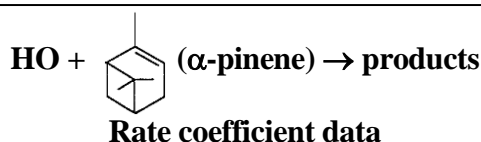


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC9

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This datasheet last evaluated: June 2019; last change in preferred values: December 2017



$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.37 \times 10^{-11} \exp[(446 \pm 76)/T]$	298-422	Kleindienst et al., 1982	FP-RF (a)
$(6.01 \pm 0.82) \times 10^{-11}$	298		
$1.63 \times 10^{-12} \exp[(1080 \pm 50)/T]$	300-435	Chuong et al., 2002	DF-RF/LIF (b)
$(6.08 \pm 0.24) \times 10^{-11}$	300		
$(6.09 \pm 0.30) \times 10^{-11}$	300	Davis and Stevens, 2005	DF-LIF (c)
$1.83 \times 10^{-11} \exp[(330 \pm 6)/T]$	238-357	Dillon et al., 2017	PLP-LIF (d)
$(5.4 \pm 0.2) \times 10^{-11}$	296		
<i>Relative Rate Coefficients</i>			
$(5.6 \pm 1.7) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR/P-GC-FID (e)
$(5.36 \pm 0.31) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR/P-GC-FID (f)
$1.17 \times 10^{-11} \exp[(436 \pm 53)/T]$	295-364	Gill and Hites, 2002	RR/P-MS (g)
$(5.04 \pm 1.23) \times 10^{-11}$	298		
$1.40 \times 10^{-11} \exp[(387 \pm 46)/T]$	240-340	Montenegro et al., 2012	RR/DF-MS (h)
$(5.36 \pm 0.94) \times 10^{-11}$	298		
$(5.06 \pm 0.75) \times 10^{-11}$	298	Dash et al. 2014	RR/P-GC-FID (i)

α-pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene

## Comments

- (a) Flash photolysis of H<sub>2</sub>O/α-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 α-pinene. *k* displayed no dependence on pressure over the studied range.
- (b) Pseudo-first order decays of HO radical concentrations (monitored by RF or LIF) were characterized in the presence of excess concentrations of α-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of either He or 90% He and 10% O<sub>2</sub>.
- (c) Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of α-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of mainly He, with O<sub>2</sub> present at ~ 1-14% of the mixture.
- (d) Pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm, in the presence of α-pinene/N<sub>2</sub> or α-pinene/air mixtures at total pressures in the range 6-211 Torr (8-280 mbar). Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of α-pinene (monitored by vacuum UV optical absorption at 184.95 nm). *k* displayed no significant dependence on bath gas or on pressure over the studied range (N.B. The 296 K data points presented below were obtained at 7.5, 96 and 197 Torr in N<sub>2</sub> and at 97 Torr in air. The reported value, tabulated above, is based on the average of the four determinations).

- (e) 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  $\alpha$ -pinene and 2-methylpropene (the reference compound) were analyzed by GC. The measured rate coefficient ratio  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 2\text{-methylpropene}) = 1.14 (\pm 30\%)$  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).
- (f) 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  $\alpha$ -pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during the CH<sub>3</sub>ONO – NO –  $\alpha$ -pinene - 2,3-dimethyl-2-butene – air irradiations. The measured rate coefficient ratio  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 0.487 \pm 0.028$  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).
- (g) 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  $\alpha$ -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  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 1\text{-butene})$ ,  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 2\text{-methylpropene})$  and  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + \textit{trans}\text{-2-butene})$  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).
- (h) 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  $\alpha$ -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,  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + \textit{isoprene})$ , 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).
- (i) HO radicals were generated by the photolysis of H<sub>2</sub>O<sub>2</sub> in nitrogen diluent at pressures in the range 800-850 Torr (1070-1130 mbar) in a 1750 cm<sup>3</sup> volume quartz vessel. The concentrations of  $\alpha$ -pinene and propene (the reference compound) were analyzed by GC-FID. The measured rate coefficient ratio  $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + \textit{propene})$  is placed on an absolute basis using  $k(\text{HO} + \textit{propene}) = 2.86 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 825 Torr (1100 mbar) (IUPAC current recommendation).

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.3 \times 10^{-11}$	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.34 \times 10^{-11} \exp(410/T)$	240-360
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.08$	298
$\Delta E/R$	$\pm 100$	

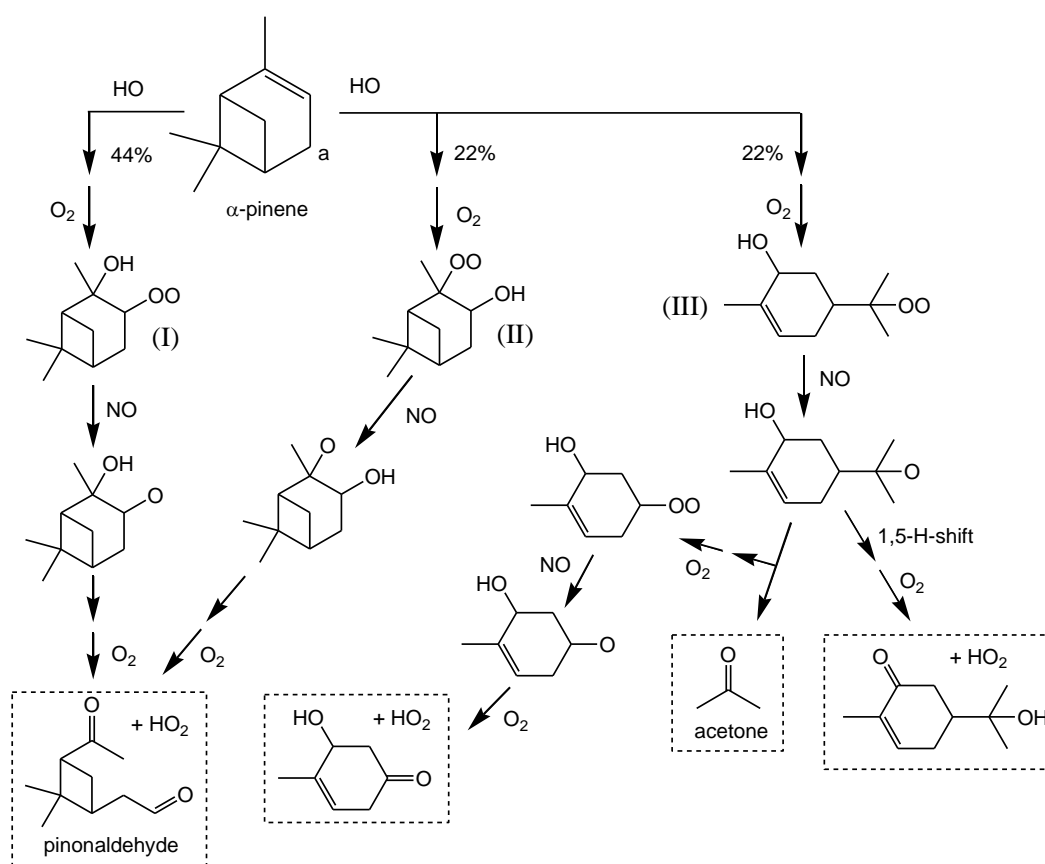
### Comments on Preferred Values

The room temperature values of  $k$  in the reported studies are in reasonable agreement. With the exception of the recent study of Dillon et al. (2017), those reported in the direct kinetics studies are consistently slightly higher (15% on average) than those reported in the relative rate studies. The direct studies of Chuong et al. (2002) and Davis and Stevens (2005) reported increased wall removal rates of HO when  $\alpha$ -pinene was present, and initial deviations from pseudo-first order HO decay, which may contribute to the small systematic difference. Chuong et al. (2002) also report a temperature dependence that is significantly higher than those reported in other temperature

dependence studies. Similar complications were not apparent in the recent direct study of Dillon et al. (2017), which reports a room temperature value of  $k$  that is comparable with those in the relative rate studies.

The preferred value of  $E/R$  is a rounded average of those reported in the relative rate studies of Gill and Hites (2002) and Montenegro et al. (2012), but is consistent with those reported in the direct studies of Kleindienst et al. (1982) and Dillon et al. (2017). The 298 K preferred value of  $k$  is an average of the room temperature values reported in all the tabulated relative rate studies, with those of Winer et al. (1976) and Atkinson et al. (1986) corrected to 298 K using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value. However, the resultant expression also provides an excellent description of the recent direct kinetics data of Dillon et al. (2017) at temperatures below 300 K.

H atom abstraction has been estimated to account for about 12 % of the reaction of HO with  $\alpha$ -pinene at 298 K (Peeters et al., 2001); with this being dominated by attack at position “a” in the schematic below, which forms a resonant radical. The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, and the schematic illustrates some features of the established and predicted subsequent chemistry in air in the presence of  $\text{NO}_x$ .



The hydroxy-substituted peroxy radicals, (I), (II) and (III), are formed from sequential addition of HO and  $\text{O}_2$ , with (III) facilitated by competitive opening of the cyclobutyl ring in the intermediate chemically-activated HO- $\alpha$ -pinene adduct. The approximate contributions of the three pathways shown are based on the calculations of Vereecken and Peeters (2000) and Peeters et al. (2001) 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 pinonaldehyde, which has been reported to be formed in yields in the range  $28 \pm 5\%$  to  $87 \pm 20\%$  in experimental studies in the presence of  $\text{NO}_x$  (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Nozière et al., 1999; Wisthaler et al., 2001; Aschmann et al., 2002). Lower yields have generally been obtained by GC analyses (Arey et al., 1990; Hakola et al., 1994; Aschmann et al., 2002) and by proton-transfer mass spectrometry (Wisthaler et al., 2001), with the higher values by *in situ* FTIR spectroscopy (Hatakeyama et al., 1991; Nozière et al., 1999). The

chemistry of (III) partially generates acetone, which has been reported to be formed in yields in the range 5-11% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000).

The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxynitrate products (not shown in the schematic). There is some disagreement in the reported yields of nitrate products, with the *in situ* FTIR determinations of total nitrate products by Nozière et al. (1999),  $18 \pm 9\%$ , and Rindelaub et al. (2015),  $26 \pm 7\%$ , being much higher than those reported specifically for the C<sub>10</sub> hydroxynitrates by Aschmann et al. (2002),  $\sim 1\%$ , and Xu et al. (2019),  $3.3 \pm 1.5\%$ , based on mass spectrometric methods (API-MS and GC-ToF-CIMS, respectively). Other products have also been observed, including formaldehyde (19%) and formic acid (7%) 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; 2002).

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. Capouet et al. (2004) calculated that peroxy radical (III) undergoes a ring closure reaction (forming a peroxide-bridged product) that dominates under most atmospheric conditions; 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  $\alpha$ -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).

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- Atkinson et al. (1986)
- ◆ Dillon et al. (2017)
- + Gill and Hites (2002) relative to 2-methylpropene
- Davis and Stevens (2005)
- ◆ Dash et al. (2014)
- ▲ Kleindienst et al. (1982)
- △ Chuong et al. (2002)
- Gill and Hites (2002) relative to but-1-ene
- ◇ Gill and Hites (2002) relative to trans-but-2-ene
- ▲ Montenegro et al. (2012)
- Recommendation

