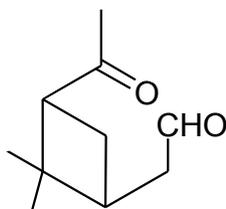


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC22

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This data sheet updated: 12th December 2007 (with revisions to the preferred values).

OH + Pinonaldehyde → products



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$4.5 \times 10^{-12} \exp[(600 \mp 100)/T]$ $(3.46 \mp 0.52) \times 10^{-11}$	297-374 297	Davis et al., 2007	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$(8.72 \pm 1.14) \times 10^{-11}$	298 ± 2	Hallquist et al., 1997	RR (b)
$(8.9 \pm 2.6) \times 10^{-11}$	300 ± 5	Glasius et al., 1997	RR (c,d)
$(9.0 \pm 1.3) \times 10^{-11}$	300 ± 5	Glasius et al., 1997	RR (c,e)
$(4.5 \pm 0.8) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (f,g)
$(4.9 \pm 1.1) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (f,h)
$(5.4 \pm 0.9) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (f,i)
$(3.0 \pm 0.8) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (d,j)
$(5.5 \pm 1.5) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (e,j)
$(4.7 \pm 0.6) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 1.0) \times 10^{-11}$	295 ± 3		
$(2.7 \pm 0.6) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (j,k)
$(3.3 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(3.9 \pm 0.4) \times 10^{-11}$	295 ± 3		
$(3.7 \pm 1.1) \times 10^{-11}$	299 ± 2	Nozière et al., 1999	RR (k,l)
$(4.2 \pm 1.1) \times 10^{-11}$	290 ± 2		
$(3.8 \pm 1.5) \times 10^{-11}$	288 ± 1		
$(4.4 \pm 0.8) \times 10^{-11}$	287 ± 1		
$(4.4 \pm 1.0) \times 10^{-11}$	289 ± 2		

Comments

- (a) Pinonaldehyde was measured by UV absorption at 185 nm prior to and after the reaction vessel and by IR absorption prior to the reaction vessel. The cited error in the 297 K rate coefficient is the estimated overall uncertainty ($\pm 15\%$).
- (b) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at 1013 ± 5 mbar pressure. The concentrations of pinonaldehyde and propene (the reference compound) were measured by FTIR spectroscopy. Wall losses of pinonaldehyde in the 153 L chamber were observed and measured in separate experiments and taken into account in the data analysis. The

measured rate coefficient ratio of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{propene})$ is placed on an absolute basis by use of a rate coefficient at 298 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

- (c) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO}$ -air or H_2O_2 -air mixtures at 987 ± 7 mbar pressure. The concentrations of pinonaldehyde and isoprene or 1,3-butadiene (the reference compounds) were measured by FTIR spectroscopy. Decays of pinonaldehyde in the dark and due to photolysis were observed in the 480 L reaction chamber used and were taken into account in the data analysis. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{isoprene}) = 0.896 \pm 0.260$ and $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + 1,3\text{-butadiene}) = 1.37 \pm 0.19$ are placed on an absolute basis by use of rate coefficients at 300 K of $k(\text{HO} + \text{isoprene}) = 9.91 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) and $k(\text{HO} + 1,3\text{-butadiene}) = 6.59 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (d) Relative to $k(\text{HO} + \text{isoprene})$.
- (e) Relative to $k(\text{HO} + 1,3\text{-butadiene})$.
- (f) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO}$ -air mixtures at 987 mbar pressure. The concentrations of pinonaldehyde and propene, 1-butene or *m*-xylene (the reference compounds) were measured by GC. No measurable decays (<5%) of pinonaldehyde were observed due to dark decays to the walls of the 7000 L Teflon chamber used or due to photolysis at wavelengths >300 nm. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{propene}) = 1.70 \pm 0.29$, $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + 1\text{-butene}) = 1.56 \pm 0.33$ and $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + m\text{-xylene}) = 2.35 \pm 0.35$ are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{HO} + 1\text{-butene}) = 3.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + m\text{-xylene}) = 2.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (g) Relative to $k(\text{HO} + \text{propene})$.
- (h) Relative to $k(\text{HO} + 1\text{-butene})$.
- (i) Relative to $k(\text{HO} + m\text{-xylene})$.
- (j) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO}$ -air or H_2O_2 -air mixtures at 1013 mbar pressure. The concentrations of pinonaldehyde and reference compound (isoprene, 1,3-butadiene or cyclohexane) were measured by FTIR spectroscopy. Wall losses and photolysis was observed in the various chambers used (ranging from 405 to 1080 L volume) and were taken into account in the data analysis. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{isoprene})$, $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + 1,3\text{-butadiene})$ and $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{cyclohexane})$ are placed on an absolute basis by use of rate coefficients at 295 K of $k(\text{HO} + \text{isoprene}) = 1.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation), $k(\text{HO} + 1,3\text{-butadiene}) = 6.76 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003) and $k(\text{HO} + \text{cyclohexane}) = 6.90 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003; Atkinson and Arey, 2003).
- (k) Relative to $k(\text{HO} + \text{cyclohexane})$.
- (l) Experiments carried out in the ~180000 L volume EUPHORE chamber with HO radicals being generated by the dark reaction of ozone with 2,3-dimethyl-2-butene in air at ~1 bar pressure. The concentrations of pinonaldehyde and cyclohexane were monitored during the experiments by FTIR spectroscopy (pinonaldehyde and cyclohexane) and also by HPLC after derivatization for pinonaldehyde and by GC for cyclohexane. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{cyclohexane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003; Atkinson and Arey, 2003).

Preferred Values

$$k = 3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$k = 5.2 \times 10^{-12} \exp(600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290-380 K.

Reliability

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

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α -pinene. Pinonaldehyde is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are from four relative rate studies carried out at around room temperature and a recent absolute rate study carried out over the temperature range 297-374 K (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998; Nozière et al., 1999; Davis et al., 2007). At room temperature the measured rate coefficients range over a factor of ~ 3 , with those measured by Hallquist et al. (1997) and Glasius et al. (1997) being a factor of ~ 2 higher than those of Alvarado et al. (1998), Nozière et al. (1999) and Davis et al. (2007), possibly because of unresolved wall adsorption problems. The preferred values are based on the absolute rate study of Davis et al. (2007) and the relative rate studies of Alvarado et al. (1998), carried out in a large volume Teflon chamber, and Nozière et al. (1999), carried out in various chambers of volume ranging from 405 L to ~ 180000 L. After correction to 298 K using the temperature dependence of Davis et al. (2007), the rate coefficients measured by Alvarado et al. (1998) have been aggregated into an average of $4.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and those measured in the extensive study of Nozière et al. (1999) have been aggregated into an average rate coefficient from the indoor chambers with photolytic production of HO radicals of $3.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an average rate coefficient from the EUPHORE chamber study (with dark production of HO radicals) of $3.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A simple average of these three relative rate coefficients and the absolute rate coefficient of Davis et al. (2007) (corrected to 298 K as described above), which are in agreement within their experimental uncertainties, leads to the preferred 298 K rate coefficient. The temperature dependence of Davis et al. (2007) is accepted and combined with the preferred 298 K rate coefficient to derive the pre-exponential factor.

The reaction proceeds by H-atom abstraction from the various C-H bonds, including from the CHO group. By analogy with other aldehydes (IUPAC, 2007), the negative temperature dependence suggests that a substantial fraction of the reaction proceeds by H-atom abstraction from the CHO group.

References

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- Recommendation
- Hallquist et al. (1997)
- ▲ Glasius et al. (1997)
- ▲ Alvarado et al. (1998)
- Noziere et al. (1999), indoor chamber
- ▽ Noziere et al. (1999), EUPHORE chamber
- ◆ Davis et al. (2007)

