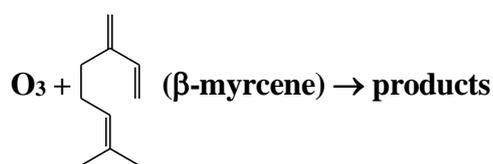


Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC24

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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>			
1.25×10^{-15}	295 ± 1	Grimsrud et al., 1975	F-CL
$(5.7 \pm 1.6) \times 10^{-16}$	298 ± 1	Bernard et al., 2012	F-CL (a)
<i>Relative Rate Coefficients</i>			
$(5.01 \pm 0.81) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (b)
$(4.59 \pm 0.57) \times 10^{-16}$	296 ± 2	Witter et al., 2002	RR-GC (c)
$2.33 \times 10^{-15} \exp[-(521 \pm 109)/T]$	298-318	Kim et al., 2011	RR-MS (d)
$(4.05^{+0.31}_{-0.29}) \times 10^{-16}$	298		
$(4.90 \pm 0.69) \times 10^{-16}$	303 ± 1	Bernard et al., 2012	RR-IR (e,f)
$(3.82 \pm 0.38) \times 10^{-16}$	304 ± 1		RR-IR (e,g)

myrcene is 7-methyl-3-methylene-octa-1,6-diene

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 -myrcene, in a flow reactor at a total pressure of ~ 1 bar.
- The concentrations of a series of alkenes (including β -myrcene 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 $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{limonene})$ is placed on an absolute basis using $k(\text{O}_3 + \text{limonene}) = 2.16 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- The concentrations of β -myrcene and 2-methyl-but-2-ene (the reference compound) were monitored by GC in reacting O_3 - β -myrcene - 2-methyl-but-2-ene - *m*-xylene (the HO radical scavenger) - air mixtures in a flow system at 100 mbar pressure. The measured rate coefficient ratio $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 1.17 \pm 0.06$ is placed on an absolute basis using $k(\text{O}_3 + 2\text{-methyl-but-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson and Arey, 2003).
- The concentrations of β -myrcene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O_3 - β -myrcene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm^3 volume quartz vessel at ~ 1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The

measured rate coefficient ratios $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{trans-but-2-ene})$ are placed on an absolute basis using $k(\text{O}_3 + \text{trans-but-2-ene}) = 7.0 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

- (e) The concentrations of β -myrcene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O_3 - myrcene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~ 1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{cyclohexene}) = 5.7 \pm 0.8$ and $k(\text{O}_3 + \beta\text{-myrcene})/k(\text{O}_3 + \text{cis-cyclooctene}) = 1.0 \pm 0.1$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.60 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and $k(\text{O}_3 + \text{cis-cyclooctene}) = 3.82 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 304 K (Atkinson and Arey, 2003).
- (f) Relative to $k(\text{O}_3 + \text{cyclohexene})$.
- (g) Relative to $k(\text{O}_3 + \text{cis-cyclooctene})$.

Preferred Values

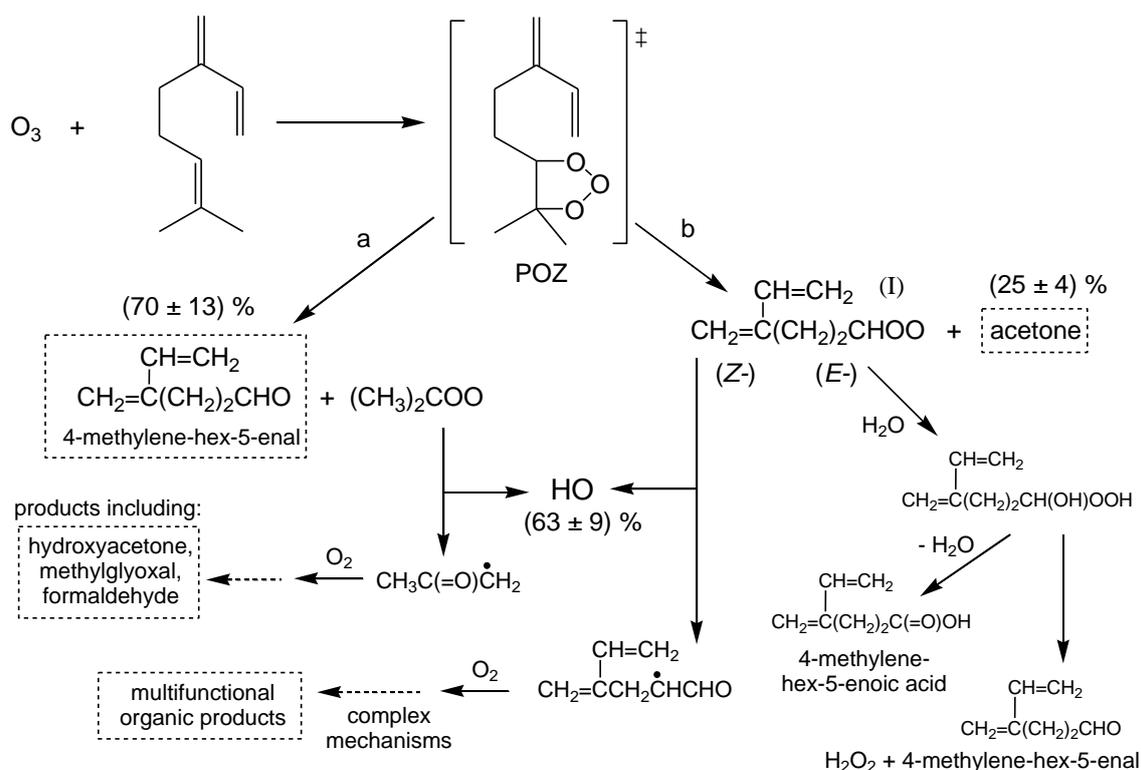
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.7×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.69 \times 10^{-15} \exp(-520/T)$	290-320
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	± 300	290-320

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Kim et al. (2011). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1990), Witter et al. (2002), Kim et al. (2011) and Bernard et al. (2012), 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 earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for β -myrcene, and also for several other terpenes, appear to be systematically high

The reaction may proceed by initial addition of O_3 to any of the three C=C bonds in β -myrcene. Comparison of k for the reaction of O_3 with β -myrcene with that reported for the reaction of O_3 with the β -myrcene oxidation product 4-methylene-hex-5-enal, which retains the two conjugated terminal C=C bonds (Baker et al., 2004), suggests that the reaction of O_3 with β -myrcene occurs predominantly ($\approx 97\%$) at the internal C=C bond; and this is largely supported by the observed product distribution and yields in reported product studies.

The addition of O_3 to the internal C=C bond in β -myrcene forms a "primary ozonide (POZ)" which rapidly decomposes to form two sets of "primary" carbonyl product plus Criegee intermediate, as shown in the schematic below. Acetone has been reported to be formed with a yield of $(25 \pm 4)\%$ (Reissell et al., 1999; 2002; Ruppert et al., 1999; Orlando et al., 2000; Newland et al., 2020), and 4-methylene-hex-5-enal with a yield of $(70 \pm 13)\%$ (Reissell et al., 2002). This suggests important contributions from both decomposition channels, (a) and (b), as shown in the schematic, but with the dominance of channel (a) being consistent with that typically observed for primary ozonides formed from alkenes of generic structure $\text{R}_1(\text{R}_2)\text{C}=\text{CHR}_3$ (Rickard et al., 1999).



The Criegee intermediates are only partially stabilized under atmospheric conditions, with a preferred stabilized Criegee intermediate (sCI) yield of 0.46 ± 0.15 recommended at atmospheric pressure, based on the determination Newland et al. (2020). The dimethyl-substituted Criegee intermediate (CH_3)₂COO (whether excited or stabilized) decomposes almost exclusively to form HO radicals and the acetyl radical (see discussion in data sheet Ox_VOC41), the further chemistry of which leads to the formation of a number of products, including hydroxyacetone and formaldehyde. These products have been reported to be formed with respective yields of 19 % (Ruppert et al., 1999) and (26 – 51) % (Ruppert et al., 1999; Lee et al., 2006) from the ozonolysis of β -myrcene. A contribution (< 3 %) to the formaldehyde yield also probably results from the minor ozonolysis of the terminal C=C bonds in β -myrcene. HO radicals have been reported to be formed with a yield of (63 ± 9) % (Aschmann et al., 2002).

The *Z*- conformer of Criegee intermediate (I), formed in channel (b), may also decompose to form HO radicals and the β -oxo-dienyl radical shown in the schematic. HO formation via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) is unavailable for the *E*- conformer. If stabilized, this is likely to react predominantly with H_2O under atmospheric conditions, potentially forming additional 4-methylene-hex-5-enal and H_2O_2 , or 4-methylene-hex-5-enoic acid, as shown in the schematic.

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- Atkinson et al. (1990)
- Kim et al. (2011)
- Bernard et al. (2012), relative (cyclohexene)
- Recommendation
- ▲ Witter et al. (2002)
- Bernard et al. (2012), absolute
- Bernard et al. (2012), relative (cis-cyclooctene)

