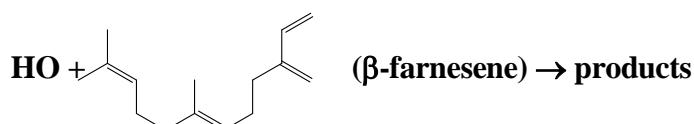


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx\_VOC108

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This datasheet last evaluated: December 2017; last change in preferred values: December 2017



## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(2.88 \pm 0.15) \times 10^{-10}$	313-423	Kim et al., 2011	RR-MS (a)
$(1.74 \pm 0.09) \times 10^{-10}$	$296 \pm 2$	Kourtchev et al., 2012	RR-FTIR (b),(c)
$(1.61 \pm 0.18) \times 10^{-10}$	$296 \pm 2$	Kourtchev et al., 2012	RR-FTIR (b),(d)

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

## Comments

- The concentrations of  $\beta$ -farnesene and 2-methylpropene (the reference compound) were monitored by MS during UV photolysis of  $\text{H}_2\text{O}_2$  -  $\beta$ -farnesene - 2-methylpropene - He mixtures in a  $160 \text{ cm}^3$  volume quartz vessel at  $\sim 1$  bar pressure. The measured rate coefficient ratios,  $k(\text{HO} + \beta\text{-farnesene})/k(\text{HO} + 2\text{-methylpropene})$ , were placed on an absolute basis using  $k(\text{HO} + 2\text{-methylpropene}) = 9.47 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1997), which agrees with the current IUPAC recommendation to within 0.5 % over the studied temperature range. The resultant values of  $k$  displayed no significant temperature dependence, and the reported rate coefficient was based on the mean of the measured values.
- The concentrations of *trans*- $\beta$ -farnesene and cyclohexa-1,3-diene or  $\alpha$ -terpinene (the reference compounds), were monitored by long path FTIR during UV photolysis of  $\text{H}_2\text{O}_2$  - *trans*- $\beta$ -farnesene - reference compound mixtures in a  $3.91 \text{ m}^3$  FEP chamber at  $0.1\text{--}1 \text{ mbar}$  above atmospheric pressure of purified air. The measured rate coefficient ratios,  $k(\text{HO} + \text{i}-\beta\text{-farnesene})/k(\text{HO} + \text{cyclohexa-1,3-diene}) = (1.06 \pm 0.04)$  and  $k(\text{HO} + \text{i}-\beta\text{-farnesene})/k(\text{HO} + \alpha\text{-terpinene}) = (0.46 \pm 0.01)$ , are placed on an absolute basis using  $k(\text{HO} + \text{cyclohexa-1,3-diene}) = 1.64 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003) and  $k(\text{O}_3 + \alpha\text{-terpinene}) = 3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC current recommendation) at  $296 \text{ K}$ . Gas phase carbonyl products were also identified, following photolysis of  $\text{HONO}$  - *trans*- $\beta$ -farnesene - air mixtures, as  $\text{O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatives (GC-MS)}$ , by collection on denuders.
- Relative to cyclohexa-1,3-diene.
- Relative to  $\alpha$ -terpinene.

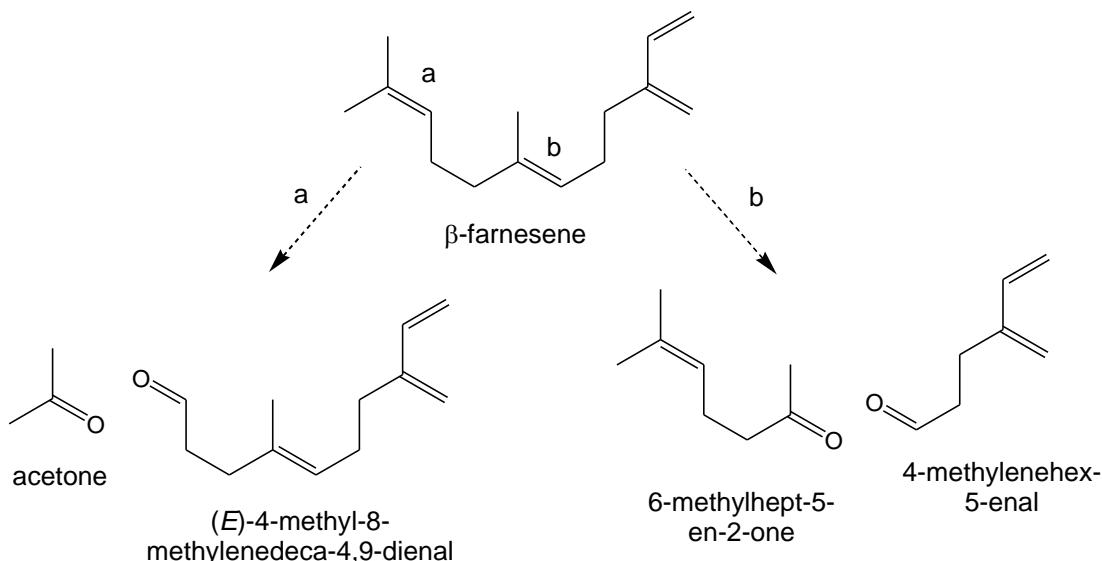
## Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.3 \times 10^{-10}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.3 \times 10^{-10}$	296-430
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.3$	298
$\Delta E/R$	$\pm 200$	

### Comments on Preferred Values

The preferred value of  $k$  is the average of the temperature-independent determination of Kim et al. (2011) and the room temperature determination of Kourtchev et al. (2012) (based on the mean of their two values), recommended for the temperature range 296-430 K. The reported values in the two studies differ by a factor of 1.7, and this is reflected in the assigned uncertainty. Additional studies are required to reduce this uncertainty.

Structure-activity methods (e.g. Vereecken and Peeters, 2001; Peeters et al., 2007) predict that the reaction should proceed mainly by addition of HO to the C=C bonds; but with a non-negligible contribution from H-atom abstraction, which results in formation of resonance-stabilized allyl radicals from attack at all (saturated carbon) sites. Kourtchev et al. (2012) reported evidence for HO addition to the two isolated C=C bonds ("a" and "b"), through detection of the corresponding carbonyl end products (acetone, (*E*)-4-methyl-8-methylenedeca-4,9-dienal, 4-methylenehex-5-enal and 6-methylhept-5-en-2-one), shown in the schematic below:



As presented by Kourtchev et al. (2012), these can be formed from the NO-catalyzed chemistry via intermediate  $\beta$ -hydroxy peroxy and oxy radical intermediates. They also reported detection of 4-oxopentanal, which may be formed from secondary oxidation of both (*E*)-4-methyl-8-methylenedeca-4,9-dienal and 6-methylhept-5-en-2-one. Addition of HO to the conjugated diene system is expected to be significant, although no evidence has been reported for the likely carbonyl end products (e.g. 6,10-dimethyl-2-methylene-undeca-5,9-dienal, 7,11-dimethyl-dodeca-1,6,10-trien-3-one and formaldehyde). Similarly, a significant contribution from H-atom abstraction chemistry also requires experimental confirmation.

## References

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