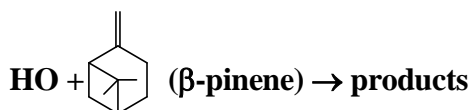


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC99

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This datasheet last evaluated: June 2019; 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>Absolute Rate Coefficients</i>			
$2.36 \times 10^{-11} \exp[(358 \pm 58)/T]$	297-423	Kleindienst et al., 1982	FP-RF (a)
$(7.76 \pm 1.10) \times 10^{-11}$	297		
$9.96 \times 10^{-12} \exp[(610 \pm 50)/T]$	300-435	Chuong et al., 2002	DF-RF/LIF (b)
$(7.72 \pm 0.44) \times 10^{-11}$	300		
$(7.68 \pm 0.72) \times 10^{-11}$	298	Davis et al. 2005	DF-LIF (c)
<i>Relative Rate Coefficients</i>			
$(6.54 \pm 0.99) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR/P-GC-FID (d)
$(7.81 \pm 0.51) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR/P-GC-FID (e)
$1.46 \times 10^{-11} \exp[(468 \pm 50)/T]$	295-364	Gill and Hites, 2002	RR/P-MS (f)
$(7.03 \pm 1.60) \times 10^{-11}$	298		
$1.91 \times 10^{-11} \exp[(416 \pm 17)/T]$	240-340	Montenegro et al., 2012	RR/DF-MS (g)
$(7.80 \pm 1.35) \times 10^{-11}$	298		
$(8.72 \pm 2.60) \times 10^{-11}$	298	Dash and Rajakumar, 2013	RR/P-GC-FID (h)

β-pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane

### Comments

- Flash photolysis of H<sub>2</sub>O/β-pinene mixtures in Ar (buffer gas) at total pressures in the range 50-200 Torr (67-270 mbar) under slow flow conditions. Pseudo-first order decays of HO radical concentrations (monitored by RF) were characterized in the presence of excess concentrations of β-pinene.  $k$  displayed no dependence on pressure over the studied range.
- Pseudo-first order decays of HO radical concentrations (monitored by RF or LIF) were characterized in the presence of excess concentrations of β-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of either He or 90% He/10% O<sub>2</sub>.
- Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of β-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of mainly He, with O<sub>2</sub> present at ~1-4% of the mixture.
- HO radicals were generated by the photolysis of NO<sub>x</sub> – organic – air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of β-pinene and 2-methylpropene (the reference compound) were analyzed by GC during the experiments. The measured rate coefficient ratio  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + 2\text{-methylpropene}) = 1.33 (\pm 30\%)$  is placed on an absolute basis using  $k(\text{HO} + 2\text{-methylpropene}) = 4.92 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 305 K (IUPAC current recommendation).
- HO radicals were generated by the photolysis of CH<sub>3</sub>ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-pinene and 2,3-

dimethyl-2-butene (the reference compound) were analyzed by GC during UV irradiation of CH<sub>3</sub>ONO - NO -  $\beta$ -pinene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 0.710 \pm 0.046$  is placed on an absolute basis using  $k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 1.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003).

- (f) HO radicals were generated by the photolysis of H<sub>2</sub>O<sub>2</sub> in helium diluent in a 192 cm<sup>3</sup> volume quartz vessel. The concentrations of  $\beta$ -pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + 1\text{-butene})$ ,  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + 2\text{-methylpropene})$  and  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + \textit{trans}\text{-2-butene})$  are placed on an absolute basis using  $k(\text{HO} + 1\text{-butene}) = 6.6 \times 10^{-12} \exp(465/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k(\text{HO} + 2\text{-methylpropene}) = 9.4 \times 10^{-12} \exp(505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k(\text{HO} + \textit{trans}\text{-2-butene}) = 1.0 \times 10^{-11} \exp(553/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC current recommendations).
- (g) HO radicals were generated by the reaction of H<sub>2</sub>O with F atoms (formed from F<sub>2</sub> discharge), and added to flowing mixtures containing  $\beta$ -pinene and isoprene (the reference compound) in helium at a total pressure of 1-8 Torr (1.3-11 mbar). The measured rate coefficient ratios,  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + \textit{isoprene})$ , are placed on an absolute basis using the rate coefficient expression  $k(\text{HO} + \textit{isoprene}) = 2.7 \times 10^{-11} \exp(370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC current recommendation).
- (h) HO radicals were generated by the photolysis of H<sub>2</sub>O<sub>2</sub> in nitrogen diluent at pressures in the range 800 Torr (1070 mbar) in a 1750 cm<sup>3</sup> volume quartz vessel. The concentrations of  $\beta$ -pinene and 2-methylpropene (the reference compound) were analyzed by GC-FID. The measured rate coefficient ratio  $k(\text{HO} + \beta\text{-pinene})/k(\text{HO} + 2\text{-methylpropene})$  is placed on an absolute basis using  $k(\text{HO} + 2\text{-methylpropene}) = 5.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (IUPAC current recommendation).

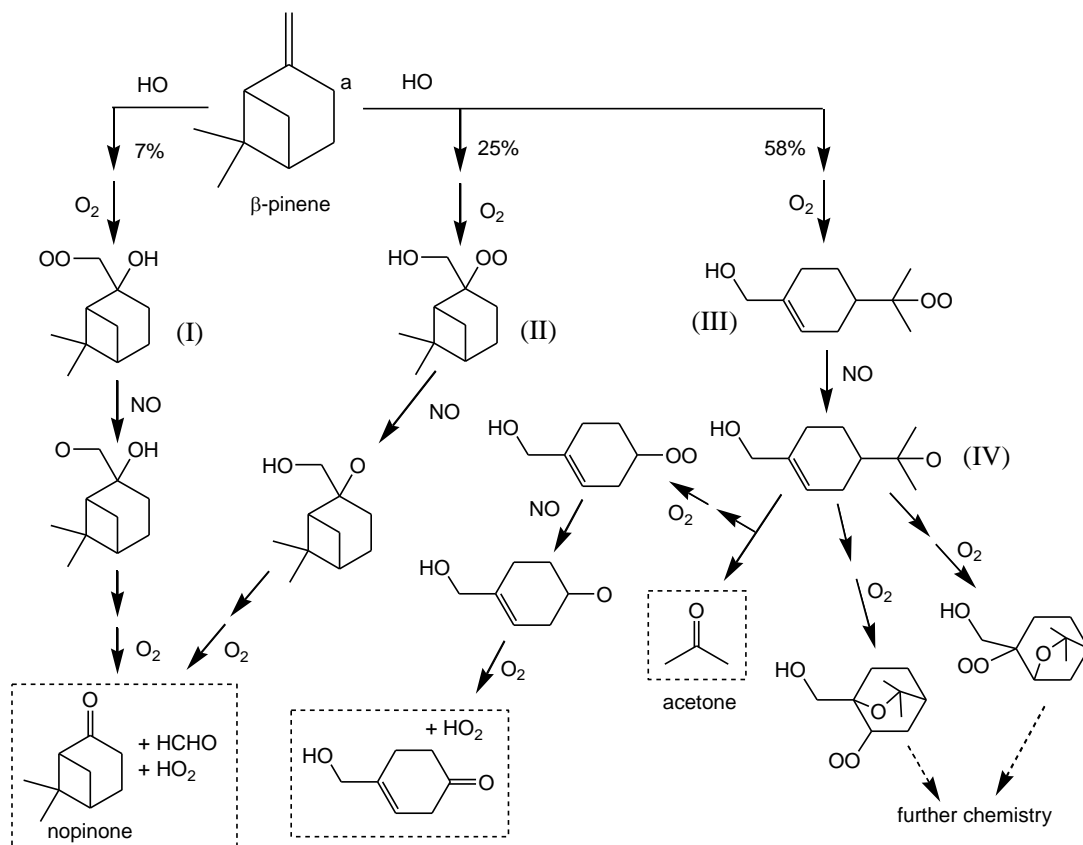
### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.6 \times 10^{-11}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.62 \times 10^{-11} \exp(460/T)$	240-420
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.05$	298
$\Delta E/R$	$\pm 150$	

### Comments on Preferred Values

The preferred value of  $E/R$  is a rounded average of those reported in the four tabulated temperature-dependence studies, with the assigned uncertainty range encompassing the set of values. The 298 K preferred value of  $k$  is the average of the room temperature values reported in all the tabulated studies, with those of Winer et al. (1976), Kleindienst et al. (1982), Atkinson et al. (1986) and Choung et al. (2002) corrected to 298 K using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

H atom abstraction has been estimated to account for about 10 % of the reaction of HO with  $\beta$ -pinene at 298 K (Vereecken and Peeters, 2012); with position “a” in the schematic below (forming a resonant radical) being the most important attack site. The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, and the schematic illustrates some established and predicted features of the subsequent chemistry in air in the presence of NO<sub>x</sub>.



The hydroxy-substituted peroxy radicals, (I), (II) and (III), are formed from sequential addition of HO and O<sub>2</sub>, with (III) facilitated by competitive opening of the cyclobutyl ring in the intermediate chemically-activated HO-β-pinene adduct. The approximate contributions of the three pathways shown are based on the calculations of Vereecken and Peeters (2012) for 298 K and 1 bar. The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates nopinone, which has been reported to be formed with a yield of about 25-30% in experimental studies in the presence of NO<sub>x</sub> (Arey et al. 1990; Hakola et al., 1994; Wisthaler et al., 2001). Its co-product, formaldehyde, has been reported to be formed with a higher yield of 45 ± 8 % (Orlando et al., 2000), consistent with its additional formation from other sources in the system. The chemistry of (III) partially generates acetone, which has been reported to be formed in yields in the range 2-13% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000). Its low yield may be explained by the operation of competing channels for oxy radical intermediate (IV), such as the illustrated ring closure reactions postulated by Vereecken and Peeters (2004; 2012).

The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxynitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of about 25% by Ruppert et al. (1999). Other products have also been observed, including formic acid (2%) by Orlando et al. (2000); and product signals consistent with a number of higher molecular weight dihydroxycarbonyl, hydroxynitrate and dihydroxynitrate products by Aschmann et al. (1998).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low NO<sub>x</sub> levels. These include bimolecular reactions with HO<sub>2</sub> and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products. Unimolecular isomerization reactions may also be available for complex peroxy radical intermediates. Vereecken and Peeters (2004) calculated that peroxy radical (III) undergoes a ring closure reaction (forming a peroxide-bridged product) that dominates at ≤ 1 ppb NO; and Berndt et al. (2016) have postulated that auto-oxidation reaction sequences, initiated by isomerization of peroxy radical (III) and involving a

number of subsequent peroxy radical isomerization reactions, may account for the observed rapid formation of highly oxidized multifunctional organic compounds from the HO-initiated oxidation of  $\beta$ -pinene in chamber experiments. The role of unimolecular isomerization reactions has recently been confirmed by Xu et al. (2019), who experimentally and theoretically characterized a number of competitive ring-closure and H-atom shift reactions for peroxy radical (III).

## References

- Arey, J., Atkinson, R. and Aschmann, S. M.: *J. Geophys. Res.*, 95, 18546, 1990
- Aschmann, S. M., Reissell, A., Atkinson, R. and Arey, J.: *J. Geophys. Res.*, 103, 25553, 1998.
- Aschmann, S. M., Atkinson, R. and Arey, J.: *J. Geophys. Res.*, 107 (D14), ACH 6, 2002.
- Atkinson, R. and Arey, J.: *Chem. Rev.*, 103, 4605, 2003.
- Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: *Int. J. Chem. Kinet.*, 18, 287, 1986.
- Berndt, T., Richters, S., Jokinen, T., Hyttinen, N., Kurtén, T., Otkjær, R. V., Kjaergaard, H. G., Stratmann, F., Herrmann, H., Sipila, M., Kulmala, M. and Ehn, M.: *Nat. Commun.*, 7, 13677, 2016.
- Chuong, B., Davis, M., Edwards, M. and Stevens, P. S.: *Int. J. Chem. Kinet.*, 34, 300, 2002.
- Gill, K. J. and Hites, R. A.: *J. Phys. Chem. A*, 106, 2538, 2002.
- Dash, M. R. and Rajakumar, B.: *Atmos. Environ.*, 79, 161, 2013.
- Davis, M. E., Tapscott, C. and Stevens, P. S.: *Int. J. Chem. Kinet.*, 37, 522, 2005.
- Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: *J. Atmos. Chem.*, 18, 75, 1994.
- Kleindienst, T. E., Harris, G. W. and Pitts Jr., J. N.: *Environ. Sci. Technol.*, 16, 844, 1982.
- Montenegro, A., Ishibashi, J. S. A., Lam, P. and Li, Z.: *J. Phys. Chem. A*, 116, 12096, 2012.
- Nozière, B., Barnes, I. and Becker, K.-H.: *J. Geophys. Res.*, 104, 23645, 1999.
- Orlando, J. J., Nozière, B., Tyndall, G. S., Orzechowska, G., Paulson, S. E. and Rudich, Y.: *J. Geophys. Res.*, 105, 11561, 2000.
- Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: *J. Geophys. Res.*, 104, 13869, 1999.
- Ruppert, L., Becker, K. H., Nozière, B., Spittler, M.: Development of monoterpene oxidation mechanisms: results from laboratory and smog chamber studies. Borrell, P.M., Borrell, P. (eds.) *Transport and Chemical Transformation in the Troposphere. Proceedings of the EUROTRAC-2 Symposium '98*, pp. 63–68. WIT, Southampton, UK, 1999.
- Vereecken, L. and Peeters, J.: *J. Phys. Chem. A*, 108, 5197, 2004.
- Vereecken, L. and Peeters, J.: *Phys. Chem. Chem. Phys.*, 14, 3802, 2012.
- Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: *J. Phys. Chem.*, 80, 1635, 1976.
- Wisthaler, A., Jensen, N. R., Winterhalter, R., Lindinger, W. and Hjorth, J.: *Atmos. Environ.*, 35, 618, 2001.
- Xu, L., Møller, K. H., Crouse, J. D., Otkjær, R. V., Kjaergaard, H. G., and Wennberg, P. O.: *J. Phys. Chem. A*, 123, 1661, 2019.

- Winer et al. (1974)
- Atkinson et al. (1986)
- Gill and Hites (2002) relative to but-1-ene
- ◇ Gill and Hites (2002) relative to trans-but-2-ene
- ▲ Montenegro et al. (2012)
- Recommendation
- ▲ Kleindienst et al. (1982)
- △ Chuong et al. (2002)
- + Gill and Hites (2002) relative to 2-methylpropene
- Davis et al. (2005)
- ◆ Dash and Rajakumar (2013)

