_3 + \text{cis-cyclooctene}) = 3.81 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K (Atkinson and Arey, 2003).
- (k) Relative to $k(\text{O}_3 + \text{cyclohexene})$.
- (l) Relative to $k(\text{O}_3 + \text{cis-cyclooctene})$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.2×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.91 \times 10^{-15} \exp(-770/T)$	290-370
<i>Reliability</i>		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 300	290-370

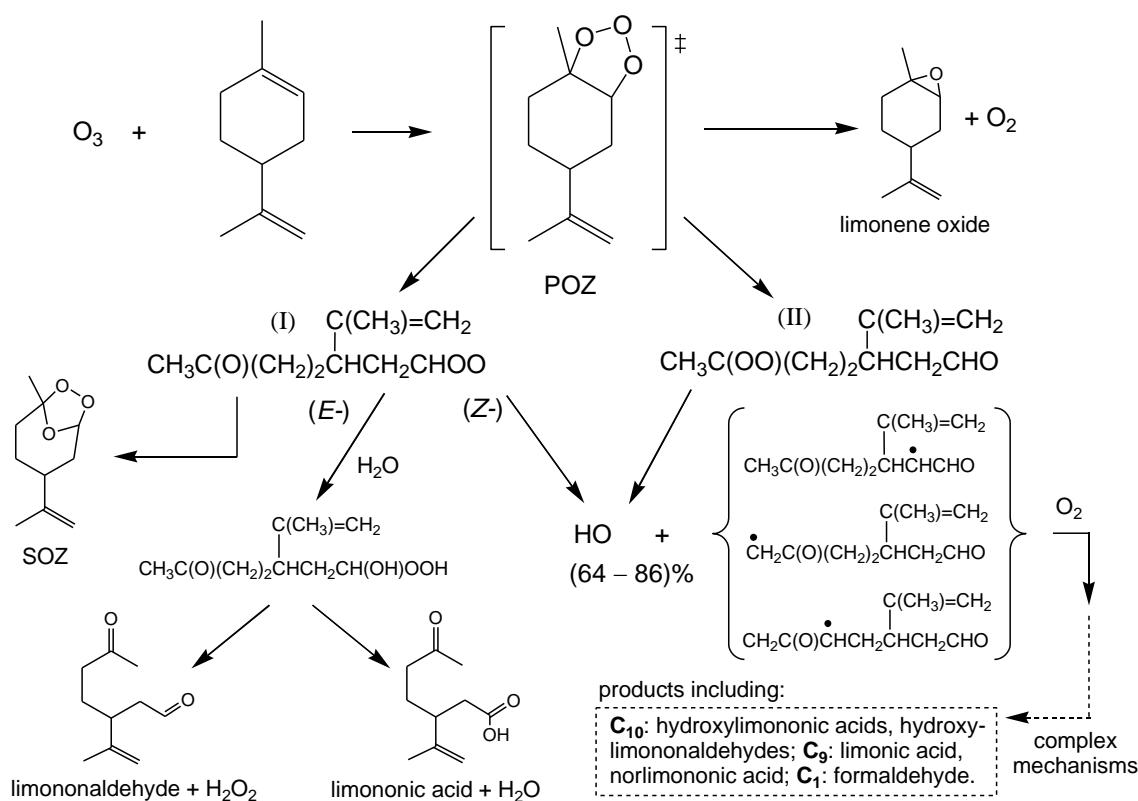
Comments on Preferred Values

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), Khamaganov and Hites (2001), Witter et al. (2002) and Bernard et al. (2012), which are in very good agreement. The absolute rate coefficient determinations of Zhang et al. (1994) and Bernard et al. (2012) provide measurements of k that are approaching a factor of two higher than the relative rate determinations. The reason for this consistent

discrepancy is currently unknown. The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for limonene, and also for several other terpenes, appear to be systematically high. The preferred temperature dependence is based on that reported by Khamaganov and Hites (2001), with the pre-exponential factor adjusted to return the 298 K preferred value.

The reaction may proceed by initial addition of O₃ to either of the endocyclic or exocyclic C=C bonds in limonene. Comparison of *k* for the reaction of ozone with limonene with that reported for the reaction of ozone with the limonene oxidation product, limononaldehyde (3-isopropenyl-6-oxo-heptanal), which retains the “exocyclic” C=C bond (Calogirou et al., 1999), suggests that the reaction of O₃ with limonene occurs predominantly (≈ 95 %) at the endocyclic bond. Support for this comes from the low reported yield (≈ 2 %) of the product limona ketone (4-acetyl-1-methylcyclohexene), which is an expected significant product of the ozonolysis of the exocyclic bond (Grosjean et al., 1993; Forester and Wells, 2009).

The addition of O₃ to the endocyclic C=C bond in limonene forms 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 Criegee intermediates are only partially stabilized under atmospheric conditions, with a preferred stabilized Criegee intermediate (sCI) yield of 0.27 ± 0.12 recommended at atmospheric pressure, based on Sipilä et al. (2014). As shown in the schematic, they mainly decompose to form HO radicals, which are expected to be formed in conjunction with a number of β-oxo alkenyl radicals. HO radical yields in the range 64 % – 86 % (preferred value 66 ± 4 %) have been reported (Atkinson et al., 1992; Aschmann et al., 2002; Herrmann et al., 2010; Forester and Wells, 2011). The further chemistry of the β-oxo alkenyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (Glasius et al., 2000; Warscheid and Hoffmann, 2001; Leungsakul et al., 2005; Nørgaard et al., 2013), and also formaldehyde, which has been reported to be formed with a yield of 10 % (Grosjean et al., 1993) and 19 % (Ruppert et al., 1999). A contribution (< 5 %) to the formaldehyde yield also probably results from the minor ozonolysis of the exocyclic C=C bond in limonene.

Products likely to be produced from alternative reactions of the Criegee intermediates have also been detected, for example the “secondary ozonide (SOZ)” (Nørgaard et al., 2013), which can potentially be formed from ring closure of either (I) or (II). Limononaldehyde (3-isopropenyl-6-oxo-heptanal) has been reported to be formed in low yield (between 0.4 % and 4 %) from the ozonolysis of limonene (Glasius et al., 2000; Clausen et al., 2001; Forester et al., 2009) under nominally dry conditions. Although no systematic investigations of the effect of water vapour on its yield have apparently been reported, limononaldehyde is predicted to be formed with H₂O₂ from reaction of H₂O with the *E*- conformer of Criegee intermediate (I). Some support for this comes from the reported high yield (≈ 33 %) of H₂O₂ from limonene ozonolysis at close to 100 % relative humidity (Hewitt and Kok, 1991).

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