IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC20

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

HO + $CH_3C(O)CH_2CH_3$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.3 \times 10^{-12} \exp[-(170 \pm 120)/T]$	240-440	Wallington and Kurylo, 1987	FP-RF
$(1.15 \pm 0.10) \times 10^{-12}$	296		
$1.51 \times 10^{-12} \exp[-(60 \pm 61)/T]$	243-372	Le Calvé et al., 1998	PLP-LIF
$(1.19 \pm 0.18) \times 10^{-12}$	298		
$1.35 \times 10^{-12} \exp[-(78 \pm 52)/T]$	228-388	Jiménez et al., 2005	PLP-LIF
$(1.04 \pm 0.07) \times 10^{-12}$	298		
$3.84 \times 10^{-24} T^4 \exp[(1038 \pm 11)/T]$	213-598	Carr et al., 2008	PLP-LIF
$(1.06 \pm 0.06) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(3.4 \pm 1.0) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (a)
2.74×10^{-12}	300	Cox et al., 1980	RR (b)
$(9.5 \pm 0.9) \times 10^{-13}$	295 ± 2	Cox et al., 1981	RR (b)
$(9.1 \pm 1.6) \times 10^{-13}$	297	Edney et al., 1986	RR (c)

Comments

(a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures, and the concentrations of 2-butanone and 2-methylpropene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanone)/k(HO + 2-methylpropene) = 0.07 (±30%) is placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of 2-butanone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratios k(HO + 2-butanone)/k(HO + ethene) are placed on an absolute basis by use of rate coefficients at atmospheric pressure of k(HO + ethene) = 8.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and 8.65×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson, 1997).

(c) HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of 2-butanone and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanone)/k(HO + propane) is placed on an absolute basis by use of a rate coefficient of k(HO + propane) = 1.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 297 K (IUPAC, 2007).

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5 \times 10^{-12} \exp(-90/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

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

Comments on Preferred Values

The measured rate coefficients exhibit a significant amount of scatter, ranging from $\sim 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} to $\sim 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. The absolute rate coefficients of Wallington and Kurylo (1987) and Le Calvé et al. (1998) are higher than those of Jiménez et al. (2005) and Carr et al. (2008), and this difference becomes more pronounced at lower temperatures (<295 K). Photolysis of 2-butanone may have contributed to the measured 2-butanone loss rates in the relative rate studies of Winer et al. (1976) and Cox et al. (1980). The rate coefficients of Wallington et al. (1987), Le Calvé et al. (1998) and Carr et al. (2008) suggest curvature in the Arrhenius plot. An un-weighted least-squares analysis of the absolute rate coefficients of Wallington et al. (1987), Le Calvé et al. (1998), Jiménez et al. (2005) and Carr et al. (2008), using the three-parameter expression $k = CT^2 \exp(-D/T)$, results in $k = 3.28 \times 10^{-18} T^2 \exp(402/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213-598 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 245 K and is derived from the above three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.

Cox et al. (1981) observed acetaldehyde as a product of the HO radical reaction with 2-butanone, with a formation yield of 0.62 ± 0.02. Acetaldehyde is expected to arise from 2-butanone after H-atom abstraction from the CH_2 group, and hence the fraction of the overall HO radical reaction with 2-butanone proceeding via

$$HO + CH_3C(O)CH_2CH_3 \rightarrow H_2O + CH_3C(O)CHCH_3$$

is ~0.62.

References

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.

Carr, S. A., Baeza-Romero, M. T., Blitz, M. A., Price, B. J. S. and Seakins, P. W.: Int. J. Chem. Kinet., 40, 504, 2008.

Cox, R. A., Derwent, R. G. and Williams, M. R.: Environ. Sci. Technol., 14, 57, 1980.

Cox, R. A., Patrick, K. F. and Chant, S. A.: Environ. Sci. Technol., 15, 587, 1981.

Edney, E. O., Kleindienst, R. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.

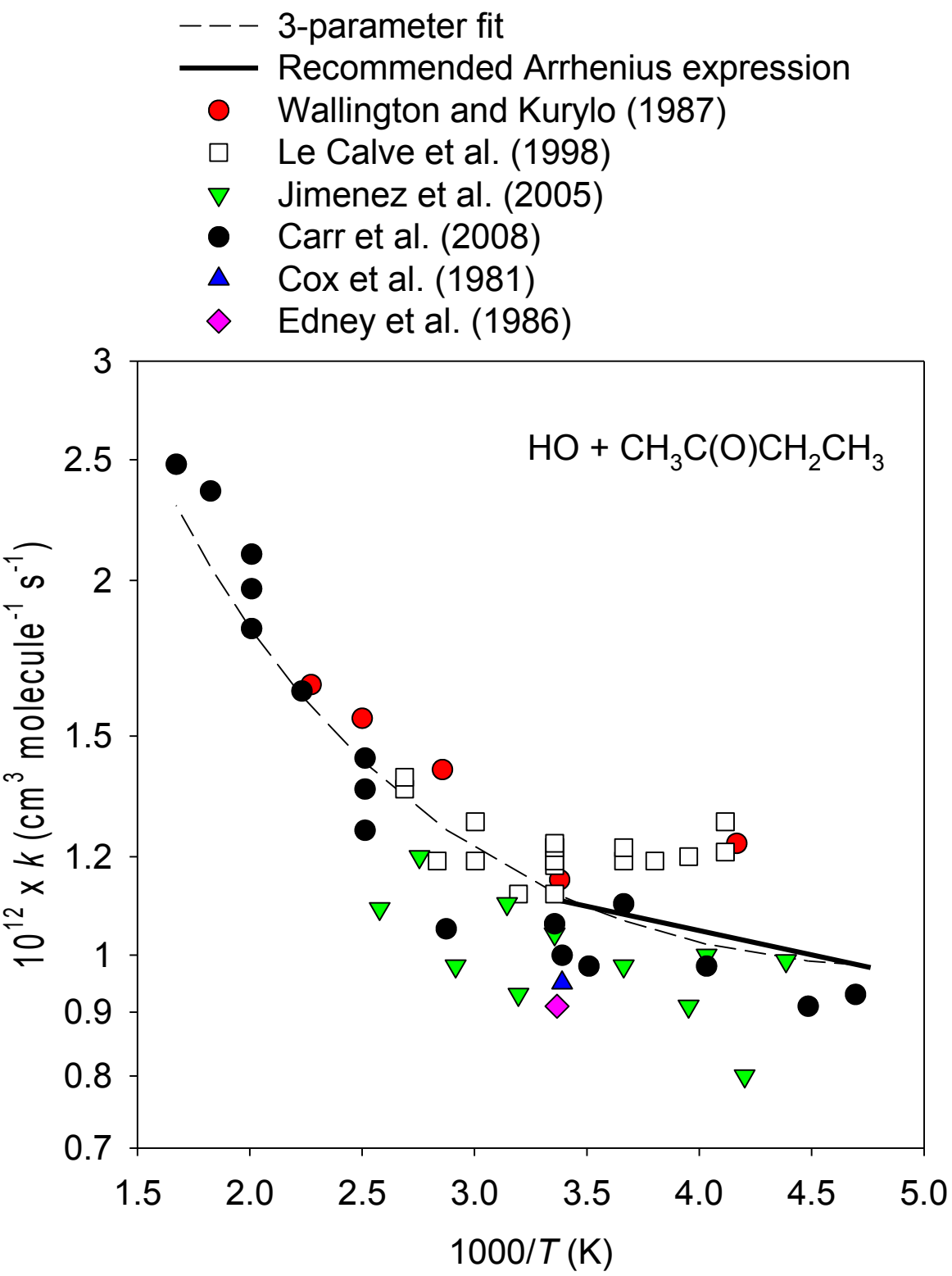
IUPAC: http://iupac.pole-ether.fr, 2013.

Jiménez, E., Ballesteros, B., Martínez, E. and Albaladejo, J.: Environ. Sci. Technol., 39, 814, 2005.

Le Calvé, S., Hitier, D., Le Bras, G. and Mellouki, A.: J. Phys. Chem. A, 102, 4579, 1998.

Wallington, T. J. and Kurylo, M. J.: J. Phys. Chem., 91, 5050, 1987.

Winer, A. M., Lloyd, A. C., Darnall, K. R. and Pitts Jr., J. N.: J. Phys. Chem., 80, 1635, 1976.


3-parameter fit
Recommended Arrhenius expression
Wallington and Kurylo (1987)
Le Calve et al. (1998)
Jimenez et al. (2005)
Carr et al. (2008)
Cox et al. (1981)
Edney et al. (1986)
HO + CH3C(O)CH2CH3
10^12 x k (cm^3 molecule^-1 s^-1)
1000/T (K)
3
2.5
2
1.5
1.2
1
0.9
0.8
0.7
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0