IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet olOx2; IV.A4.267

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This datasheet last evaluated: June 2015; last change in preferred values: June 2001.

HO + CF_3I → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-13}$	295	Garraway and Donovan, 1979	FP-RA
$(3.1 \pm 0.5) \times 10^{-14}$	300	Brown et al., 1990	DF-RF
$5.8 \times 10^{-12} \exp[-(1359 \pm 133)/T]$	281-443	Berry et al., 1998	FP-RF (a)
$(5.9 \pm 1.4) \times 10^{-14}$	292		
$2.1 \times 10^{-11} \exp[-(2000 \pm 140)/T]$	271-370	Gilles et al., 2000	PLP-LIF (b)
$(2.35 \pm 0.54) \times 10^{-14}$	296		

Comments

(a) The measured rate coefficients were observed to increase with flash energy (which affects both the initial concentration of HO radicals and the amount of CF_3I photolysis products). The cited rate coefficients at each temperature were obtained from extrapolation to zero flash energy. Theoretical calculations indicated that the dominant channel is that to form CF_3 + HOI.

(b) No effect on the rate coefficient of varying the laser fluence by a factor of ~5 was observed when 351 nm pulsed laser photolysis of HONO was used as the HO radical source. However, a significant effect of laser fluence was observed when using 248 nm pulsed laser photolysis of O_3 in the presence of H_2O to generate HO radicals. The cited rate coefficients and Arrhenius expression were obtained from experiments using 351 nm photolysis of HONO as the HO radical source. The CF_3I concentrations were monitored by UV/visible absorption spectroscopy.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.6×10^{-14}	298
k /cm^3 molecule^{-1} s^{-1}	$2.1 \times 10^{-11} \exp(-2000/T)$	270-370

Reliability

$\Delta \log k$	± 0.2	298
Δ E/R	± 500	

Comments on Preferred Values

Studies of this reaction have the potential for secondary reactions (including, in the pulsed photolysis systems, with CF_3I photolysis products), reactions with impurities, and/or heterogeneous wall reactions (Brown et al., 1990; Wayne et al., 1992; Berry et al., 1998; Gilles et al., 2000). The preferred values are based on the more extensive study of Gilles et al. (2000) in which HONO photolysis at 351 nm was used to generate HO radicals with no apparent problems due to secondary reactions and with the CF_3I concentrations being monitored by UV/visible absorption spectroscopy.

References

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Brown, A. C., Canosa-Mas, C. E. and Wayne, R. P.: Atmos. Environ. 24A, 361, 1990.
Garraway, J. and Donovan, R. J.: J. Chem. Soc., Chem. Comm. 1108, 1979.
Gilles, M. K., Talukdar, R. K. and Ravishankara, A. R.: J. Phys. Chem. A 104, 8945, 2000.
Wayne, R. P., Canosa-Mas, C. E., Heard, A. C. and Parr, A. D.: Atmos. Environ. 26A, 2371, 1992.