Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC36

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

$$HO + CH_3C(O)OH \rightarrow H_2O + CH_2C(O)OH \quad (1)$$
$$\rightarrow H_2O + CH_3C(O)O \quad (2)$$
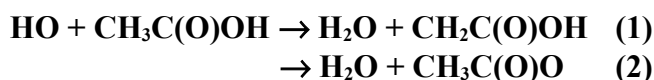
Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-12} \exp[-(170 \pm 20)/T]$	298-440	Dagaut et al., 1988	FP-RF (a)
$(7.4 \pm 0.6) \times 10^{-13}$	298		
$(8.67 \pm 0.65) \times 10^{-13}$	296.8	Singleton et al., 1989	PLP-RA
$(5.63 \pm 0.44) \times 10^{-13}$	326.2		
$(4.88 \pm 0.17) \times 10^{-13}$	356.4		
$(4.09 \pm 0.14) \times 10^{-13}$	396.8		
$(3.95 \pm 0.07) \times 10^{-13}$	446.2		
$2.2 \times 10^{-14} \exp[(1012 \pm 80)/T]$	229-300	Butkovskaya et al., 2004	DF-CIMS (b)
$(6.6 \pm 1.1) \times 10^{-13}$	300		
$2.52 \times 10^{-14} \exp[(1010 \pm 150)/T]$	273-373	Vimal and Stevens, 2006	DF-RF (c)
$(7.42 \pm 0.12) \times 10^{-13}$	300		
$2.9 \times 10^{-9} \exp(-6030/T)$	287-802	Khamaganov et al., 2006	PLP-LIF (d)
$+ 1.50 \times 10^{-13} \exp(515/T)$			
$(8.5 \pm 0.9) \times 10^{-13}$	298		
$5.38 \times 10^{-14} \exp[(740 \pm 51)/T]$	256-357	Huang et al., 2009	DF-LIF
$(6.77 \pm 0.14) \times 10^{-13}$	295		
Relative Rate Coefficients			
$(6.5 \pm 0.5) \times 10^{-13}$	296 ± 2	Crunaire et al., 2006	RR (e)

Comments

(a) Rate coefficient also measured at 240 K where the major species present was expected to be the dimer. Assuming that the monomer and dimer were equally reactive towards the HO radical (but see Butkovskaya et al., 2004), a rate coefficient of $(6.4 \pm 0.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 240 K was obtained.

(b) Experiments were carried out in a turbulent flow system at ~200 Torr (267 mbar) pressure. Combined with the rate data of Singleton et al. (1989), the expression $k = 2.45 \times 10^{-16}$ $(T/298)^{5.24} \exp[(2358 \pm 189)/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 229-446 K was obtained. The CO$_2$ yield was measured by CIMS to be $64 \pm 17\%$, independent of temperature over the range 249-298 K.

(c) Experiments were carried out at 5 Torr (6.7 mbar) total pressure, except at 300 K where the pressure was varied over the range 2-5 Torr (2.7-6.7 mbar), with no effect on the measured rate coefficient. Rate coefficients were also measured for the reactions of HO radials with CD$_3$C(O)OD (263-323 K) and CD$_3$C(O)OH (300 K).

(d) Carried out at total pressures of 50 and 100 Torr (67 and 133 mbar) of Ar or N$_2$ diluent.

(e) HO radicals were generated from the photolysis of CH$_3$ONO in air at 760 Torr (1.013 bar) pressure in a 300 L Teflon chamber. The concentrations of acetic acid and methanol (the

reference compound) during the experiments were measured by GC. Corrections were made for the presence of acetic acid dimer, which was assumed to be unreactive towards HO radicals based on the data of Singleton et al. (1989). The measured rate coefficient ratio of k(HO + CH$_3$C(O)OH)/k(HO + CH$_3$OH) = 0.73 ± 0.05 is placed on an absolute basis using a rate coefficient of k(HO + CH$_3$OH) = 8.9×10^{-13} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation). Formation yields of CO$_2$ were measured from the HO + CH$_3$C(O)OH (78 ± 13%) and HO + CH$_3$C(O)OD (36 ± 7%) reactions using CRDS.

Preferred Values

$k = 6.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.0 \times 10^{-14}$ exp(850/T) cm^3 molecule^{-1} s^{-1} over the temperature range 220-300 K.

Reliability
Δlog k = ± 0.10 at 298 K.
Δ(E/R) = ± 250 K.

*Comments on Preferred Values*

At room temperature, the rate coefficients of Dagaut et al. (1988), Singleton et al. (1989), Butkovskaya et al. (2004), Vimal and Stevens (2006), Crunaire et al. (2006), Khamaganov et al. (2006) and Huang et al. (2009) are in reasonable agreement. However, the measured temperature dependencies disagree significantly. Dagaut et al. (1988) observed the rate coefficient to increase with increasing temperature, while Singleton et al. (1989), Butkovskaya et al. (2004), Vimal and Stevens (2006), Khamaganov et al. (2006) and Huang et al. (2009) observed the rate coefficient to decrease with increasing temperature up to ~550 K. Above ~550 K, Khamaganov et al. (2006) observed the rate coefficient to increase rapidly with increasing temperature. While the rate coefficients measured by Singleton et al. (1989), Vimal and Stevens (2006), Khamaganov et al. (2006) and Huang et al. (2009) all decrease with increasing temperature over the range 296-446 K, the rate coefficients of Khamaganov et al (2006) are higher than those of Singleton et al. (1989), which in turn are higher than those of Vimal and Stevens (2006) and Huang et al. (2009). The three-parameter expression $k = CT^2$ exp(-D/T) was fitted to the rate coefficients of Butkovskaya et al. (2004), Vimal and Stevens (2006), Crunaire et al. (2006) and Huang et al. (2009), and those of Singleton et al. (1989) and Khamaganov et al. (2006) at temperatures <400 K, resulting in $k = 8.40 \times 10^{-20}$ T^2 exp(1356/T) cm^3 molecule^{-1} s^{-1} over the temperature range 229-399 K. Fitting only rate coefficients measured at ≤350 K or ≤300 K resulted in very similar fits. The preferred Arrhenius expression, $k = A$ exp(-B/T), is centered at 255 K and is derived from the three-parameter equation with $A = C$ e^2 T^2 and $B = D + 2T$. The three-parameter expression $k = 8.40 \times 10^{-20}$ T^2 exp(1356/T) cm^3 molecule^{-1} s^{-1} results in rate coefficients which are 11-15% lower over the temperature range 229-446 K than those calculated from the rate expression presented by Butkovskaya et al. (2004) from combination of their data and those of Singleton et al. (1989), of $k = 2.45 \times 10^{-16}$ (T/298)$^{5.24}$ exp(2358/T) cm^3 molecule^{-1} s^{-1}.

The rate coefficients of Singleton et al. (1989) and Vimal and Stevens (2006) for the reactions of the HO radical with CH$_3$C(O)OH, CD$_3$C(O)OH and CD$_3$C(O)OD indicate that at room temperature the major reaction channel involves overall H-atom abstraction from the OH bond [channel (2)]:

$$HO + CH_3C(O)OH \rightarrow H_2O + CH_3C(O)O$$
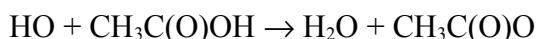
This is confirmed by the measured CO$_2$ yields, of 64 ± 17% over the temperature range 249-298 K (Butkovskaya et al. (2004), 64 ± 14% at 290 K (De Smedt et al., 2005) and 78 ± 13% at 296 ± 2 K (Crunaire et al., 2006), with the CO$_2$ arising from decomposition of the CH$_3$C(O)O radical:
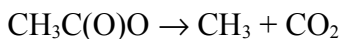
$$CH_3C(O)O \rightarrow CH_3 + CO_2$$

The lower CO_2 yield from the HO + $CH_3C(O)OD$ reaction (36 ± 7%) measured by Crunaire et al. (2006) is consistent with the significant deuterium isotope effect of k(HO + $CD_3C(O)OH$)/k(HO + $CD_3C(O)OD$) = 3.4 (Singleton et al., 1989) and 7.1 (Vimal and Stevens, 2006). Hence it appears that k_2/k ~0.7 over the temperature range 250-300 K (Butkovskaya et al., 2004; De Smedt et al., 2005; Crunaire et al., 2006).

References

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