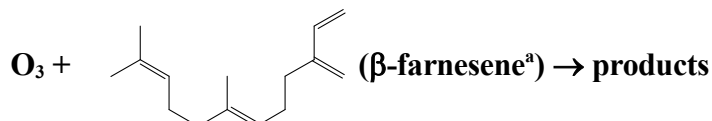


Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC36

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>)

This datasheet last evaluated: June 2015; last change in preferred values: June 2015



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(4.12 \pm 0.17) \times 10^{-16}$	296 ± 2	Kourtchev et al., 2009	RR-FTIR (b), (c)
$(4.01 \pm 0.12) \times 10^{-16}$	296 ± 2	Kourtchev et al., 2009	RR-FTIR (b), (d)
$(4.19 \pm 0.11) \times 10^{-16}$	296 ± 2	Kourtchev et al., 2009	RR-FTIR (b), (e)
$1.80 \times 10^{-12} \exp[-(2348 \pm 329)/T]$	$298-318$	Kim et al., 2011	RR-MS (f)
$(6.81^{+1.70}_{-1.36}) \times 10^{-16}$	298		

Comments

- (a) (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene.
- (b) The concentrations of *trans*-β-farnesene and cycloocta-1,5-diene, *cis*-cyclooctene or γ-terpinene (the reference compounds), with carbon monoxide to scavenge HO radicals, were monitored by long path FTIR in a 3.91 m³ FEP chamber at 0.1–1 mbar above atmospheric pressure of purified air in the presence of O₃. The measured rate coefficient ratios, $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-farnesene})/k(\text{O}_3 + \text{cycloocta-1,5-diene}) = (2.71 \pm 0.11)$, $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-farnesene})/k(\text{O}_3 + \textit{cis}\text{-cyclooctene}) = (1.04 \pm 0.03)$ and $k(\text{O}_3 + \textit{trans}\text{-}\beta\text{-farnesene})/k(\text{O}_3 + \gamma\text{-terpinene}) = (2.79 \pm 0.07)$, are placed on an absolute basis using $k(\text{O}_3 + \text{cycloocta-1,5-diene}) = 1.52 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{O}_3 + \textit{cis}\text{-cyclooctene}) = 3.86 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Cuisick and Atkinson, 2005) and $k(\text{O}_3 + \gamma\text{-terpinene}) = 1.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation) at 296 K. Gas phase carbonyl products were also identified as O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatives (GC-MS), following collection on denuders.
- (c) Relative to cycloocta-1,5-diene.
- (d) Relative to *cis*-cyclooctene.
- (e) Relative to γ-terpinene.
- (f) The concentrations of β-farnesene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O₃ - β-farnesene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm³ volume quartz vessel at ~1 bar pressure, with acetaldehyde being present to scavenge HO

radicals. The measured rate coefficient ratios, $k(\text{O}_3 + \beta\text{-farnesene})/k(\text{O}_3 + \text{trans-but-2-ene})$, are placed on an absolute basis using $k(\text{O}_3 + \text{trans-but-2-ene}) = 6.6 \times 10^{-15} \exp(-1060/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.6×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.5 \times 10^{-12} \exp(-2350/T)$	290-320

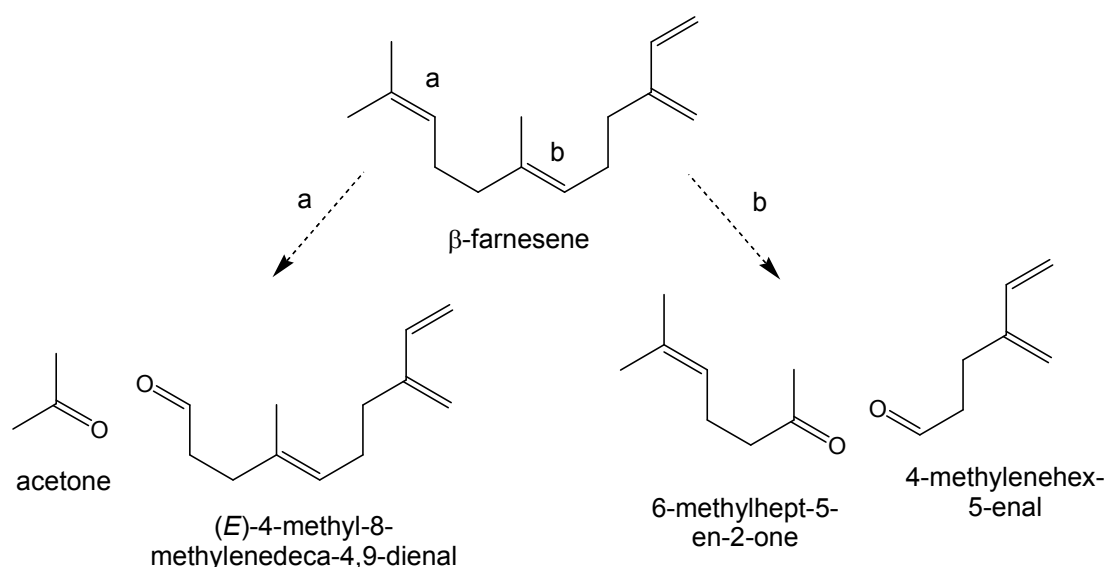
Reliability

$\Delta \log k$	± 0.25	298
$\Delta E/R$	± 500	290-320

Comments on Preferred Values

The preferred value of E/R is based on the sole temperature dependence study of Kim et al. (2011). The preferred 298 K rate coefficient is an average of those of Kourtchev et al. (2009) (corrected to 298 K using the preferred temperature dependence) and Kim et al. (2011), which are in reasonable agreement. The pre-exponential factor is adjusted to fit the 298 K preferred value. Confirmatory studies of the temperature dependence are required.

Structure-activity methods based on a summation of the rate coefficients for simple alkene and diene structures (e.g. Calvert et al., 2000) predict a rate coefficient that agrees with the preferred value to within a factor of 1.5. These methods also predict that the reaction should proceed mainly via O_3 addition to the two non-conjugated methyl-substituted $\text{C}=\text{C}$ bonds (“a” and “b”) with about equal probability at 298 K. Some support for this has been provided by the product study of Kourtchev et al. (2009), who detected the formation of the corresponding primary carbonyl products (acetone, (*E*)-4-methyl-8-methylenedeca-4,9-dienal, 4-methylenehex-5-enal, 6-methylhept-5-en-2-one), as shown below.



Kourtchev et al. (2009) also reported detection of 4-oxopentanal, which may be formed from the secondary ozonolysis of both (*E*)-4-methyl-8-methylenedeca-4,9-dienal and 6-methylhept-5-en-2-one; and methylglyoxal, which may be formed from reactions of the Criegee intermediate $[(\text{CH}_3)_2\text{COO}]^*$, the expected initial co-product of (*E*)-4-methyl-8-methylenedeca-4,9-dienal. Further product and

mechanistic studies are required.

References

Calvert, J. G., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G.: The mechanisms of atmospheric oxidation of alkenes, Oxford University Press, New York, ISBN 0-19-513177-0, 2000.

Cusick, R. D. and Atkinson, R.: *Int. J. Chem. Kinet.*, 37, 183, 2005.

Kim, D., Stevens, P. S. and Hites, R. A.: *J. Phys. Chem. A*, 115, 500, 2011.

Kourtchev, I., Bejan, I., Sodeau, J. R., and Wenger, J. C: *Atmos. Environ.*, 43, 3182, 2009.

