IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC30

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This data sheet updated: 12th December 2007 (with no revision of the preferred values).

$HO + CH_3OCH_3 \rightarrow H_2O + CH_3OCH_2$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.29 \times 10^{-11} \exp[-(388 \pm 151)/T]$	299-424	Perry et al., 1977	FP-RF
$(3.50 \pm 0.35) \times 10^{-12}$	299		
$1.04 \times 10^{-11} \exp[-(372 \pm 34)/T]$	295-442	Tully and Droege, 1987	PLP-LIF
$(2.95 \pm 0.12) \times 10^{-12}$	295		
$6.7 \times 10^{-12} \exp[-(300 \pm 70)/T]$	240-440	Wallington et al., 1988	FP-RF
$(2.49 \pm 0.22) \times 10^{-12}$	296		
$(2.35 \pm 0.24) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$6.38 \times 10^{-12} \exp[-(234 \pm 34)/T]$	230-372	Mellouki et al., 1995	PLP-LIF
$(2.82 \pm 0.21) \times 10^{-12}$	295		
$3.39 \times 10^{-24} T^{4.11} \exp[(1221 \pm 252)/T]$	295-650	Arif et al., 1997	PLP-LIF
$(2.95 \pm 0.21) \times 10^{-12}$	295		
$3.02 \times 10^{-20} T^{2.85} \exp[(618 \pm 13)/T]$	295-618	Bonard et al., 2002	PLP-LIF
$(2.67 \pm 0.07) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(2.11 \pm 0.21) \times 10^{-12}$	295 ± 3	Wallington et al., 1989	RR (a)
$(2.97 \pm 0.66) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
2.41×10^{-12}	263	DeMore and Bayes, 1999	RR (c,d)
2.47×10^{-12}	273		
2.70×10^{-12}	293		
2.72×10^{-12}	298		
3.03×10^{-12}	313		
3.23×10^{-12}	333		
3.39×10^{-12}	351		
3.04×10^{-12}	295	DeMore and Bayes, 1999	RR (c,e)
3.25×10^{-12}	305		
3.16×10^{-12}	318		
3.42×10^{-12}	328		
3.81×10^{-12}	336		
3.62×10^{-12}	345		
3.86×10^{-12}	364		
3.18×10^{-12}	306	DeMore and Bayes, 1999	RR (c,f)
3.33×10^{-12}	324		
3.62×10^{-12}	351		
3.82×10^{-12}	361		

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. The concentrations of dimethyl ether and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(CH_3OCH_3)/k(n\text{-butane}) = 0.918 \pm 0.090$ is placed on an absolute basis by using a rate coefficient of $k(n\text{-butane}) = 2.30 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at atmospheric pressure. The concentrations of dimethyl ether and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(CH_3OCH_3)/k$(cyclohexane) is placed on an absolute basis by use of a rate coefficient of k(cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of O_3 at 254 nm in the presence of water vapor. The concentrations of dimethyl ether and the reference compound were measured by GC.

(d) Relative to k(HO + *n*-butane). The measured rate coefficient ratios k(HO + dimethyl ether)/k(HO + *n*-butane) are placed on an absolute basis by use of a rate coefficient of k(HO + *n*-butane) = $1.81 \times 10^{-17} T^2 \exp(114/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(e) Relative to k(HO + *n*-pentane). The measured rate coefficient ratios k(HO + dimethyl ether)/k(HO + *n*-pentane) are placed on an absolute basis by use of a rate coefficient of k(HO + *n*-pentane) = $2.52 \times 10^{-17} T^2 \exp(158/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(f) Relative to k(HO + cyclohexane). The measured rate coefficient ratios k(HO + dimethyl ether)/k(HO + cyclohexane) are placed on an absolute basis by use of a rate coefficient of k(HO + cyclohexane) = $3.26 \times 10^{-17} T^2 \exp(262/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

Preferred Values

$k = 2.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.7 \times 10^{-12} \exp(-215/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The reported room temperature absolute (Perry et al., 1977; Tully and Droege, 1987; Wallington et al., 1988; Nelson et al., 1990; Mellouki et al., 1995; Arif et al., 1997; Bonard et al., 2002) and relative (Nelson et al., 1990; Wallington et al., 1989; DeMore and Bayes, 1999) rate coefficients exhibit appreciable scatter, covering a range of a factor of 1.6. The measured temperature dependencies (Perry et al., 1977; Tully and Droege, 1987; Wallington et al., 1988; Mellouki et al., 1995; Arif et al., 1997; Bonard et al., 2002; Bonard et al., 2002; Wallington et al, 1989) are in reasonable agreement. The preferred values are based on the absolute rate coefficient studies of Tully and Droege (1987), Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002), the rate coefficients of which are in good agreement and which are between those of the other two absolute temperature-dependent studies of Perry et al. (1977) and Wallington et al. (1988).

Because Arrhenius plots of the data of Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002) show curvature, the rate coefficients of Tully and Droege (1987), Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002) have been fitted to the expression $k = CT^2 \exp(-D/T)$, resulting in $k = 1.14 \times 10^{-17} T^2 \exp(303/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-650 K. The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered at 260 K and is derived from the three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The rate coefficients determined by DeMore and Bayes

(1999) relative to that for the reaction of HO radicals with *n*-butane are in excellent agreement with the recommendation; however the rate coefficients determined by DeMore and Bayes (1999) relative to those for the reactions of HO radicals with *n*-pentane and cyclohexane are uniformly ~10% higher than the preferred values.

The significant deuterium isotope effect observed by Tully and Droege (1987) indicates that reaction proceeds by initial H-atom abstraction.

References

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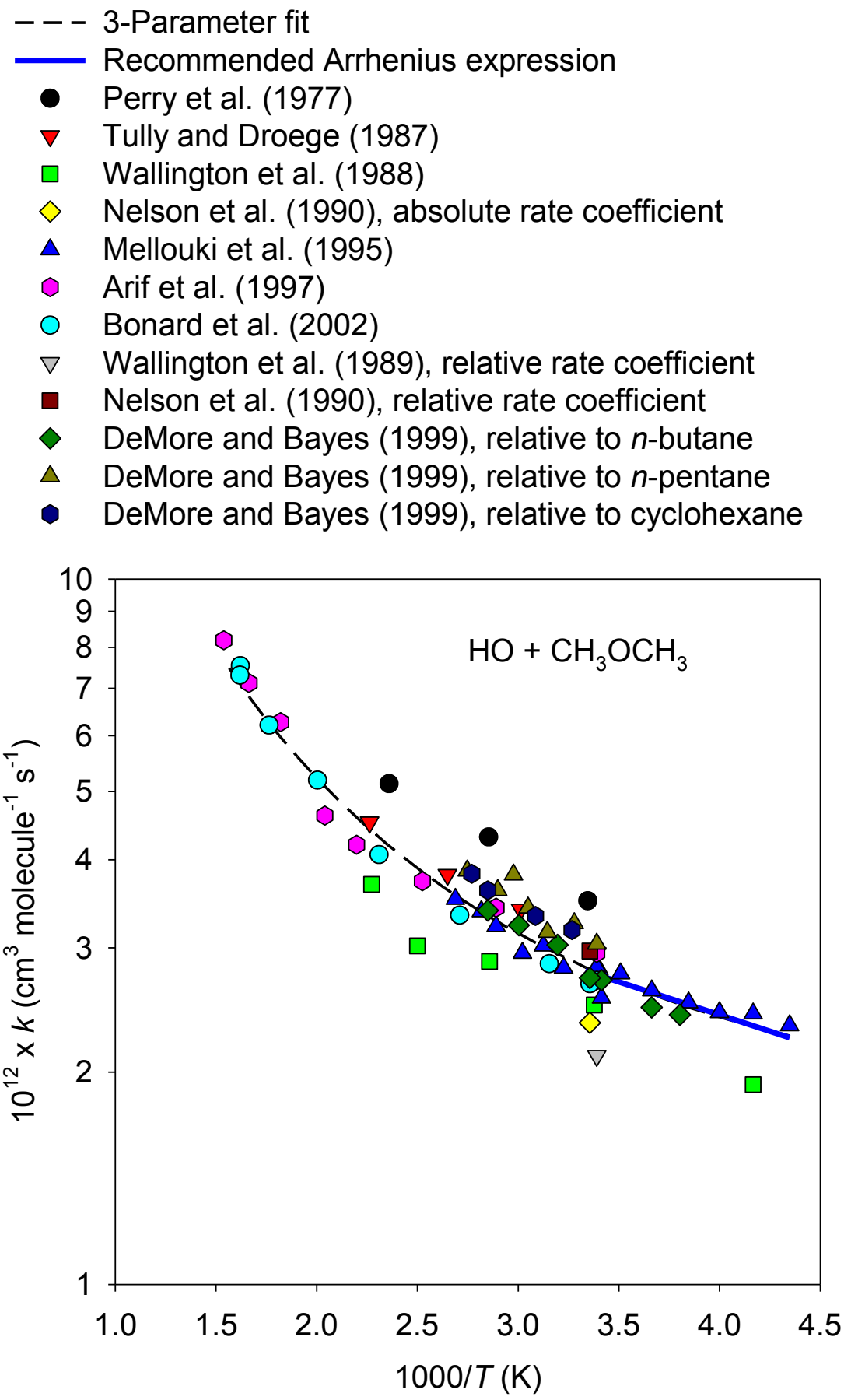
3-Parameter fit
Recommended Arrhenius expression
Perry et al. (1977)
Tully and Droege (1987)
Wallington et al. (1988)
Nelson et al. (1990), absolute rate coefficient
Mellouki et al. (1995)
Arif et al. (1997)
Bonard et al. (2002)
Wallington et al. (1989), relative rate coefficient
Nelson et al. (1990), relative rate coefficient
DeMore and Bayes (1999), relative to n-butane
DeMore and Bayes (1999), relative to n-pentane
DeMore and Bayes (1999), relative to cyclohexane
HO + CH3OCH3
10^12 x k (cm^3 molecule^-1 s^-1)
1000/T (K)
10
9
8
7
6
5
4
3
2
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5