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$OH(X^2\Pi) + OH(X^2\Pi) \rightarrow O(^3P) + H_2O(X^1A_1)$

Thermodynamic Data

$\Delta H^o_{298} = -\ 70.3$ kJ mol^{-1} (1)

Rate Coefficient Data *k*

k / cm^3 $molecule^{-1}$ s^{-1}	T / K	Reference	Ref
Rate Coefficient Measurements			
$k = (3.2\pm0.8)\times10^{-13}\times\exp[(242)/T]$	250-580K	Wagner and Zellner, 1981	(2)
$k = (7.1\pm1)\times10^{-13}\times\exp[(210(\pm40)/T]$	233-360K	Bedjanian *et al*, 1999	(3)
$k = 2.7\times10^{-13}\times\exp[(446(\pm37)/T]$	220-320K	Sun and Li, 2004	(4)
$k = (2.7\pm0.9)\times10^{-12}$	298K	Bhang and Macdonald, 2007	(5)
+ various measurement at 300K and at higher temperatures.			
Theory			
$k = 6.19\times10^{-14}\times(T/273)^{2.62}\times\exp[944/T]$	233-2000K	Harding *et al*, 1988	(6)
Review			
$k = 1.48\times10^{-12}$	298K	Atkinson et al, 2004	(7)
$k = 6.2\times10^{-14}\times(T/298)^{2.60}\times\exp[945/T]$	200-350K	Atkinson et al, 2004	(7)

Comments

The $OH + OH \rightarrow H_2O + O$ reaction is slightly exothermic (-70.3 kJ mol^{-1}). There is several experimental determinations of this rate constant in the range 220-2000K and at various pressure (apart the $OH + OH \rightarrow H_2O + O$ reaction there is also the three body $OH + OH + M \rightarrow H_2O_2 + M$ (-210.3 kJ mol^{-1}) pressure dependant reaction). From the experimental (3) and theoretical (6,8) works, the various aspect of this reaction is well understood: in a first step there is formation, without barrier in the entrance channel, of a van der Waals complex H_2O_2 , not the stable molecule, which can evaluate through a barrier (380K) toward $H_2O + O$. The presence of the barrier explains the increase of the rate constant at high temperature. However there is also an increase between 330 K and 220K resulting in negative temperature dependence due to an increase of the tunneling effect with decreasing of the temperature (the lifetime of the H_2O_2 adducts increase more quickly than the width of the barrier). The various measurement can been show on this Figure from Bedjanian *et al* (3):

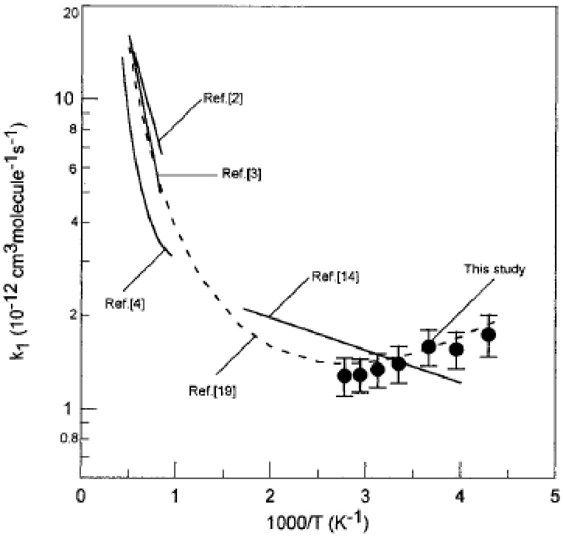

Figure 8. Reaction $OH + OH \rightarrow O + H_2O$ (1): summary of results from temperature dependence studies of the reaction rate constant.

Atkinson et al (7) have fitted the experimental data between 200 and 350 K: $k=6.2\times10^{-14}\times(T/298)^{2.60}\times\exp(945(\pm250)/T)$ with $\Delta\log(k) = \pm0.15$ at 298 K (confidence interval of 95%)(Atmos. Chem. Phys. 4 (2004) p 1514) equivalent to $F_{298} = (10^{\Delta\log(k)})^{0.5} = 1.2$ (in KIDA we use 1σ uncertainty) and $g = 0.5\times\Delta E/R = 125$. However, this expression can’t be extrapolated at very low temperature (it’s give $k(10K)=1.2\times10^{+24}$!!!). The rate constant is certainly higher at low temperature as the lifetime of the adduct is certainly very long at very low temperature. To have a precise value, we need to do additional calculations. However the high pressure limit of the rate constant for the $OH + OH \rightarrow H_2O_2$ ($(2.6 \pm 0.8)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, practically independent of temperature.(9,10)) can be considered as an upper limit for the $OH + OH \rightarrow O + H_2O$.

Preferred Values

T=200-350K :

$k(T) = 6.2\times10^{-14}\times(T/273)^{2.62}\times\exp(945/T)$ cm^3 $molecule^{-1}$ s^{-1}

Reliability

F=1.2   g = 125

g defined by$F(T)=F(298)*\exp(-g|1/T-1/298|)$

($F = 10^{\Delta\log(k)}$ (95%confidence) or $F_{298} = (10^{\Delta\log(k)})^{0.5}$ (1σ uncertainty))

10K:

$k(10K) = 1.0\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}

Reliability

F=3

Comments on Preferred Values

In the 200-350 K range there various coherent experimental measurements as well as theoretical study(6).

Even if there is no measurement at temperature below 200K, as there is no barrier for the H_2O_2 van der Waals complex formation and the tunneling more efficient with a lower energy in this complex, the rate constant is certainly higher than 2.0×10^{-12} $cm^3.molecule^{-1}.s^{-1}$. The high pressure limit of the rate constant for the $OH + OH \rightarrow H_2O_2$ ($(2.6 \pm 0.8)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) can be considered as an upper limit for the $OH + OH \rightarrow O + H_2O$.

References

(1) DL Baulch, CT Bowman, CJ Cobos, RA Cox, T Just, JA Kerr, MJ Pilling, D Stocker, J Troe, W Tsang, RW Walker, J Warnatz: J. Phys. Chem. Ref. Data 34 (2005) 757-1397.

(2) G Wagner, R Zellner: Ber. Bunsenges. Phys. Chem. 85 (1981) 1122.

(3) Y Bedjanian, GL Bras, G Poulet: J. Phys. Chem. A 103 (1999) 7017.

(4) H Sun, Z Li: Chem. Phys. Lett. 399 (2004) 33-38.

(5) M-K Bahng, RG Macdonald: J. Phys. Chem. A 111 (2007) 3850-61.

(6) LB Harding, AF Wagner: 22nd International Symposium on Combustion (1988) 983.

(7) R Atkinson, DL Baulch, RA Cox, JN Crowley, RF Hampson, RG Hynes, ME Jenkin, MJ Rossi, J Troe: Atmos. Chem. Phys. 4 (2004) 1461 - 738.

(8) SP Karkach, VI Osherov: J. Chem. Phys. 110 (1999) 11918.

(9) R Forster, M Frost, D Fulle, HF Hamann, H. Hippler, A Schlepegrell, J Troe: J. Chem. Phys. 103 (1995) 2949.

(10) D Fulle, HF Hamann, H Hippler, J Troe: J. Chem. Phys. 105 (1996) 1001.