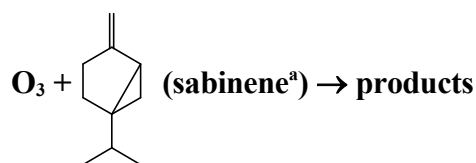


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC28

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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>			
$(8.07 \pm 0.83) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990a	S-CL/GC (c)
$(6.2 \pm 2.1) \times 10^{-17}$	297 ± 1	Bernard et al., 2012	F-CL (c)
<i>Relative Rate Coefficients</i>			
$(9.36 \pm 1.02) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990b	RR-GC (d)
$(9.03 \pm 0.77) \times 10^{-16}$	303 ± 1	Bernard et al., 2012	RR-IR (e,f)
$(8.40 \pm 1.15) \times 10^{-16}$	303 ± 1		RR-IR (e,g)

Comments

- (a) 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.
- (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 sabinene (measured by GC-FID). Experiments were carried out at a total pressure of 980 mbar in a 160 L Teflon 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 sabinene, in a flow reactor at a total pressure of ~1 bar.
- (d) The concentrations of a series of alkenes (including sabinene 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 $k(\text{O}_3 + \text{sabinene})/k(\text{O}_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(\text{O}_3 + \alpha\text{-pinene}) = 9.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (e) The concentrations of sabinene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O₃ - sabinene - reference compound - cyclohexane (HO radical scavenger) - air mixtures in a 7300 L Teflon chamber at ~1 bar pressure. The measured rate coefficient ratios, $k(\text{O}_3 + \text{sabinene})/k(\text{O}_3 + \text{cyclohexene}) = 1.05 \pm 0.09$, and $k(\text{O}_3 + \text{sabinene})/k(\text{O}_3 + \text{cis-cyclooctene}) = 0.22 \pm 0.03$, are placed on an absolute basis using $k(\text{O}_3 + \text{cyclohexene}) = 8.60 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{O}_3 + \text{cis-cyclooctene}) = 3.82 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K (Atkinson and Arey, 2003).

- (f) Relative to $k(\text{O}_3 + \text{cyclohexene})$.
 (g) Relative to $k(\text{O}_3 + \text{cis-cyclooctene})$.

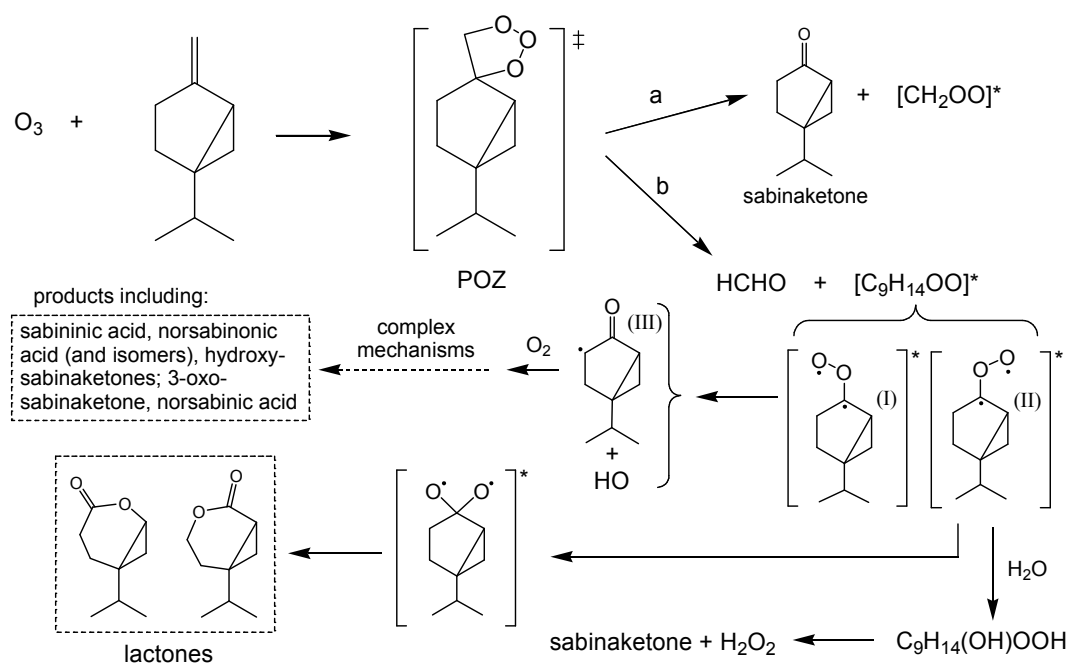
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	8.2×10^{-17}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is the average of the determinations of Atkinson et al. (1990a; 1990b) and Bernard et al. (2012), which are in good agreement.

The reaction proceeds by initial addition of O_3 to the $\text{C}=\text{C}$ 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:



Sabinaketone (5-isopropyl-bicyclo[3.1.0]hexan-2-one) has been reported to be formed with yields in the range (35 – 50) % (Hakola et al., 1994; Yu et al., 1999; Chiappini et al., 2006), and HCHO with a yield of (52 ± 9) % (Chiappini et al., 2006), providing evidence for the significant participation of both decomposition channels, (a) and (b).

In the absence of other information, it is assumed that the reactions of the Criegee intermediate $[\text{CH}_2\text{OO}]^*$ formed in channel (a) are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene (see datasheets Ox_VOC3 and Ox_VOC5). These partially form HCOOH , which has been reported to be formed with a yield of (17 ± 7) % from the ozonolysis of sabinene (Chiappini et al., 2006). The chemistry of $[\text{CH}_2\text{OO}]^*$ also probably leads to a relatively small overall yield (≤ 8 %) of HO radicals. The majority of the

reported HO production from sabinene ozonolysis, $\approx 30\%$ (Atkinson et al., 1992; Chew and Atkinson, 1996), 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, as discussed for a structurally similar Criegee intermediate formed from β -pinene by Rickard et al. (1999); and this would help explain the relatively low HO yield from sabinene ozonolysis. The alternative well-documented decomposition route for conformer (II), via a dioxirane intermediate (e.g. Johnson and Marston, 2008), leads to the formation of lactones (6-isopropyl-2-oxa-bicyclo[4.1.0]heptan-3-one and/or 6-isopropyl-3-oxa-bicyclo[4.1.0]heptan-2-one), the detection of which has been reported by Griesbaum and Miclaus (1998) and Chiappini et al. (2006). Conformer (II) may also potentially react with H_2O under atmospheric conditions, potentially forming H_2O_2 and additional sabinaketone.

The generation of HO from conformer (I) 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 (Yu et al., 1999; Warscheid and Hoffmann, 2001; Chiappini et al., 2006).

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