IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet SOx78

This data sheet last evaluated: June 2011; last change in preferred values: June 2011.

$$O(^1D) + SO_2F_2 \rightarrow O(^3P) + SO_2F_2 \quad (1)$$
$$\rightarrow \text{products} \quad (2)$$

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

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients, k			
$(1.3 \pm 0.2) \times 10^{-10}$	220-300	Dillon et al., 2008	LP-LIF/RF (a)
$9.0 \times 10^{-11} \exp[(98 \pm 41)/T]$	199-351	Zhao et al. 2010	LP-RF (b)
Relative Rate Coefficients			
$k_2 = (4.9 \pm 0.14) \times 10^{-11}$	298	Dillon et al., 2008	(c)
Branching ratios			
$k_1 / k_2 = 0.55 \pm 0.04$	225-296	Dillon et al., 2008	(a)
$k_1 / k_2 = 0.42 \exp[(73 \pm 60)/T]$	199-351	Zhao et al. 2010	(b)

Comments

(a) $O(^1D)$ ($\sim 2 \times 10^{11}$ molecule cm^{-3}) was generated in the 248 nm photolysis of O_3 in He. In LIF experiments, the kinetics of formation of OH in a competing reaction (with pentane, hexane or H_2O) was used to derive the overall rate coefficient ($k_1 + k_2$). Resonance fluorescence detection was used to derive the yield of $O(^3P)$ (relative to $O(^1D) + N_2$).

(b) $O(^1D)$ was generated in the 248 nm photolysis of O_3 in He. The kinetics of formation of $O(^3P)$ was used to derive both the overall rate coefficient ($k_1 + k_2$) and the $O(^3P)$ yield, which was measured relative to the known $O(^3P)$ yield from O_3 photolysis.

(c) O_3 photolysed at 254 nm in a 44 L quartz reactor. Depletion of SO_2F_2 and N_2O (reference reactant) were monitored in-situ by FTIR. The 298 K rate constant ratio $k(O(^1D) + SO_2F_2) / k(O(^1D) + N_2O)$ of 0.411 ± 0.012 was placed on an absolute basis using $k(O(^1D) + N_2O \rightarrow \text{products}) = 1.19 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2011).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	$8.85 \times 10^{-11} \exp(106/T)$	190-350
k_1/k	$0.47 \exp(40/T)$	190-350
Reliability		
$\Delta \log k$	± 0.15	190-350

Δ E/R	± 100	190-350
Δ k_1/k	± 0.1	190-350
Δ (E_x/R –E/R)	± 50	

Comments on Preferred Values

Both studies of the overall rate coefficient, k are in excellent agreement. The preferred, temperature dependent expression was obtained by weighted, least-squares fitting to both datasets, which results in a slight, negative activation energy. The measurements of the branching ratio for physical quenching (k_1/k) via measurements of $O(^3P)$ formation are also in good agreement, with both datasets consistent with an almost temperature independent value of 0.55 ± 0.05. The value obtained at 199 K by Zhao et al. (2010), is somewhat higher, possibly indicating an increase to lower temperatures. Fitting to both datasets results in the temperature dependence of k_1/k given in the preferred values. k_2 can be calculated from: $k_2 = k(1-k_1/k)$.

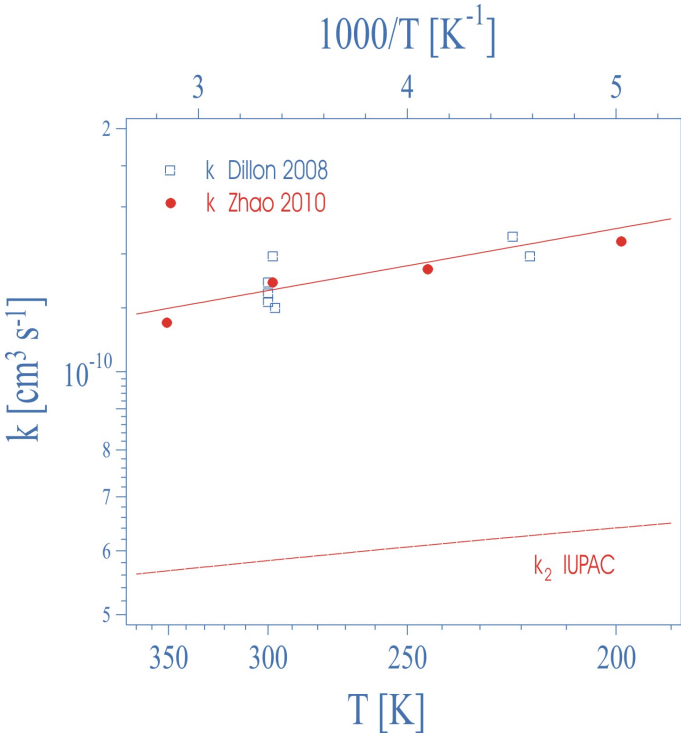
The relative rate study of Dillon et al., was sensitive only to reaction pathways which remove SO_2F_2 (i.e. k_2). The value obtained at room temperature was $k_2 = (4.9 \pm 0.14) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The value calculated from the expression for k_2 given above is 5.8 x 10^{-11} cm^3 molecule^{-1} s^{-1}, some 18 % larger. The good agreement between relative rate values of k_2 and those calculated from k and k_1 which Dillon et al., reported is due to their use of a larger rate coefficient (1.4 x 10^{-10} cm^3 molecule^{-1} s^{-1}) for the reference reaction of $O(^1D)$ with N_2O.

The products of k_2 are not well characterised, though Dillon et al report formation of F atoms at an estimated yield of 20 %.

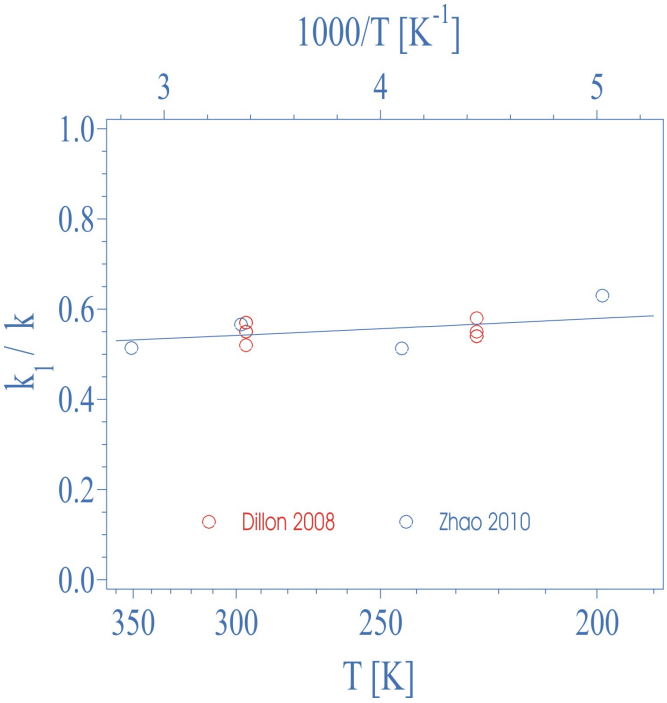
References

Dillon, T. J., Horowitz, L. and Crowley, J. N.: Atmos. Chem. Phys. 8, 1547-1557, 2008.

Zhao, Z. J., Laine, P. L., Nicovich, J. M. and Wine, P. H.: Proc. Natl. Acad. Sci. U. S. A. 107, 6610-6615, 2010.



Upper curve: Measured overal rate coefficients (k) and Arrhenius fit to both datasets. Lower curve: k_2 (calculated from preferred values of k and k_1 / k)



Measured values of k_1 / k and Arrhenius fit to both datasets.