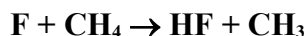


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC1

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 12th February 2004.



$$\Delta H^\circ = -131.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$5.5 \times 10^{-10} \exp[-(580 \pm 150)/T]$	250-350	Wagner, Warnatz and Zetzsch, 1971 ¹	DF-MS
7.9×10^{-11}	298		
7.2×10^{-11}	298	Kompa and Wanner, 1972 ²	(a)
$(6.0 \pm 6.0) \times 10^{-11}$	298	Clyne, McKenney and Walker, 1973 ³	DF-MS
$(5.72 \pm 0.30) \times 10^{-11}$	298	Fasano and Nogar, 1982 ⁴	(b)
$(5.3 \pm 0.3) \times 10^{-11}$	294	Moore, Smith and Stewart, 1994 ⁵	(c)
<i>Relative Rate Coefficients</i>			
$9.0 \times 10^{-11} \exp(-137/T)$	253-348	Foon and Reid, 1971 ⁶	RR (d)
5.7×10^{-11}	298		
$1.3 \times 10^{-10} \exp(-215/T)$	180-410	Persky, 1996, 1998 ⁷	RR (e)
6.2×10^{-11}	298		

Comments

- Flash photolysis of WF₆. Overall rate coefficient was obtained by monitoring the decay of the HF chemical laser emission.
- Infrared multiphoton dissociation of SF₆ in a mixture of CH₄, D₂ and Ar. First-order decay of [F] was monitored by chemiluminescence from either HF or DF. Dependence of decay rate on mixture composition gave values for k and for $k(\text{F} + \text{D}_2)$.
- Time-resolved vibrational chemiluminescence from HF monitored following the production of F atoms in the presence of CH₄ by pulsed laser photolysis of F₂ at 266 nm. Rate coefficient values were also reported at 218 K, 179 K and 139 K, with the values increasing at temperatures below about 200 K.
- Competitive fluorination-consumption technique. Value of k derived from measured ratio $k/k(\text{F} + \text{H}_2) = 0.82 \exp(313/T)$ and $k(\text{F} + \text{H}_2) = 1.1 \times 10^{-10} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.⁸
- Competitive study using DF-MS technique. Value of k derived from measured ratio $k/k(\text{F} + \text{D}_2) = 1.21 \exp(420/T)$, the kinetic isotope effect $k(\text{F} + \text{H}_2)/k(\text{F} + \text{D}_2) = 1.04 \exp(185/T)$,⁹ and $k(\text{F} + \text{H}_2) = 1.1 \times 10^{-10} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$k = 6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.3 \times 10^{-10} \exp(-215/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180 K to 410 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred value at room temperature is based on the room temperature values reported in Wagner *et al.*,¹ Kompa and Wanner,² Clyne *et al.*,³ Fasano and Nogar,⁴ Moore *et al.*,⁵ Foon and Reid⁶ and Persky.⁷ The preferred temperature dependence is that reported by Persky.⁷ Results reported in this study are preferred over the temperature dependences reported in the much earlier studies of Wagner *et al.*¹ and Foon and Reid.⁶

References

- ¹ H. Gg. Wagner, J. Warnatz, and C. Zetzsch, *An. Assoc. Quim. Argentina* **59**, 169 (1971).
- ² K. L. Kompa and J. Wanner, *Chem. Phys. Lett.* **12**, 560 (1972).
- ³ M. A. A. Clyne, D. J. McKenney, and R. F. Walker, *Can. J. Chem.* **51**, 3596 (1973).
- ⁴ D. M. Fasano and N. S. Nogar, *Chem. Phys. Lett.* **92**, 411 (1982).
- ⁵ C. M. Moore, I. W. M. Smith, and D. W. A. Stewart, *Int. J. Chem. Kinet.* **26**, 813 (1994).
- ⁶ R. Foon and G. P. Reid, *Trans. Faraday Soc.* **67**, 3513 (1971).
- ⁷ A. Persky, *J. Phys. Chem.* **100**, 689 (1996); *Chem. Phys. Lett.* **298**, 390 (1998); Erratum, *Chem. Phys. Lett.* **306**, 416 (1999).
- ⁸ IUPAC, 2013. <http://iupac.pole-ether.fr>
- ⁹ A. Persky, *J. Chem. Phys.* **59**, 3612 (1973).