

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC9

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This data sheet last evaluated: 17th December 2007 (with no revision of the preferred values).

HO + α -pinene \rightarrow products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	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
$(6.01 \pm 0.82) \times 10^{-11}$	298		
$1.63 \times 10^{-12} \exp[(1080 \pm 50)/T]$	300-435	Choung et al., 2002	DF-RF (a)
$(6.08 \pm 0.24) \times 10^{-11}$	300		
<i>Relative Rate Coefficients</i>			
$(5.6 \pm 1.7) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR (b)
$(5.35 \pm 0.31) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR (c)
$1.17 \times 10^{-11} \exp[(436 \pm 53)/T]$	295-364	Gill and Hites, 2002	RR (d)
$(5.05 \pm 1.23) \times 10^{-11}$	298		

Comments

- (a) Experiments carried out at 5 Torr (6.7 mbar) of He or 90% He + 10% O₂.
- (b) HO radicals were generated by the photolysis of NO_x – organic – air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of α -pinene and 2-methylpropene (the reference compound) were analyzed by GC during the experiments. 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 by use of a rate coefficient at 305 K of $k(\text{HO} + 2\text{-methylpropene}) = 4.94 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
- (c) HO radicals were generated by the photolysis of CH₃ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of α -pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during the CH₃ONO – NO – α -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 by use of a rate coefficient at 294 K of $k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 1.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
- (d) HO radicals were generated by the photolysis of H₂O₂ in helium diluent in a 192 cm³ volume quartz vessel. The concentrations of α -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 by use of rate coefficients of $k(\text{HO} + 1\text{-butene}) = 6.55 \times 10^{-12} \exp(467/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{HO} + 2\text{-methylpropene}) = 9.47 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \textit{trans}\text{-2-butene}) = 1.01 \times 10^{-11} \exp(550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).

Preferred Values

$k = 1.2 \times 10^{-11} \exp(440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290-430 K

$k = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

At room temperature, the rate coefficients of Winer et al. (1976), Kleindienst et al. (1982), Atkinson et al. (1986), Gill and Hites (2002) and Choung et al. (2002) are in good agreement, as are the temperature dependencies obtained by Kleindienst et al. (1982) and Gill and Hites (2002). The temperature dependence obtained by Chuong et al. (2002) at 6.7 mbar pressure is significantly higher than those of Kleindienst et al. (1982) and Gill and Hites (2002), possibly because of fall-off effects above 300 K (although no evidence was obtained to support this conclusion). The preferred temperature dependence is based on those obtained by Kleindienst et al. (1982) and Gill and Hites (2002), and the preferred 298 K rate coefficient is the average of the measurements of Kleindienst et al. (1982), Atkinson et al. (1986) (corrected to 298 K using the preferred temperature dependence) and Gill and Hites (2002). The pre-exponential factor is adjusted to fit the 298 K preferred value.

A number of product studies have been carried out at room temperature and atmospheric pressure of air (see Atkinson and Arey (2003b) and references therein). The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, resulting in two hydroxyalkyl radicals which then add O₂ to form two 1,2-hydroxyalkyl peroxy radicals. H-atom abstraction almost certainly occurs to a minor extent, with acetone (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000) being one of the likely products. Subsequent reactions of these 1,2-hydroxyalkyl peroxy radicals with NO, NO₂, HO₂ radicals, organic peroxy radicals and NO₃ radicals will lead to the products formed in the atmosphere. In the presence of NO such that organic peroxy radicals react dominantly with NO, the products observed (and their reported yields) are: pinonaldehyde, 28 ± 5% to 87 ± 20% (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Nozière et al., 1999; Wisthaler et al., 2001; Aschmann et al., 2002) with the lower yields being 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) and the higher values by *in situ* FTIR spectroscopy (Hatakeyama et al., 1991; Nozière et al., 1999); acetone, 5-11% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000), formic acid, 7% (Orlando et al., 2000); organic nitrates, 18 ± 9% (Nozière et al., 1999); a molecular weight 184 (dihydroxycarbonyl), ~19% (Aschmann et al., 2002); a molecular weight 200 product, ~11% (Aschmann et al., 2002), and molecular weight 215 C₁₀-hydroxynitrates and molecular weight 231 C₁₀-dihydroxynitrates (Aschmann et al., 1998, 2002).

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son et al. (1986)
- ▲ Gill and Hites (2002), relative to 1-butene
- ▼ Gill and Hites (2002), relative to 2-methylpropene
- ◆ Gill and Hites (2002), relative to trans-2-butene
- ◆ Gill and Hites (2002), relative to trans-2-butene
- Choung et al. (2002)
- Recommendation

