

Author: Ian Smith (University of Cambridge, UK)



Thermodynamic Data

$$\Delta H_{298}^{\circ}(1) = -57 \text{ kJ mol}^{-1}$$

$$\Delta H_{298}^{\circ}(2) = -158 \text{ kJ mol}^{-1}$$

Thermochemical data are taken from ref. 3

Rate Coefficient Data ($k = k_1 + k_2$)

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T / K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$(8 \pm 4) \times 10^{-10}$	300	Fehsenfeld, 1976 ¹	(a)
$(12 \pm 5) \times 10^{-10}$	295 ± 5	Milligan and McEwan, 2000 ²	(b)
<i>Theoretical Evaluations</i>			
$11.9 \times 10^{-10} (T/\text{K})/300)^{-0.144}$	0 – 70	Bettens, Hansen and Collin ⁴	(c)
$9.4 \times 10^{-10} (T/\text{K})/300)^{-0.320}$	70 – 500	Bettens, Hansen and Collins ⁴	(c)
$1.14 \times 10^{-9} (T/\text{K})/300)^{-0.156} \exp(-1.41/T)$	5 – 400	Klippenstein et al., 2010 ⁵	(d)
<i>Reviews and Evaluations</i>			
$(8 \pm 4) \times 10^{-10}$	all temperatures	UMIST database	
$(8 \pm 4) \times 10^{-10}$	all temperatures	OSU website	

Comments

(a) A very short paper with few experimental details. Flowing afterglow technique: production of H_3^+ described in ref. 3, no details of how of O-atom concentration were estimated. No measurements of branching ratio.

(b) Experiment employs a SIFT technique to generate and select H_3^+ ions. O atoms from microwave discharge of O_2/He . Reaction of $\text{CH}_3^+ + \text{O}$ (which it is claimed has a well-established rate coefficient) was used to calibrate the O-atom concentrations. Error takes into account uncertainties in estimating O-atom concentrations. Branching ratios are found to be $k_1/(k_1 + k_2) = 0.7$ and $k_2/(k_1 + k_2) = 0.3$.

(c) Results of a quasiclassical trajectory study on an *ab initio* potential energy surface,⁴ provides a temperature-dependence for k . The branching ratios were calculated to be $k_1/(k_1 + k_2) = 0.94$ and $k_2/(k_1 + k_2) = 0.06$, independent of collision energy.

(d) Kinetics predicted from a combination of transition state theory, trajectory calculations and master equation analysis employing potential energy surface from high level quantum chemical calculations.

Preferred Values

$$k(298 \text{ K}) = (1.2 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(10 \text{ K}) = (1.7 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(T) = 1.14 \times 10^{-9} (T/300)^{-0.156} \exp(-1.41/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_1/(k_1 + k_2) = (0.7 \pm 0.2) \text{ and } k_2/(k_1 + k_2) = (0.3 \pm 0.2), \text{ independent of temperature.}$$

Reliability

$$\Delta \log k = \pm 0.15 ; F_0 = 1.4 ; g = 0$$

Comments on Preferred Values

Both the OSU and UMIST databases accept Fehsenfeld's room temperature value from 1976,¹ and (apparently) assume (a) that reaction (1) to $\text{OH}^+ + \text{H}_2$ is dominant, and (b) that the rate coefficient is independent of temperature. Unfortunately, Fehsenfeld gives no details of how the O-atoms were generated and their concentration estimated. A follow-up paper that was supposed to give these details could not be found.

Milligan and McEwan² do give details. In effect, they measure the rate coefficient relative to that for $\text{CH}_3\text{O}^+ + \text{O}$. Their assessment of errors seems well founded, their value of $k(298 \text{ K})$ and the branching ratio at 298 K (and the uncertainties in both quantities) are accepted.

Both Fehsenfeld¹ and Milligan and McEwan² only give room temperature values of the rate coefficient. The latter authors point out $k(298 \text{ K})$ is close to the value expected from the Langevin model ($17 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), on which basis one might expect no temperature-dependence.

Bettens *et al.*⁴ provide a thorough theoretical analysis of this reaction. Their findings include: (a) that the capture cross-section is greater than that given by the Langevin model due to the long-range ion-quadrupole forces between H_3^+ and $\text{O}(^3\text{P})$; and (b) that only *ca.*

80% of the 'captured' trajectories lead to reaction. They assume that reaction occurs only on the lowest triplet surface correlating with reactants and reduce their calculated by a factor taking account of the spin-orbit states in $\text{O}(^3\text{P}_j)$. Together with (a) and (b), the value of $k(298 \text{ K})$ obtained is close to that obtained by Milligan and McEwan² and to that estimated by a Langevin analysis.

The calculations of Klippenstein *et al.*⁵ are in fair agreement with those of Bettens *et al.*⁴, both in respect of the absolute values of the rate coefficients and their T -dependence, and again with the limited experimental data. They do not provide information on the branching ratio. We adopt their recommended T -dependence (in recognition of their more sophisticated treatment of spin-orbit effects) and the branching ratio from ref. 2.

We adopt the value of $k(298 \text{ K})$ and the expression for $k(T)$ from Klippenstein *et al.* In view of the good agreement between the two sets of calculations and their agreement with the experimental values of $k(298 \text{ K})$, the uncertainties in the recommendations are quite small.

References

¹ F. C. Fehsenfeld, *Astrophys. J.* **209**, 638 (1976).

² D. B. Milligan and M. J. McEwan, *Chem. Phys. Lett.* **319**, 482 (2000).

³ F. C. Fehsenfeld, W. Lindinger and D. L. Albritton, *J. Chem. Phys.* **63**, 443 (1975).

⁴ R. P. A. Bettens, T. A. Hansen and M. A. Collins, *J. Chem. Phys.* **111**, 6322 (1999).

⁵ S. J. Klippenstein, Y. Georgievskii and B. J. McCall, *J. Phys. Chem. A*, **114**, 278 (2010).