IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx111

This data sheet last evaluated: September 2011; last change in preferred values: September 2011.

$$Cl + CHF_3 \rightarrow HCl + CF_3$$

$\Delta H° = 17.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.3 \pm 1.5) \times 10^{-16}$	298	Jourdain et al., 1976	FT-MS (a)
Relative Rate Coefficients			
$4.6 \times 10^{-13} \exp[-(3520)/T]$	303-399	Coomber and Whittle, 1966	RR (b)
3.4×10^{-18}	298		

Comments

(a) The reaction rate coefficient was measured using a flow reactor, employing a microwave discharge in Cl_2 for the generation of Cl atoms with mass spectrometric detection of reactants and products. Experiments were performed in 0.3-3 Torr of helium diluent.

(b) The reaction rate coefficients were measured using a competitive method with Cl atoms generated via photolysis of Cl_2 at 366 nm (mercury lamp). The expression in the table above was derived from the measured ratios k_{CH4}/k_{C2F5H} =12.4 exp[(1450±40)/RT] and k_{C2F5H}/k_{CHF3} = 1.16 exp[(3080±70)/RT])which leads to k_{CH4}/k_{CHF3} = 14.4 exp[(4530±80)/RT]) = 14.4 exp[(2280±40)/T]). Using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ (Atkinson et al., 2006) gives $k(Cl + CHF_3) = 4.6 \times 10^{-13} \exp(-3520/T)$cm^3 molecule^{-1} s^{-1}. At 298 K this expression gives $k(Cl + CHF_3) = 3.4 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	$<6 \times 10^{-16}$	298

Comments on Preferred Values

The rate coefficient reported by Jourdain et al. at 298 K is two orders of magnitude greater than that obtained from extrapolation of the data from Coomber and Whittle. The reaction endothermicity of 17.9 kJ mol^{-1} provides a lower limit for the activation energy (Ea/R = 2150) which combined with

an estimate of 1 x 10^{-12} for the A factor gives an upper limit of $k(Cl + CHF_3) < 7 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. In the absolute rate study by Jourdain et al. a contribution from reaction with reactive impurities is difficult to exclude. The study by Coomber and Whittle gives a rate coefficient ratio of $k(Cl + CH_4)/k(Cl + C_2HF_5) = 144$ which is approximately a factor of two lower than the ratio of the recommended rate coefficients $k(Cl + CH_4)/k(Cl + C_2HF_5) = 385$ (Atkinson et al., 2006; 2008). The recommended upper limit of $k(Cl + CHF_3) < 6 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K is based on the result from Jourdain et al.

References

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