IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC6

This data sheet updated: 4th June 2013 (with no revision of preferred values).

$$HO + C_3H_8 \rightarrow H_2O + CH_3CH_2CH_2 \quad (1)$$
$$\rightarrow H_2O + CH_3CHCH_3 \quad (2)$$

$\Delta H°(1) = -73.7$ kJ·mol^{-1}
$\Delta H°(2) = -87.9$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.62 \pm 0.67) \times 10^{-11}$	1220±15	Bott and Cohen, 1984	SH-RA
$(2.19 \pm 0.60) \times 10^{-11}$	1074	Smith et al., 1985	LH-LIF
$(1.20 \pm 0.18) \times 10^{-12}$	295 ± 2	Baulch, Campbell, and Saunders 1985	DF-RF
$1.04 \times 10^{-16}\ T^{1.72} \exp(-145/T)$	293-854	Droege and Tully, 1986	PLP-LIF
$(1.10 \pm 0.04) \times 10^{-12}$	293		
$(1.21 \pm 0.10) \times 10^{-12}$	297 ± 2	Abbatt, Demerjian, and Anderson, 1990	DF-LIF
$(1.22 \pm 0.08) \times 10^{-12}$	298	Mac Leod et al., 1990	PLP-LIF
$9.81 \times 10^{-12} \exp[-(650 \pm 30)/T]$	233-363	Mellouki et al., 1994	PLP-LIF
$(1.05 \pm 0.09) \times 10^{-12}$	295		
$1.01 \times 10^{-11} \exp[-(657 \pm 46)/T]$	233-376	Talukdar et al., 1994	PLP-LIF
$(1.11 \pm 0.04) \times 10^{-12}$	298		
$(1.09 \pm 0.03) \times 10^{-12}$	300	Donahue, Anderson, and Demerjian, 1998	DF-LIF
$(1.37 \pm 0.04) \times 10^{-12}$	325		
$(1.46 \pm 0.04) \times 10^{-12}$	340		
$(1.60 \pm 0.09) \times 10^{-12}$	360		
$(1.85 \pm 0.06) \times 10^{-12}$	375		
$(1.83 \pm 0.10) \times 10^{-12}$	390		
$(3.626 \pm 0.247) \times 10^{-13}$	190	Clarke et al., 1998	DF-LIF
$(4.136 \pm 0.127) \times 10^{-13}$	200		
$(4.864 \pm 0.095) \times 10^{-13}$	213		
$(5.602 \pm 0.063) \times 10^{-13}$	225		
$(6.475 \pm 0.053) \times 10^{-13}$	238		
$(7.532 \pm 0.051) \times 10^{-13}$	250		
$(8.691 \pm 0.147) \times 10^{-13}$	265		
$(1.129 \pm 0.0159) \times 10^{-12}$	295		
$(1.276 \pm 0.0182) \times 10^{-12}$	310		
$(1.356 \pm 0.0140) \times 10^{-12}$	325		
$(1.480 \pm 0.0136) \times 10^{-12}$	340		
$(1.640 \pm 0.0229) \times 10^{-12}$	360		
$(1.15 \pm 0.1) \times 10^{-12}$	298	Carl and Crowley, 2001	PLP-RF
$(1.17 \pm 0.1) \times 10^{-12}$	298		
$5.81 \times 10^{-17}\ T^{1.83} \exp(-167/T)$	210-480	Kozlov et al., 2003	FP-RF

$(1.13 \pm 0.02) \times 10^{-12}$	298		
1.04×10^{-12}	296	Amedro et al., 2012	PLP-LIF/FAGE (a)

Comments

(a) FAGE setup permitting measurement of OH and HO_2 in a flow system at 1 bar, with detection limit of HO approx. 1×10^6 molecules cm^{-3}.

Preferred Values

$k = 1.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.
$k = 7.6 \times 10^{-12} \exp(-585/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200-300 K.

Reliability

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

Comments on Preferred Values

The absolute rate coefficient data of Bott and Cohen (1984), Smith et al. (1985), Droege and Tully (1986), Abbatt et al. (1990), Mac Leod et al. (1990), Mellouki et al. (1994), Talukdar et al. (1994), Donahue et al. (1998) and Clarke et al. (1998) were used to derive the preferred value. These data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.65 \times 10^{-17} T^2 \exp(-87/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 190-1220 K. The rate coefficients recently measured by Kozlov et al (2003) are in agreement with the preferred value to within 5% over the entire temperature range studied (210-480 K). The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K, and is derived from the three-parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The preferred Arrhenius expression predicts a rate coefficient at 190 K which is within 4% of that measured by Clarke et al. (1998). The relative rate coefficients of Atkinson et al. (1982), Baulch et al. (1983), Edney et al. (1986), Nielsen et al. (1991), Finlayson-Pitts et al. (1993) and DeMore and Bayes (199) are in good agreement with the recommended expression, as are the absolute rate coefficients of Tully et al. (1983) (judged to be superseded by the study of Droege and Tully, 1986), Baulch et al. (1985), Schiffman et al. (1991) and Carl and Crowley (2001).

Droege and Tully[4] also measured rate coefficients for the reaction of the HO radical with fully and partially deuterated propanes, and derived a value of $k_1/k_2 = 226 T^{-0.64} \exp(-816/T)$, leading to $k_1 = 3.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and $k_2 = 8.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

References

Abbatt, J. P. D., Demerjian, K. L. and Anderson, J. G.: J. Phys. Chem., 94, 4566, 1990.

Atkinson, R., Aschmann, S. M., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 14, 781, 1982.

Baulch, D. L., Campbell, I. M. and Saunders, S. M.: J. Chem. Soc. Faraday Trans. 1, 81, 259, 1985.

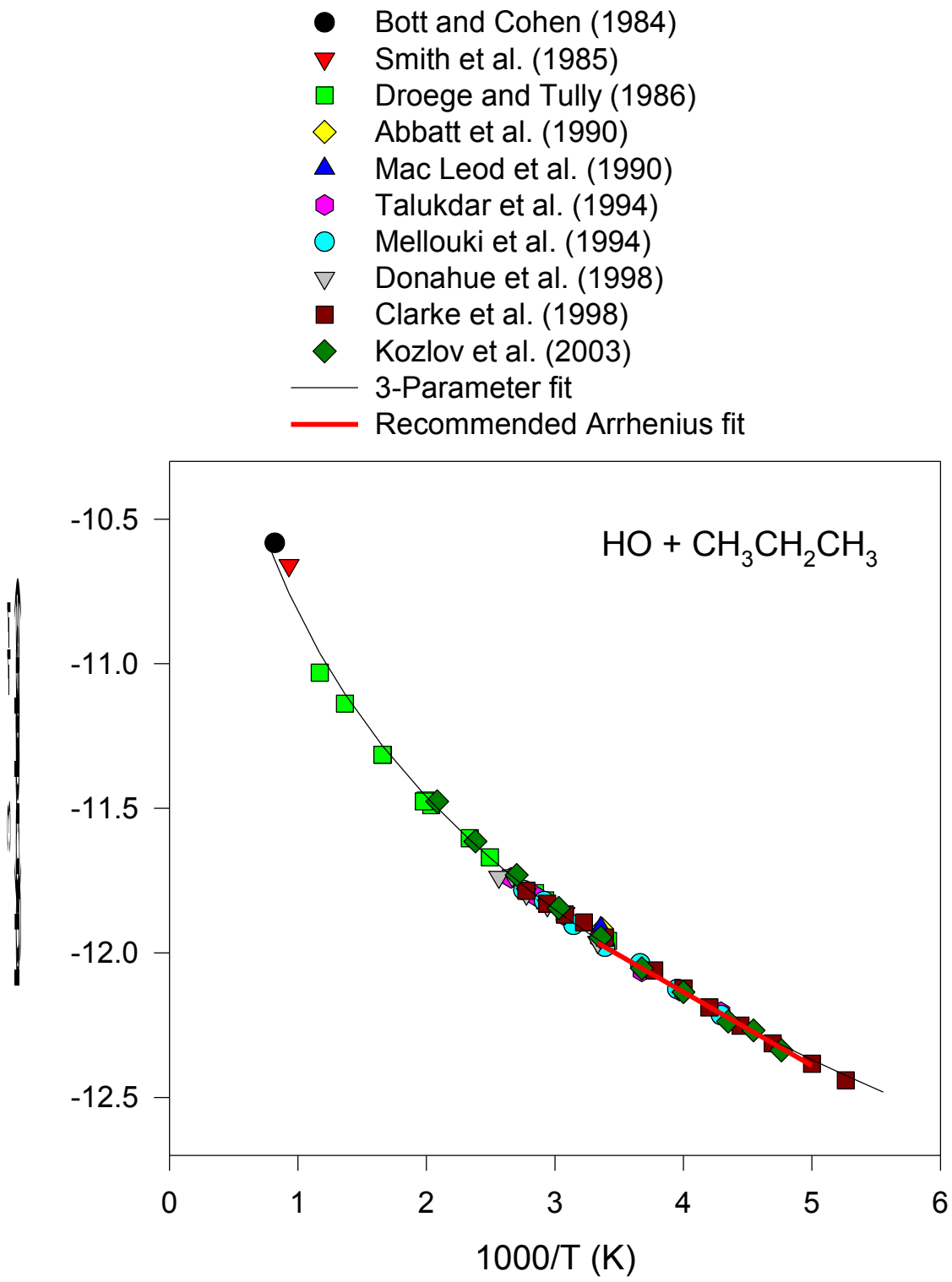
Baulch, D. L., Craven, R. J. B., Din, M., Drysdale, D. D., Grant, S., Richardson, D. J., Walker, A. and Watling, G.: J. Chem. Soc., Faraday Trans. 1, 79, 689, 1983)

Bott, J. F. and Cohen, N.: Int. J. Chem. Kinet., 16, 1557, 1984.

Carl, S. A. and Crowley, J. N.: Atmos. Chem. Phys., 1, 1, 2001)

Clarke, J. S., Kroll, J. H., Donahue, N. M. and Anderson, J. G.: J. Phys. Chem. A, 102, 9847, 1998.

DeMore, W. B. and Bayes, K. D.: J. Phys. Chem. A, 103, 2649, 1999.
Donahue, N. M., Anderson, J. G. and Demerjian, K. L.: J. Phys. Chem. A., 102, 3121, 1998.
Droege, A. T. and Tully, F. P.: J. Phys. Chem., 90, 1949, 1986.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
Finlayson-Pitts, B. J., Hernandez, S. K. and Berko, H. N.: J. Phys. Chem., 97, 1172, 1993.
Kozlov, S. N., Orkin, V. L., Huie, R. E. and Kurylo, M. J.: J. Phys. Chem. A, 107, 1333, 2003.
Mac Leod, H., Balestra, C., Jourdain, J. L., Laverdet, G. and Le Bras, G.: Int. J. Chem. Kinet., 22, 1167, 1990.
Mellouki, A., Téton, S., Laverdet, G., Quilgars, A. and Le Bras, G.: J. Chim. Phys., 91, 473, 1994.
Nielsen, O. J., Sidebottom, H. W., Donlon, M. and Treacy, J.: Int. J. Chem. Kinet., 23, 1095, 1991.
Schiffman, A., Nelson, Jr., D. D., Robinson, M. S. and Nesbitt, D. J.: J. Phys. Chem., 95, 2629, 1991.
Smith, G. P., Fairchild, P. W., Jeffries, J. B. and Crosley, D. R.: J. Phys. Chem., 89, 1269 , 1985.
Talukdar, R. K., Mellouki, A., Gierczak, T., Barone, S., Chiang, S.-Y. and Ravishankara, A. R.: Int. J. Chem. Kinet., 26, 973, 1994.
Tully, F. P., Ravishankara, A. R. and Carr, K.: Int. J. Chem. Kinet., 15, 1111, 1983.


Bott and Cohen (1984)
Smith et al. (1985)
Droege and Tully (1986)
Abbatt et al. (1990)
Mac Leod et al. (1990)
Talukdar et al. (1994)
Mellouki et al. (1994)
Donahue et al. (1998)
Clarke et al. (1998)
Kozlov et al. (2003)
3-Parameter fit
Recommended Arrhenius fit
HO + CH3CH2CH3
-10.5
-11.0
-11.5
-12.0
-12.5
0
1
2
3
4
5
6
1000/T (K)