Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC36

O_3 + (β-farnesene) $\rightarrow$ products
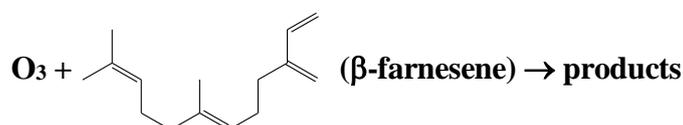
Rate coefficient data

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

β-farnesene is (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene

Comments

(a) 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 m^3 FEP chamber at 0.1–1 mbar above atmospheric pressure of purified air in the presence of O_3. The measured rate coefficient ratios, $k(O_3 + trans$-β-farnesene$)/k(O_3 +$ cycloocta-1,5-diene$) = (2.71 \pm 0.11)$, $k(O_3 + trans$-β-farnesene$)/k(O_3 + cis$-cyclooctene$) = (1.04 \pm 0.03)$ and $k(O_3 + trans$-β-farnesene$)/k(O_3 + $γ-terpinene$) = (2.79 \pm 0.07)$, are placed on an absolute basis using $k(O_3 +$ cycloocta-1,5-diene$) = 1.52 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, $k(O_3 + cis$-cyclooctene$) = 3.86 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (Cuisick and Atkinson, 2005) and $k(O_3 + $γ-terpinene$) = 1.5 \times 10^{-16}$ cm^3 molecule^{-1} 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.
(b) Relative to cycloocta-1,5-diene.
(c) Relative to *cis*-cyclooctene.
(d) Relative to γ-terpinene.
(e) The concentrations of β-farnesene and *trans*-but-2-ene (the reference compound) were monitored by MS in reacting O_3 - β-farnesene - *trans*-but-2-ene - acetaldehyde - He mixtures in a 160 cm^3 volume quartz vessel at ~1 bar pressure, with acetaldehyde being present to scavenge HO radicals. The measured rate coefficient ratios, $k(O_3 + $β-farnesene$)/k(O_3 + trans$-but-2-ene$)$, are placed on an absolute basis using $k(O_3 + trans$-but-2-ene$) = 6.6 \times 10^{-15} \exp(-1060/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

<div align="center">**Preferred Values**</div>

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.6×10^{-16}	298
k /cm^3 molecule^{-1} s^{-1}	1.5×10^{-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 C=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.

acetone

(*E*)-4-methyl-8-methylenedeca-4,9-dienal

6-methylhept-5-en-2-one

4-methylenehex-5-enal

β-farnesene
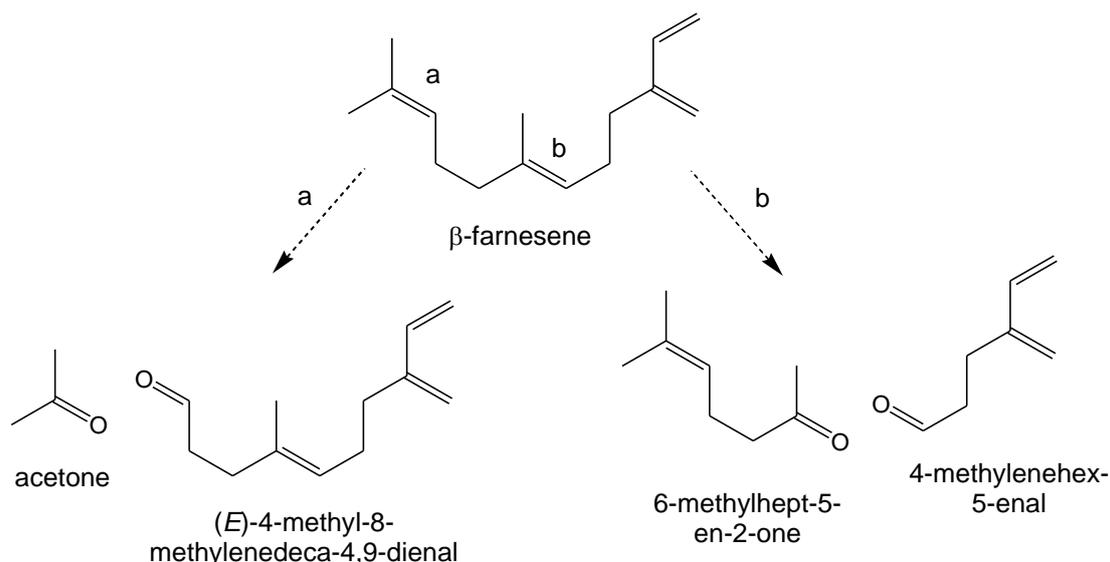
Kourtchev et al. (2009) also reported detection of 4-oxopentanal, which may be formed from the secondary ozonolysis of both (*E*)-4-methyl-8-methylenedeca-4,9-dienal and 6-methylhept-5-en-2-one; and methylglyoxal, which may be formed from reactions of the Criegee intermediate (CH$_3$)$_2$COO, the expected 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.