

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet of FOx86; VII.A2.1

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This datasheet last evaluated: June 2014; last change in preferred values: June 2009.



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.9 \pm 0.7) \times 10^{-13}$	296	Howard and Evenson (1976)	DF-LMR (a)
$(3.94 \pm 0.53) \times 10^{-13}$	297	Paraskevopoulos et al. (1981)	FP-RA (b)
$2.96 \times 10^{-13} (T/300)^{2.59} \exp[-(28 \pm 75/T)]$	295-789	Kasner et al. (1990)	FP-LIF (c)
$2.4 \times 10^{-11} \exp(-1082/T)$	295-360	Markert and Nielsen (1992)	PR-RA (d)
$(4.3 \pm 0.5) \times 10^{-13}$	295		
$1.5 \times 10^{-13} T^{0.5} \exp(-637/T)$	223-426	Herndon et al. (2001)	PLP-LIF (e)
$(2.92 \pm 0.12) \times 10^{-13}$	296		

Comments

- (a) HO radicals were generated by the reaction of H atoms with NO₂ in 0.1-1.0 kPa (1-10 mbar) of helium diluent.
- (b) HO radicals produced by the flash photolysis of H₂O ($\lambda \geq 165$ nm) in 20-30 Torr (27-40 mbar) of helium diluent.
- (c) HO radicals were produced by the 193 nm (ArF excimer laser) photolysis of N₂O to produce O(¹D) atoms in the presence of H₂O in 1 bar of helium diluent.
- (d) HO radicals were produced by the pulsed radiolysis of argon (1 bar) containing 15 mbar of H₂O.
- (e) HO radicals were produced by either the photolysis of HONO at 355 nm (third harmonic Nd:YAG laser) or the photolysis of H₂O₂ at 248 nm (KrF excimer laser) in approximately 100 Torr (133 mbar) of helium diluent.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.7×10^{-13}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$4.25 \times 10^{-12} \exp(-727/T)$	220-400
<i>Reliability</i>		
$\Delta \log k$	0.1	298
$\Delta E/R$	± 200	

Comments on Preferred Values

The room temperature rate coefficients reported by Howard and Evenson (1976), Paraskevopoulos et al. (1981), Kasner et al. (1990), and Markert and Nielsen (1992) are in excellent agreement. However, there is disagreement between the temperature dependences reported by Kasner

et al. (1990) and Markert and Nielsen (1992). The data of Markert and Nielsen (1992) are more scattered than those from Kasner et al. (1990). The rate coefficients reported by Herndon et al. (2001) lie approximately 20-30% below those from the other studies. Herndon et al. (2001) argue that the presence of reactive impurities and/or complications caused by photolysis or radiolysis of the C₂H₅Cl sample may have led to overestimation of $k(\text{OH} + \text{C}_2\text{H}_5\text{Cl})$ in previous studies. However, the discharge flow experiments by Howard and Evenson (1976) would not suffer from photolysis or radiolysis of the C₂H₅Cl sample. Also, the impact of an unsaturated reactive impurity such as ethene or isobutene would be reduced at the low pressures used. Averaging the results obtained by Howard and Evenson (1976), Paraskevopoulos et al. (1981), Kasner et al. (1990), and Herndon et al. (2001) gives our recommendation of $k(\text{HO} + \text{C}_2\text{H}_5\text{Cl}) = 3.71 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Fitting the three parameter equation $k = CT^2 \exp(-D/T)$ to the data from Herndon et al. (2001) gives $k = 5.19 \times 10^{-18} T^2 \exp(-131/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which when centered at 298 K with $A = C e^2 T^2$ and $B = D + 2T$ gives $k = 3.41 \times 10^{-12} \exp(-727/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Adjusting the A factor to match the 298 K recommendation of $k(\text{HO} + \text{C}_2\text{H}_5\text{Cl}) = 3.71 \times 10^{-13}$ gives our recommended Arrhenius expression of $k = 4.25 \times 10^{-12} \exp(-727/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

References

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