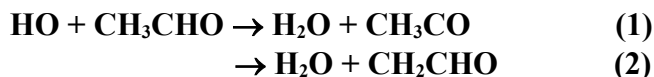


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_VOC12

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated May 2009 (with revision of the preferred values).



$$\Delta H^\circ(1) = -123.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -102.7 \text{ kJ}\cdot\text{mol}^{-1}$$

## Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.55 \pm 0.39) \times 10^{-11}$	300	Morris et al., 1971	DF-MS
$6.87 \times 10^{-12} \exp[(257 \pm 151)/T]$	299-426	Atkinson and Pitts, 1978	FP-RF
$(1.60 \pm 0.16) \times 10^{-11}$	299		
$7.1 \times 10^{-12} \exp[(165 \pm 91)/T]$	253-424	Semmes et al., 1985	FP-RF
$(1.22 \pm 0.27) \times 10^{-11}$	298		
$5.52 \times 10^{-12} \exp[(307 \pm 52)/T]$	244-528	Michael et al., 1985	DF-RF
$(1.47 \pm 0.28) \times 10^{-11}$	298		
$8.6 \times 10^{-12} \exp[(200 \pm 60)/T]$	297-517	Dóbé et al., 1989	DF-RF/LIF
$(1.69 \pm 0.34) \times 10^{-11}$	298 ± 2		
$(1.7 \pm 0.3) \times 10^{-11}$	298	Balestra-Garcia et al., 1992	PLP-RF
$(1.44 \pm 0.25) \times 10^{-11}$	298	Tyndall et al., 1995	DF-LIF
$4.31 \times 10^{-12} \exp[(309 \pm 19)/T]$	295-550	Taylor et al., 1996	PLP-LIF
$1.23 \times 10^{-11}$	295		
$4.4 \times 10^{-12} \exp[(366 \pm 30)/T]$	202-348	Sivakumaran and Crowley, 2003	PLP-LIF
$1.50 \times 10^{-11}$	298		
$1.67 \times 10^{-11}$	296	Wang et al., 2003	PLP-IRS
$(1.546 \pm 0.222) \times 10^{-11}$	297	Taylor et al., 2006	PLP-LIF (a)
$(1.690 \pm 0.154) \times 10^{-11}$	297		
$(1.083 \pm 0.130) \times 10^{-11}$	383		
$1.5 \times 10^{-11}$	295	Vöhringer-Martinez et al., 2007	PLP-LIF (b,c)
$1.6 \times 10^{-11}$	295	Vöhringer-Martinez et al., 2007	PLP-LIF (b,d)
$5.32 \times 10^{-12} \exp[(315 \pm 40)/T]$	204-373	Zhu et al., 2008	PLP-LIF
$(1.52 \pm 0.15) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(1.62 \pm 0.18) \times 10^{-11}$	298 ± 2	Niki et al., 1978	RR (e)
$(1.28 \pm 0.43) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (f)
$(1.62 \pm 0.10) \times 10^{-11}$	298 ± 2	Scollard et al., 1993	RR (g)
$(1.44 \pm 0.08) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (h)
<i>Branching Ratios</i>			
$k_1/k = 0.93 \pm 0.18$	296	Cameron et al., 2002	(i)
$k_2/k = 0.051^{+0.024}_{-0.017}$	298	Butkovskaya et al., 2004	(j)

## Comments

- a) Rate coefficients were measured at 297, 383, 600, 672, 859 and 860 K, using the pulsed laser photolysis of HONO and of N<sub>2</sub>O in the presence of H<sub>2</sub>O as sources of HO radicals. The measured rate coefficients were uniformly 20-30% higher than the earlier values from this group (Taylor et al., 1996). Rate coefficients were also measured for HO + CH<sub>3</sub>CDO at 297, 298, 383, 600 and 860 K and for HO + CD<sub>3</sub>CHO at 297, 602 and 861 K. The reported deuterium isotope effects  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CH}_3\text{CDO})$  were 1.68 at 297 K, 1.77 at 298 K, 1.61 at 383 K, 1.39 at 600 K and 1.10 at 860 K, and those for  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CD}_3\text{CHO})$  were 0.88 at 297 K, 1.10 at 602 K and 1.64 at 861 K.
- b) Rate coefficients were measured at 60, 77, 106, 118 and 295 K, in the presence and absence of water vapor (at concentrations ranging from  $1.5 \times 10^{15}$  molecule cm<sup>-3</sup> at 60 K to  $7.8 \times 10^{15}$  molecule cm<sup>-3</sup> at 295 K). At temperatures in the range 60-118 K the presence of water vapor increased the measured rate coefficient significantly, by a factor of ~2 at 60 K. At 295 K, no effect of  $7.8 \times 10^{15}$  molecule cm<sup>-3</sup> of water vapor on the rate coefficient was observed within the experimental uncertainties.
- c) In the absence of added water vapor.
- d) In the presence of  $7.8 \times 10^{15}$  molecule cm<sup>-3</sup> of water vapor.
- e) Relative rate method. HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH<sub>3</sub>CHO and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{ethene}) = 1.9 \pm 0.2$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and atmospheric pressure (Atkinson, 1997).
- f) Relative rate method. HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH<sub>3</sub>CHO and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{ethene}) = 1.50 \pm 0.50$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and atmospheric pressure (Atkinson, 1997).
- g) Relative rate method. HO radicals were generated from the photolysis of CH<sub>3</sub>ONO in air, and the concentrations of CH<sub>3</sub>CHO and ethene (the reference compound) were measured during the experiments by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and atmospheric pressure (Atkinson, 1997).
- h) Relative rate method. HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of acetaldehyde and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + 1\text{-butene}) = 0.458 \pm 0.024$  is placed on an absolute basis by use of a rate coefficient of  $k(\text{HO} + 1\text{-butene}) = 3.14 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K and atmospheric pressure of air (Atkinson, 1997; IUPAC, current recommendation).
- i) Obtained from the yields of CH<sub>3</sub>CO radicals per HO radical reacting with CH<sub>3</sub>CHO. CH<sub>3</sub>CO formation was monitored by UV absorption at 220 nm.
- j) Obtained from the yield of vinoxy (CH<sub>2</sub>CHO) radicals, with vinoxy being measured by proton-transfer-ionization mass spectrometry.

### Preferred Values

$k = 1.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K.

$k = 4.7 \times 10^{-12} \exp(345/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> over the temperature range 200-380 K.

$k_1/k = 0.95$  at 298 K

$k_2/k = 0.05$  at 298 K

### Reliability

$\Delta \log k = \pm 0.06$  at 298 K.

$\Delta(E/R) = \pm 80$  K.

$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.05$  at 298 K.

### Comments on Preferred Values

The room temperature rate coefficients are in the range  $(1.2-1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with the absolute rate coefficients of Atkinson and Pitts (1978), Michael et al. (1985), Tyndall et al. (1995), Sivakumaran and Crowley (2003), Wang et al. (2003), Taylor et al. (2006), Vöhringer-Martinez et al. (2007) and Zhu et al. (2008) being in reasonably good agreement. The temperature dependences of Michael et al. (1985), Taylor et al. (1996), Sivakumaran and Crowley (2003) and Zhu et al. (2008) are in excellent agreement and also agree well with the temperature dependence measured over a smaller temperature range by Atkinson and Pitts (1978). The extensive studies of Sivakumaran and Crowley (2003) and Zhu et al. (2008) extend to significantly lower temperatures than the other temperature-dependent studies (Atkinson and Pitts, 1978; Semmes et al., 1985; Michael et al., 1985; Dóbé et al., 1989; Taylor et al., 1996, 2006), and are used as the basis for the preferred values. The preferred values are obtained from an un-weighted least-squares analysis of the rate coefficients of Sivakumaran and Crowley (2003) and Zhu et al. (2008). The data of Semmes et al. (1985) are lower than the preferred values by up to ~20%, possibly because of the reported difficulties in accurately determining the acetaldehyde concentrations (Semmes et al., 1985). While the absolute rate coefficients measured by Dóbé et al. (1989) for  $\text{CH}_3\text{CHO}$  are in good agreement with the preferred values, their measured rate coefficients for the reactions of HO radicals with the higher aldehydes  $(\text{CH}_3)_2\text{CHCHO}$  and  $(\text{CH}_3)_3\text{CCHO}$  are significantly higher, by factors of ~1.5 to 2.3, than the rate coefficients of Kerr and Sheppard (1981) and Semmes et al. (1985) (which are in good agreement).

Cameron et al. (2002), Wang et al. (2003), Vandenberk and Peeters (2003) and Butkovskaya et al. (2004) have investigated the products of this reaction using mass spectrometry (Vandenberk and Peeters, 2003; Butkovskaya et al., 2004) and IR and UV spectroscopic methods (Cameron et al., 2002; Wang et al., 2003). Vandenberk and Peeters (2003), Wang et al. (2003) and Butkovskaya et al. (2004) measured  $\text{H}_2\text{O}$  formation yields of  $86 \pm 6\%$  at 290 K, ~100% at 296 K, and  $97.7 \pm 4.7\%$  at 248 and 298 K, respectively. Cameron et al. (2002) used absorption spectroscopy to detect  $\text{CH}_3$  and  $\text{CH}_3\text{CO}$  radicals and resonance fluorescence to detect H atoms, and obtained upper limits for the formation of  $\text{CH}_3 + \text{HC(O)OH}$  (<3% at 296 K) and  $\text{H} + \text{CH}_3\text{C(O)OH}$  (<2% over the temperature range 237-296 K); the major reaction pathway was determined to be formation of  $\text{CH}_3\text{CO} + \text{H}_2\text{O}$ , with a measured yield of  $93 \pm 18\%$  at 296 K (Cameron et al., 2002). Vandenberk and Peeters (2003) measured a  $\text{HC(O)OH}$  formation yield of <3% at room temperature, in agreement with the conclusion of Cameron et al. (2002) based on the upper limit to the  $\text{CH}_3$  yield. The H atom and  $\text{CH}_3$  yields of  $5 \pm 5\%$  and <5%, respectively, measured by Wang et al. (2003) are consistent with the upper limits of Cameron et al. (2002). By direct detection of vinoxy,  $\text{CH}_2\text{CHO}$ , radicals, Butkovskaya et al. (2004) derived a branching ratio for H-atom abstraction from the  $\text{CH}_3$  group in  $\text{CH}_3\text{CHO}$  of  $5.1^{+2.4}_{-1.7}\%$ , consistent with the conclusion of Cameron et al. (2002) that H-atom abstraction from the  $\text{CH}_3$  group accounts for <25% of the overall reaction at room temperature. These product data are in agreement with H-atom abstraction being the sole reaction pathway, with H-atom abstraction from the CHO group dominating and accounting for ~95% of the overall reaction at room temperature.

D'Anna et al. (2003) have measured deuterium isotope effects at  $298 \pm 2$  K, with rate coefficient ratios of  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CH}_3\text{CDO}) = 1.42 \pm 0.10$ ,  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CD}_3\text{CHO}) = 1.13 \pm 0.04$  and  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CD}_3\text{CDO}) = 1.65 \pm 0.08$ . The rate coefficient ratios  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CH}_3\text{CDO})$  and  $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{CD}_3\text{CHO})$  at room temperature derived by Taylor et al. (2006) from absolute rate measurements are in reasonable agreement with the more

direct measurements of D'Anna et al. (2003). These deuterium isotope effects are consistent with H- (or D-) atom abstraction from the CHO (or CDO) group being dominant at room temperature.

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- Recommendation
- - - Taylor et al. (1996) Arrhenius fit
- Atkinson and Pitts (1978)
- ▼ Semmes et al. (1985)
- Michael et al. (1985)
- ◆ Balestra-Garcia et al. (1993)
- ▲ Tyndall et al. (1995)
- ◆ Sivakumaran and Crowley (2003)
- Wang et al. (2003)
- ▽ Taylor et al. (2006)
- Vohringer-Martinez et al. (2007)
- ◆ Zhu et al. (2008)

