IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx112

This data sheet last evaluated: June 2017; last change in preferred values: June 2017.

HO + CF_2=CF_2 → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.02 \pm 0.05) \times 10^{-11}$	298	Orkin et al., 1997	FP-RF (a)
$3.39 \times 10^{-12} \exp[(323\pm11)/T]$	250-370	Orkin et al., 2002	FP-RF (a)
$(1.00 \pm 0.015) \times 10^{-11}$	298		
$(8.0 \pm 0.3) \times 10^{-12}$	370	Orkin et al., 2011	FP-RF (a)
$(7.09 \pm 0.02) \times 10^{-12}$	480		
Relative Rate Coefficients			
$(1.07 \pm 0.34) \times 10^{-11}$	298	Acerboni et al., 1999	RR (b)
$(1.07 \pm 0.15) \times 10^{-11}$	298		

Comments

(a) HO radicals were generated by the photolysis of H_2O by a xenon flash lamp in 100 Torr (133 mbar) of argon diluent. HO radicals were monitored using resonance fluorescence.

(b) Photolysis of CH_3ONO in presence of C_2F_4-C_3H_6-NO and C_2F_4-cyclohexane-NO mixtures in 740 Torr (986 mbar) of air diluent was used to generate HO radicals and measure $k(C_2F_4)/k(C_3H_6)$ = 0.375±0.118 and $k(C_2F_4)/k$(cyclohexane) = 1.566±0.226. Using k(HO + C_3H_6) = 2.85×10^{-11} (Atkinson et al., 2006) and k(HO + cyclohexane) = 6.85×10^{-12} (Calvert et al., 2015) gives k(HO + C_2F_4) = $(1.07\pm0.34) \times 10^{-11}$ and $(1.07\pm0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.04×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$3.84 \times 10^{-12} \exp(297/T)$	250-500
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 100	250-500

Comments on Preferred Values

The preferred value at 298 K is an average of the absolute rate determinations by Orkin et al. (1997) and (2002) and the relative rate determination by Acerboni et al. (1999). The temperature dependence is derived from a fit to the data from Orkin et al. (2002) and (2011) with the A factor adjusted to give the recommended rate coefficient at 298K.

The reaction proceeds via addition to the >C=C< double bond. Based upon the behavior of the reaction of HO radicals with similar halogenated alkenes such as CH_2=CF_2 (Howard, 1976) it is expected that the kinetics of the reaction will be at the high pressure limit for total pressures above approximately 5 Torr (7 mbar). Consistent with this expectation there is no discernable difference between the rate coefficient measured in 100 Torr of argon diluent by Orkin et al. (1997, 2002) and that measured in 740 Torr of air by Acerboni et al. (1999). The HO radical initiated oxidation of CF_2=CF_2 will give COF_2 as the major product.

$$HO + CF_2{=}CF_2 \rightarrow HOCF_2CF_2$$
$$HOCF_2CF_2 + O_2 \rightarrow HOCF_2CF_2O_2$$
$$HOCF_2CF_2O_2 + NO/RO_2 \rightarrow HOCF_2CF_2O + NO_2/RO + O_2$$
$$HOCF_2CF_2O \rightarrow HOCF_2 + COF_2$$
$$HOCF_2 + O_2 \rightarrow HO_2 + COF_2$$

References

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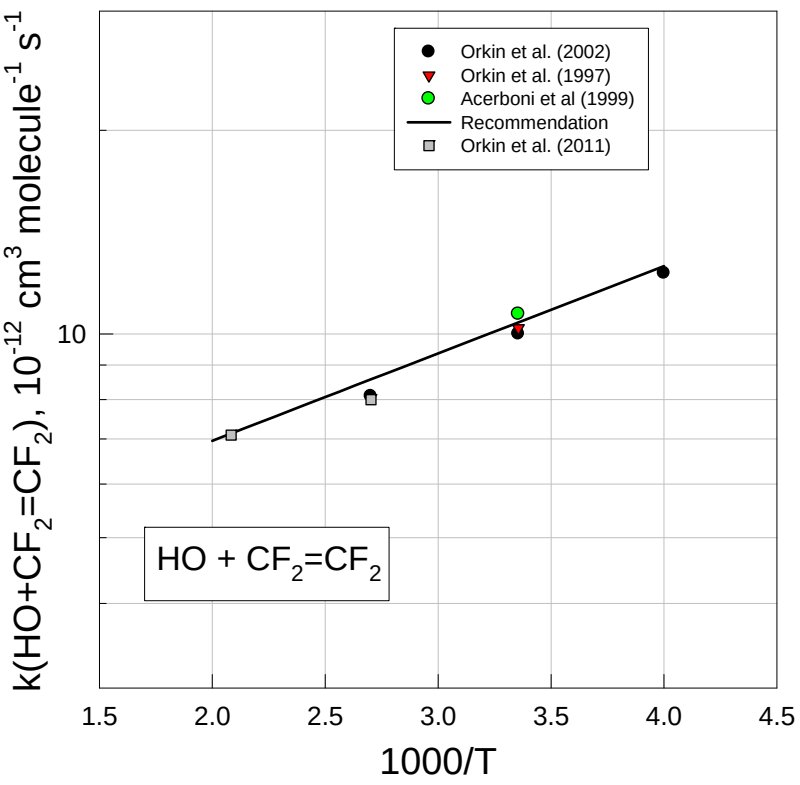
Orkin et al. (2002)
Orkin et al. (1997)
Acerboni et al (1999)
Recommendation
Orkin et al. (2011)
HO + CF2=CF2
k(HO+CF2=CF2), 10-12 cm3 molecule-1 s-1
10
1.5
2.0
2.5
3.0
3.5
4.0
4.5
1000/T