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$O(^3P) + CS(X^1\Sigma) \rightarrow CO(X^1\Sigma^+) + S(^3P)$ (1)

Thermodynamic Data

$\Delta H^o_{298}(1) = - 360.71$ kJ mol^{-1} (1)

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	
Rate Coefficient Measurements			
$(2.1 \pm 0.14) \times 10^{-11}$	305	Slage *et al*, 1975	(2)
$(2.24 \pm 0.37) \times 10^{-11}$	300	Bida *et al*, 1976	(3)
$(2.09 \pm 0.22) \times 10^{-11}$	298	Dodonov *et al*, 1976	(4)
$(2.6 \pm 0.4) \times 10^{-10} \times \exp(-760/T)$	150-300	Lilenfeld and Richardson, 1977	(5)
Theory			
$1.94 \times 10^{-11} \times \exp(-231/T)$	150-1000	Gonzalez *et al*, 1996	(6)
Reviews and Evaluations			
$2.7 \times 10^{-10} \times \exp(-760/T)$	150 – 300	Atkinson *et al*, 2004	(7)

Comments

The reactants $O(^3P) + CS(X^1\Sigma)$ correlate with three adiabatic Potential Energy Surface (PES), one of $^3A'$ and two of $^3A''$. Theoretical calculations (6,8) on this system are a little bit confused. Gonzales et al found that the $^3A'$ PES always lies energetically below the $^3A''$ PES although not far away from it, nonlinear OCS transition states have been found on both surfaces and a very shallow nonlinear OCS minimum, almost not bound if the zero point vibrational energy is included, has been found on the $^3A'$ PES. On the lowest $^3A'$ PES, they found a small barrier with an energy highly dependent on the method and varying between -0.4 and 7 kcal mol^{-1}, the best estimate (PUMP4 with BSSE) being around 2 kcal mol^{-1}. However recent DFT calculation using MPWB1K functional lead to an absence of barrier.(8) The high value of the 300 K rate constant, 2×10^{-11} molecule^{-1} s^{-1} (four measurements (2-5) in good agreements but using chain reactions) is compatible with either barrier and no barrier in the entrance valley and the only single (also using chain reactions) measurement of the temperature dependence of the rate constant , leading to a 760 K barrier, (5) may be compatible with van der Waals complex and a submerged barrier. One argument in favour of the existence of the barrier in the entrance valley is the semi-empirical "rules" proposed by Smith *et al* (9). The I.E.(CS) minus E.A.(O) is equal to (11.33 - 1.46) = 9.87 eV which is well above the 'critical value' of 8.75 eV proposed to separate 'fast' low temperature reactions from 'slow' low temperature reactions (between radicals and unsaturated molecules). On the following table are summarized the value of IE(molecule)-EA(O) for various O + unsaturated reaction ($E_0^\#$ roughly estimated from rate constant T dependency) (10)

Reaction	IE(molecule)	IE-EA	≈ $E_0^\#$(K)
O + CO	14.01	12.55	1400
O + CO_2	13.78	12.32	>1200
O + C_2H_2	11.40	9.93	1600
O + CS	**11.33**	**9.87**	**760**
O + C_2H_4	10.51	9.05	500
O + C_3H_4	10.36	8.90	960
O + CS_2	10.07	8.61	650
O + C_3H_6	9.73	8.27	0

If this hypothesis is to be believed for this reaction, it would be slow at low T. So the balances of the arguments are that O + CS will be slow at 10 K. In that case there is no reason to prefer the ab-initio rate constant (6) rather the experimental one.(5)

Preferred Values

k (150-300 K) = $2.6\times10^{-10}\times\exp(-760/T)$ cm^3 molecule^{-1} s^{-1}

Reliability

F = 1.3, g = 0 over the range 150-300K

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

References

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