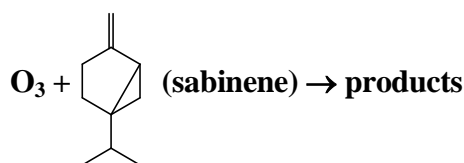


Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC28

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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>			
$(8.07 \pm 0.83) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990a	S-CL/GC (a)
$(6.2 \pm 2.1) \times 10^{-17}$	297 ± 1	Bernard et al., 2012	F-CL (b)
<i>Relative Rate Coefficients</i>			
$(9.55 \pm 1.04) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990b	RR-GC (c)
$(9.03 \pm 0.77) \times 10^{-16}$	303 ± 1	Bernard et al., 2012	RR-IR (d,e)
$(8.40 \pm 1.15) \times 10^{-16}$	303 ± 1		RR-IR (d,f)

sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane

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 sabinene (measured by GC-FID). Experiments were carried out at a total pressure of 980 mbar in a 160 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 sabinene, in a flow reactor at a total pressure of ~1 bar.
- 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 O_3 . 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 $k(\text{O}_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- The concentrations of sabinene and cyclohexene or *cis*-cyclooctene (the reference compounds) were monitored by FT-IR in reacting O_3 - 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).

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

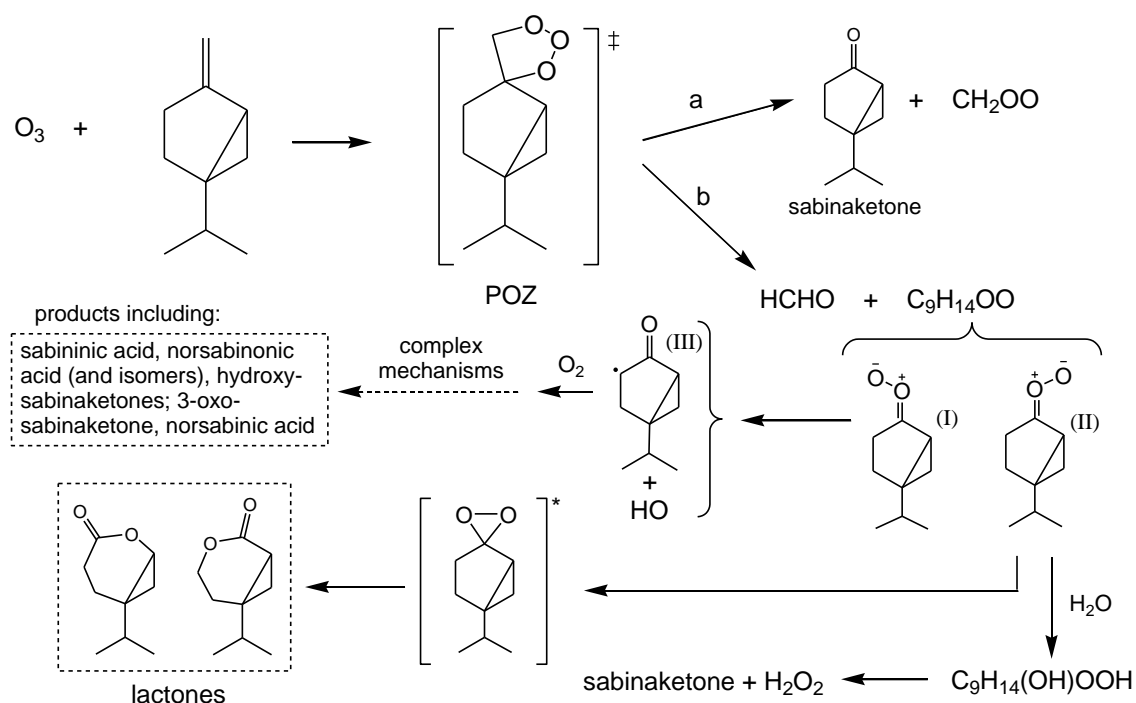
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	8.3×10^{-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 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:



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).

The Criegee intermediate, CH_2OO (formed from channel (a)), is expected to be almost fully stabilised at atmospheric pressure, by analogy with the β -pinene system (Nguyen et al., 2009). Its reaction with H_2O partially forms HCOOH (see data sheet Ox_VOC5), which has been reported to be formed with a yield of (17 ± 7) % from the ozonolysis of sabinene (Chiappini et al., 2006). The reported

HO production from sabinene ozonolysis (Atkinson et al., 1992; Aschmann et al., 2002), preferred yield $33 \pm 5 \%$, is expected to result mainly from reactions of the Criegee intermediate $C_9H_{14}OO$ 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 Nguyen et al. (2009); 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, 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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