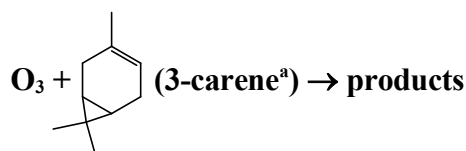


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC23

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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>			
1.2×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
$(5.20 \pm 0.56) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (b)
<i>Relative Rate Coefficients</i>			
$(4.05 \pm 0.43) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	RR-GC (c)
$(5.60 \pm 0.95) \times 10^{-17}$	295 ± 0.5	Witter et al., 2002	RR-GC (d)

Comments

- (a) 3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene.
- (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 3-carene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber. The presence of impurities in the 3-carene sample (3 % of sabinene and/or β -pinene and 2.9 % of limonene) was reported, such that the measured value of k was believed to be overestimated by up to about 20 %.
- (c) The concentrations of a series of alkenes (including 3-carene 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 $k(\text{O}_3 + 3\text{-carene})/k(\text{O}_3 + \alpha\text{-pinene})$ 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).
- (d) The concentrations of 3-carene and 2-methylbut-2-ene (the reference compound) were monitored by GC in reacting O₃- 3-carene - 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 $k(\text{O}_3 + 3\text{-carene})/k(\text{O}_3 + 2\text{-methylbut-2-ene}) = 0.143 \pm 0.018$ is placed on an absolute basis using a rate coefficient at 295 K of $k(\text{O}_3 + 2\text{-methylbut-2-ene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

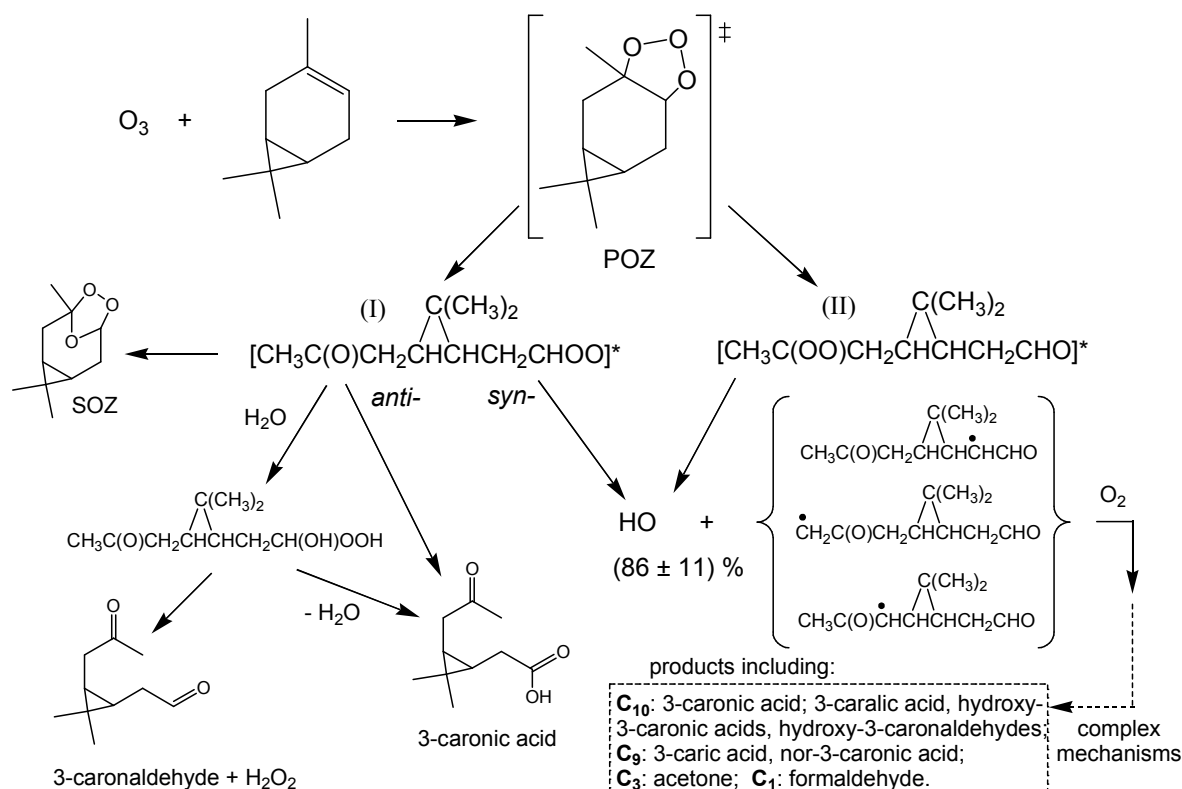
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	4.8×10^{-17}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.20	298

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) and Witter et al. (2002), which are in agreement to within their combined uncertainty limits. The absolute rate coefficient determination of Atkinson et al. (1990) was reported to be potentially influenced by the presence of reactive impurities in the 3-carene sample (see comment (b)), and is therefore not included in the average; although it is consistent with the preferred value of k . The earlier absolute rate coefficient determinations reported by Grimsrud et al. (1975) for 3-carene, and also for several other terpenes, appear to be systematically high.

The reaction proceeds by initial addition of O_3 to the $\text{C}=\text{C}$ bond in 3-carene 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 Criegee intermediates mainly decompose to form HO radicals, which are expected to be formed in conjunction with a number of β -oxo alkyl radicals. A yield of HO radical yields of (86 ± 11) % has been reported by Aschmann et al. (2002). The further chemistry of the β -oxo alkyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (Yu et

al., 1999; Glasius et al., 2000; Warscheid and Hoffmann, 2001; Ma et al., 2009); and also acetone and formaldehyde, which have been reported to be formed with respective yields of (14⁺⁸₋₄) % (Reissel et al., 1999; Orlando et al., 2000; Lee et al., 2006) and (25 ± 2) % (Lee et al., 2006).

Products likely to be produced from alternative reactions of the Criegee intermediates have also been detected, for example the “secondary ozonide (SOZ)” (Vibenholt et al., 2009), which can potentially be formed from ring closure of either (I) or (II). 3-caronaldehyde has been reported to be formed with total yields in the range (8.5 – 25) % under nominally dry conditions (Yu et al., 1999; Ma et al., 2009), with Ma et al. (2009) reporting an increasing yield with increasing relative humidity. 3-caronaldehyde is therefore likely to be formed with H₂O₂ from the reaction of H₂O with the *anti*- conformer of Criegee intermediate (I), which would also be predicted to be its dominant reaction under atmospheric conditions.

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