

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC21

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This datasheet last evaluated: August 2018; last change in preferred values: August 2018



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.0 \pm 1.7) \times 10^{-19}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (a)
<i>Relative Rate Coefficients</i>			
$(4.3 \pm 0.5) \times 10^{-19}$	298 ± 2	Johnson et al., 2000	RR-GC (b)
$(5.5 \pm 1.2) \times 10^{-19}$	298 ± 2	Gaona-Colmán et al., 2017	RR-FTIR (c)
$9.8 \times 10^{-18} \exp[(-859 \pm 53)/T]$	288-311		

camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane

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 camphene (measured by GC-FID). Experiments were carried out at a total pressure of 980 mbar in a 160 L Teflon chamber. k was corrected to account for the presence of a $\sim 10\%$ monoterpene impurity of comparable ozone reactivity in the camphene sample, which was tentatively identified as the structurally-similar monoterpene, α -fenchene.
- The concentrations of camphene and ethene (the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 50 L collapsible Teflon chamber at 760 Torr (1013 mbar) pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(O_3 + \text{camphene})/k(O_3 + \text{ethene})$ is placed on an absolute basis using $k(O_3 + \text{ethene}) = 1.55 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- The concentrations of camphene and ethene or o-cresol (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 50 L collapsible Teflon chamber at 760 Torr (1013 mbar) pressure of purified air in the presence of O_3 . Experiments performed at 298 K carried out using both ethene and o-cresol as reference compounds; with only ethene used at other temperatures. The measured rate coefficient ratios $k(O_3 + \text{camphene})/k(O_3 + \text{ethene})$ and $k(O_3 + \text{camphene})/k(O_3 + \text{o-cresol})$ are placed on an absolute basis using $k(O_3 + \text{ethene}) = 6.82 \times 10^{-15} \exp(-2500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(O_3 + \text{o-cresol}) = 2.6 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendations).

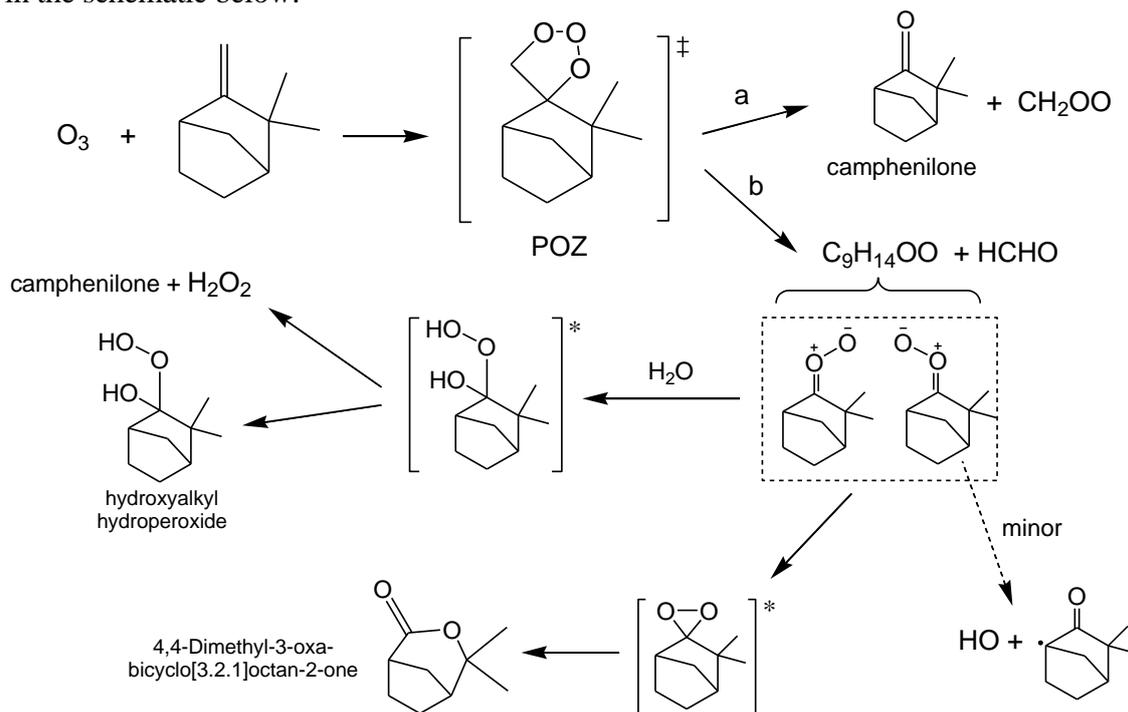
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.0×10^{-19}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$9.0 \times 10^{-18} \exp(-860/T)$	285-315
<i>Reliability</i>		
$\Delta \log k$	± 0.30	298
$\Delta E/R$	± 500	285-315

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Gaona-Colmán et al. (2017), which covered only a narrow temperature range. Confirmatory studies of the temperature dependence are required. The preferred 298 K rate coefficient is a rounded average of the relative rate determinations of Johnson et al. (2000) and Gaona-Colmán et al. (2017), which are in good agreement. The absolute determination of Atkinson et al. (1990) required correction for the presence of an impurity, but the reported value of k lies within the assigned uncertainty range in the preferred value.

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 schematic below:



Camphenilone (3,3-dimethyl-bicyclo[2.2.1]heptan-2-one) is expected to be formed in conjunction with the Criegee intermediate CH_2OO (channel (a)), and has been reported as a significant product, formed with a yield of $(36 \pm 6) \%$ (Hakola et al., 1994). Channel (b) is expected to form HCHO and the Criegee intermediate $\text{C}_9\text{H}_{14}\text{OO}$, although there have been no reported measurements of the yield of HCHO .

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). Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH_2OO under tropospheric conditions is expected to be removal via bimolecular reactions, particularly

with $(\text{H}_2\text{O})_2$. Partial stabilisation of the C_9 Criegee intermediate, $\text{C}_9\text{H}_{14}\text{OO}$ (formed from channel (b)), has also been inferred by Hasson et al. (2001), based on scavenging with added H_2O and observation of the corresponding products.

Atkinson et al. (1992) have reported an upper limit HO yield of $\leq 18\%$ for the reaction of O_3 with camphene, indicating that HO formation from the decomposition of $\text{C}_9\text{H}_{14}\text{OO}$ is also a minor route. The formation of HO via the accepted decomposition mechanism (involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate) may be inhibited owing to the only β -hydrogen in $\text{C}_9\text{H}_{14}\text{OO}$ being at the bridgehead of a constrained bicyclic structure, as discussed by Rickard et al. (1999) and Nguyen et al. (2009) for the structurally-similar isomeric Criegee intermediate formed from β -pinene ozonolysis. The alternative well-documented decomposition route, via a dioxirane intermediate (e.g. Johnson and Marston, 2008), leads to the formation of a lactone (4,4-dimethyl-3-oxa-bicyclo[3.2.1]octan-2-one), which has been reported to be a significant product (yield $\approx 20\%$) by Hakola et al. (1994). If stabilized, $\text{C}_9\text{H}_{14}\text{OO}$ may also potentially react with H_2O under atmospheric conditions. Based on the results of Hasson et al. (2001), this leads mainly to formation of the hydroxyalkyl hydroperoxide shown in the schematic, with minor formation of camphenilone and H_2O_2 .

References

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