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

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



$O_3$ + (camphene) → products

## Rate coefficient data

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

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

## Comments

(a) $k$ 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 ~10 % monoterpene impurity of comparable ozone reactivity in the camphene sample, which was tentatively identified as the structurally-similar monoterpene, α-fenchene.

(b) 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 $k(O_3 +$ camphene)$/k(O_3 +$ ethene) is placed on an absolute basis using $k(O_3 +$ ethene) = 1.55 x $10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, current recommendation).

(c) 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 $k(O_3 +$ camphene)$/k(O_3 +$ ethene) and $k(O_3 +$ camphene)$/k(O_3 +$ o-cresol) are placed on an absolute basis using $k(O_3 +$ ethene) = 6.82 x $10^{-15}$ exp(-2500/T) cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k(O_3 +$ o-cresol) = 2.6 x $10^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (IUPAC, current recommendations).

| Parameter | Value | T/K |
|---|---|---|
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $5.0 \times 10^{-19}$ | 298 |
| $k$ /cm$^3$ molecule$^{-1}$ s$^{-1}$ | $9.0 \times 10^{-18}$ exp($-860/T$) | 285-315 |

*Reliability*

| | | |
|---|---|---|
| $\Delta \log k$ | $\pm 0.30$ | 298 |
| $\Delta E/R$ | $\pm 500$ | 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:
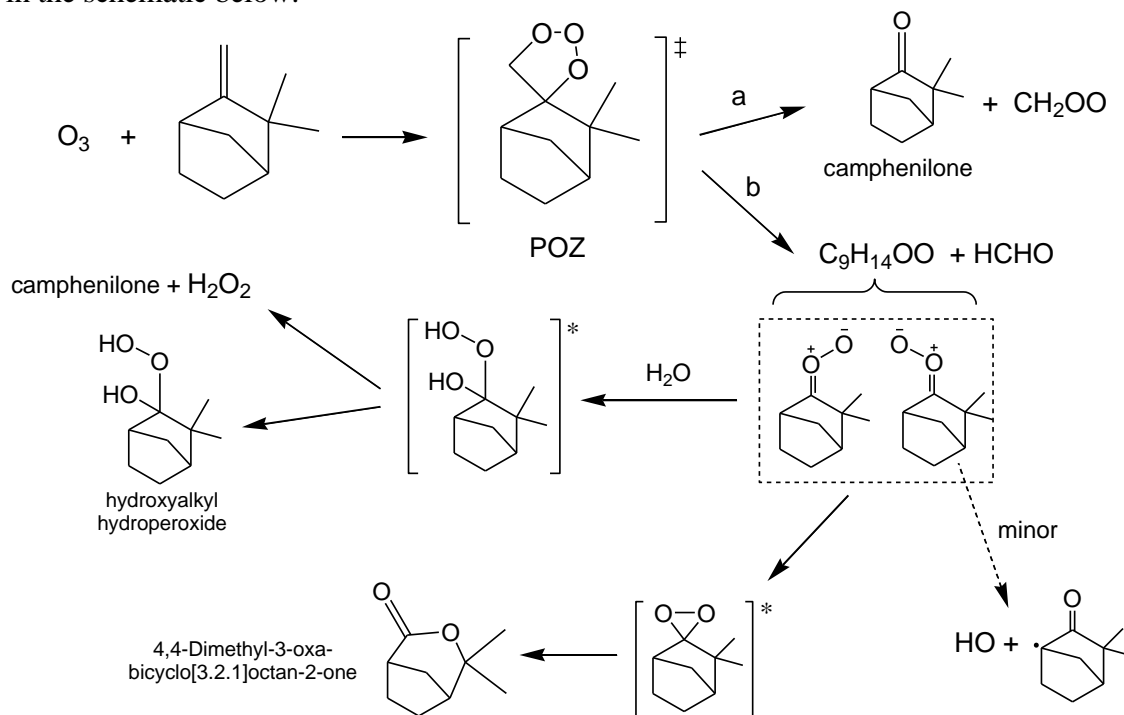


Camphenilone (3,3-dimethyl-bicyclo[2.2.1]heptan-2-one) is expected to be formed in conjunction with the Criegee intermediate CH$_2$OO (channel (a)), and has been reported as a significant product, formed with a yield of (36 ± 6) % (Hakola et al., 1994). Channel (b) is expected to form HCHO and the Criegee intermediate C$_9$H$_{14}$OO, although there have been no reported measurements of the yield of HCHO.

The Criegee intermediate, CH$_2$OO (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$_2$OO under tropospheric conditions is expected to be removal via bimolecular reactions, e.g. with

(H$_2$O)$_2$, NO$_2$ and SO$_2$. Partial stabilisation of the C$_9$ Criegee intermediate, C$_9$H$_{14}$OO (formed from channel (b)), has also been inferred by Hasson et al. (2001), based on scavenging with added H$_2$O 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 C$_9$H$_{14}$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 C$_9$H$_{14}$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 ≈ 20 %) by Hakola et al. (1994). C$_9$H$_{14}$OO may also potentially react with H$_2$O 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$_2$O$_2$.

## References

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