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$O(^3P) + OH(X^2\Pi) \rightarrow H(^2S) + O_2(X^3\Sigma^-_g)$

Thermodynamic Data

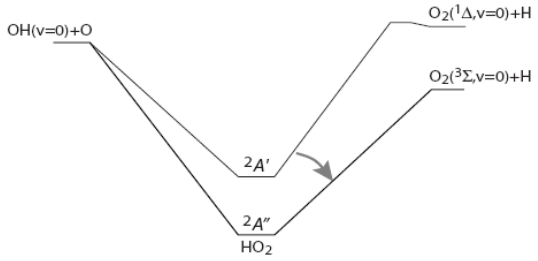
$\Delta H^o_{298} = -68.4$ kJ mol^{-1} (1)

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Ref
Rate Coefficient Measurements			
$k = (3.85\pm0.13)\times10^{-11}\times(T/298)^{-(0.50\pm0.12)}$	250-515K	Howard and Smith, 1980-81	(2,3)
$k = (3.0\pm1.15)\times10^{-11}\times(T/298)^{-(0.36\pm0.07)}$	221-499	Lewis and Watson, 1980	(4)
$(3.1\pm0.5)\times10^{-11}$		Brune et al, 1983	(5)
$k = f_{el}\times3.7\times10^{-11}\times(T/298)^{-0.24}$	158-294K	Smith and Stewart, 1994	(6)
$f_{el} = 2/[\{5 + 3\exp(-228/T) + \exp(-326/T)\}\{2 + 2\exp(-205/T)]$			(7)
$(3.17\pm0.51)\times10^{-11}$	295	Robertson and Smith, 2002	(8)
$k = 1.8\times10^{-11}\times(T/298)^{-0.32}\exp(177/T)$	136-377	Robertson and Smith, 2006	(9)
$(3.5\pm1.0)\times10^{-11}$	39-142K	Carty et al, 2006	(10)
Review			
$k = 2.4\times10^{-11}\times\exp((110\pm50)/T)$	150-500K	Atkinson et al, 2004	(11)
Theory			
No expressions are given for theoretical calculations. The range of the calculations was in general quite wide (10-5000K).			
7×10^{-11}	10K	Harding *et al*, 2000	(12)
$0.026\times(T/1000)^{1.47} + 1.92\times(1000/T)^{0.46}$	300-5000K	Troe and Ushakov, 2001	(13)
5.4×10^{-13}	10K	Xu *et al*, 2007	(14)
7.8×10^{-12}	10K	Lin *et al*, 2008	(15)
4×10^{-11}	10K	Lique *et al*, 2009	(16)
4×10^{-11}	10K	Quéméner *et al*, 2009	(17)

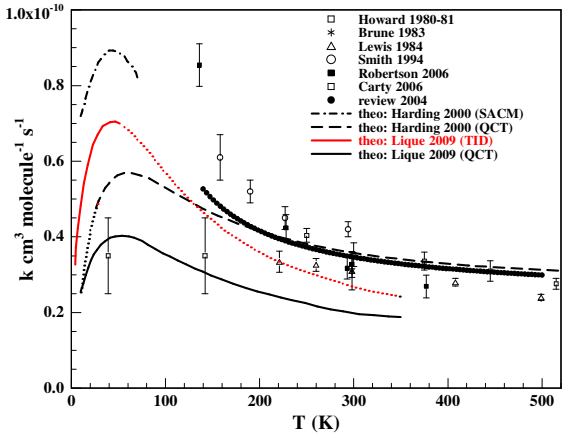
Comments

The reaction O + OH → H + O_2 is slightly exothermic (-68.4 kJ mol^{-1}). $O(^3P)$ + $OH(X^2\Pi)$ correlates with $3^2A'$ + $3^2A''$ + $3^4A'$ + $3^4A''$ surfaces. Only two surfaces ($^2A''$ + $^4A''$) correlate with the reaction products $H(^2S)$ + $O_2(X^3\Sigma^-_g)$ but the $^4A''$ surface is purely repulsive. The $^2A'$ surface, populated without barrier from O + OH, correlates only with the excited H + O_2 ($a^1\Delta_g$) product channel. So it is generally assumed that reaction only occurs over the lowest $^2A''$ surface which corresponds to the electronic ground state of the HO_2 intermediate. Nevertheless, temporary population of excited electronic states during the reaction may take place and influence the rate. (12,18,19)



The study of this reaction has attracted considerable experimental attention (2-6,8-10), and there have also been a large number

of theoretical studies using a variety of methods (12-20). The experimental rate constant is well determined between 140 K and 300K decreasing from 7×10^{-11} cm^3 molecule^{-1} s^{-1} at 140 K to 3×10^{-11} cm^3 molecule^{-1} s^{-1} at 300K. Rate constants of the reverse reaction H + O_2 → O + OH combined with calculated equilibrium constants extend the available temperature range up to about 5000 K. Between 40 K and 140 K the reaction has been studied in a CRESU (*Cinétique de Réaction en Ecoulement Supersonique Uniforme*) apparatus (10) leading to a value of k = 3.5 (±1.0) 10^{-11} cm^3 molecule^{-1} s^{-1} between 39 K and 142 K. Considering the difficulty to perform rate constant measurement between atom and radical in the CRESU experiment the given uncertainties may be widely underestimated. Quasiclassical trajectory (QCT) calculations give good agreement with experiment between 300 and 3000 K (13) and between 40 and 140 K (20) but the relatively good agreement at low temperature may be fortuitous. Indeed, the problem of QCT treatments to cope with the vibrational zero-point energy can render this method unreliable near reaction thresholds and therefore unreliable at very low temperature. However, one can consider the QCT calculation of the rate constant as a lower limit at low temperature (k(10 K) > 2×10^{-11} cm^3 molecule^{-1} s^{-1}). The reaction, which proceeds through a relatively long-lived HO_2 complex, should be amenable to a statistical treatment, based on adiabatic capture considerations. However the presence of a strong dynamical bottleneck (12,13,20) has to be taken into account. The QCT calculations indicate (13) that the reaction at low temperature is completely capture-controlled without redissociation of the HO_2 intermediate. The statistical adiabatic channel model (SACM) treats the capture process on a quantum-state selected level (12,13), the adiabatic channel potential curves showing barriers because of the dynamical bottleneck. Surface-hopping forward and backward between adiabatic channel potentials on several electronic states allow the system to avoid the dynamical bottleneck to some extent. That is the reason for the marked increase of the rate constant around 50K compared to the calculation on the ground state alone. Very low rate constants (5.4×10^{-13} and 7.8×10^{-12} cm^3 molecule^{-1} s^{-1}) at low temperature have been obtained using Time Independent Wave Packet (TDWP) methods (14,15). However TDWP methods are not suitable for the low temperature regime, because at very low energies the TDWP cross section decreases in contrast to the barrierless nature of the reaction. An accurate (but using J-shifting approximations for T > 50 K) time independent (TID) quantum mechanical calculation has been applied to this reaction by Lique et al in 2009 (16) leading to value equal to 4.7×10^{-11} cm^3 molecule^{-1} s^{-1} at 10 K. Regrettably, TID investigations of the O + OH reaction are highly computationally demanding and spin-orbit coupling and electronic fine structure of O and OH as well as surface hopping dynamics between the ground and excited potentials at large O-OH distances, has not been taken in account in this study and may notably change the calculated rate constant. Among these effects, surface hopping dynamics (nonadiabatic transitions between the lowest ^{2}A' surface, populated without barrier from O + OH but correlating only with the energetically inaccessible H + O_2 ($a^1\Delta_g$) product channel, and the ^{2}A″ surface, coupled to ^{2}A' state through Renner-Teller effect) is expected to be important at low temperature (18,19) and the rate constant may be as high as 8×10^{-11} cm^3 molecule^{-1} s^{-1} at 10 K.



Preferred Values

T=150-500K (Atkinson et al, 2004 (11)):
$k(T) = 2.4\times10^{-11} \times\exp(110(\pm50)/T)$ cm^3 molecule^{-1} s^{-1}
Reliability
$F_{300} = 1.2$, g = 50
k comprised between k(T)/F and k(T)*F
g defined by $F(T)=F_{300} *\exp(g(1/T-1/300))$
With J. Phys. Chem. Ref. Data standard:
$F_{298} = 10^{\Delta\log(k)} = 1.2$ and $g = \sigma(E^{\#})$ if $\Delta\log(k)$ and $\sigma(E^{\#})$ refer to 1σ.

T = 10-50K:
$k = 4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}
Reliability
$F_{300} = 3$, g = 0

Discussion on preferred values:
Influenced by the CRESU measurements which are the lowest temperature experimental measurements (39K) and by the TID quantum values obtained in the 10-50 K range, we propose a value of 4×10^{-11} cm^3 molecule^{-1} s^{-1} over the entire 10-50 K range. We propose a wide error limits (F=3), in part because this recommendation descends below the lowest temperature measurement at 39 K, but also in view of the disagreement observed between different experimental studies at higher temperatures, and also the wide variation of the theoretical studies. It should be noted however than, even if theory has difficulties with this reaction, the various theoretical studies give a non constant rate constant value with the temperature but a maximum near 50 K, with similar shape for all the various theoretical studies. It is clear that further measurements and calculations on this reaction are needed at very low temperatures.

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) MJ Howard, IWM Smith: Chem. Phys. Lett. 69 (1980) 40-44.

(3) MJ Howard, IWM Smith: J. Chem. Soc., Faraday Trans. 77 (1981) 997-1008.

(4) RS Lewis, RT Watson: J. Phys. Chem. 84 (1980) 3495-503.

(5) WH Brune, JJ Schwab, JG Anderson: J. Phys. Chem. 87 (1983) 4503-14.

(6) IWM Smith, DWA Stewart: J. Chem. Soc. Faraday Trans. 90 (1994) 3221-27.

(7) MM Graff, AF Wagner: J. Chem. Phys. 92 (1990) 2423-39.

(8) R Robertson, GP Smith: Chem. Phys. Lett. 358 (2002) 157-62.

(9) R Robertson, GP Smith: J. Phys. Chem. A 110 (2006) 6673-79.

(10) D Carty, A Goddard, SPK Kahler, IR Sims, IWM Smith: J. Phys. Chem. A 110 (2006) 3101-09.

(11) R Atkinson, DL Baulch, RA Cox, JN Crowley, RF Hampson, RG Hynes, ME Jenkin, MJ Rossi, J Troe: Atmos. Chem. Phys. 4 (2004) 1461-736.

(12) LB Harding, AI Maergoiz, J Troe, VG Ushakov: J. Chem. Phys. 113 (2000) 11019-34.

(13) J Troe, VG Ushakov: J. Chem. Phys. 115 (2001) 3621-28.

(14) C Xu, D Xie, P Honvault, SY Lin, H Guo: J. Chem. Phys. 127 (2007) 024304-10.

(15) SY Lin, H Guo, P Honvault, C Xu, D Xie: J. Chem. Phys. 128 (2008) 014303-11.

(16) F Lique, M Jorfi, P Honvault, P Halvick, SY Lin, H Guo, DQ Xie, PJ Dagdigian, J Klos, MH Alexander: J. Chem. Phys. 131 (2009) 221104-08.

(17) G Quéméner, N Balakrishnan, BK Kendrick: Phys. Rev. A 79 (2009) 022703-11.

(18) AI Maergoiz, EE Nikitin, J Troe, VG Ushakov In: Theory of the dynamics of elementary chemical reactions, (Ed.) Maergoiz,A.I., Nikitin, E.E., Troe, J., Ushakov, V.G.Lendvay,G., NATO ASI Kluwer, Dordrecht (2004) 21-44 (2004) 21-44.

(19) A Li, D Xie, R Dawes, AW Jasper, J Ma, H Guo: J. Chem. Phys. 133 (2010) 144306-14.

(20) M Jorfi, P Honvault, P Bargueno, T Gonzalez-Lezana, P Larregaray, L Bonnet, P Halvick: J. Chem. Phys. 130 (2009) 184301-11.