IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A1.38 oFOx38

This data sheet last evaluated: March 2005.

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$$

$\Delta H° = -148$ kJ mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.1) \times 10^{-29}$ [He]	295	Ryan and Plumb, 1982	DF-MS (a)
$(1.9 \pm 0.2) \times 10^{-29} (T/300)^{-4.7}$ [N_2]	233-373	Caralp, Lesclaux,and Dognon, 1986	PLP-MS (b)
$(2.5 \pm 0.3) \times 10^{-29}$ [N_2]	295	Breheny, Hancock and Morrell, 2001	PLP-CL(c)

Comments

(a) Microwave discharge-flow system coupled to quadrupole MS. CF_3 radicals monitored by MS. Measurements over the range 0.7-11 mbar, extrapolated with $F_c \approx 0.4$ and $k_\infty \approx 8.0 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}.

(b) Pulsed laser photolysis–MS study over the range 0.3-16 mbar. Extrapolation with $F_c \approx 0.6$ and $k_\infty \approx 9.0 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}.

(c) Pulsed laser photolysis-IR chemiluminescence study of CF_3I in the presence of NO_2 and O_2, using IR emission from the reaction $CF_3 + NO_2$ for detection. Pressure range 2.7-150 mbar. Extrapolation with $F_c \approx 0.6$ and $k_\infty \approx 2.55 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}, using data up to 800 mbar from relative rate measurements by Kaiser et al. (1995).

Preferred Values

$k_0 = 2.2 \times 10^{-29} (T/300)^{-4.7}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1.5$.

Comments on Preferred Values

The preferred values are an average of the low pressure results from Caralp et al. (1986), and Breheny et al. (2001) which appear well consistent with the measurements in He from Ryan and Plumb (1982). Differences in k_∞ and F_c, used in the extrapolation, only slightly influence the preferred k_0 because all measurements extended to pressures close to the low pressure limit of k.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.0×10^{-11}	298	Cooper et al., 1980	PR (a)
Relative Rate Coefficients			
$(3.92 \pm 0.25) \times 10^{-12}$	271-363	Kaiser, Wallington and Hurley, 1995	PR (b)

Comments

(a) Pulse radiolysis of CF_3Cl. CF_3O_2 detected by UV absorption spectroscopy near 260 nm. Measurements in 920 mbar of Ar.

(b) UV irradiation of $CF_3I/CH_4/Cl_2/N_2/O_2$ mixtures and observation of loss of CF_3 and CH_4. Measurement of the ratio $k(CF_3 + O_2)/k(CF_3 + Cl_2)$ as a function of the pressure and calibration of this ratio at low pressures against $k_0(CF_3 + O_2)$ from Caralp et al., (1986). Inspection of the spectra recorded by Cooper et al. (1980) and comparison with more recently detected spectra of CF_3O_2 indicates that the rate of $CF_3 + O_2$ was not observed by Cooper et al. (1980).

Preferred Values

$k_\infty = 4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1.5$.

Comments on Preferred Values

Since the measurements of Cooper et al. (1980) were shown not to lead to k_∞, the results from the relative rate measurements from Kaiser et al. (1995) are preferred. They are similar to values for k_∞ for $CCl_3 + O_2$ from Luther et al. (2001) for which n = -1.4 was measured. Using an estimated $F_c = 0.39$ independent of the temperature, all results (except those from Cooper et al. (1980)) are consistently represented and the remaining uncertainty of k_∞ does not impact on k_0.
The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of k:

=((2.2e-29*(T/300)^-4.7)*M*(4.0e-12))/((2.2e-29*(T/300)^-4.7)*M+(4.0e-12))*10^(log10(0.39)/(1+(log10((2.2e-29*(T/300)^-4.7)*M/(4.0e-12))/(0.75-1.27*log10(0.39)))^2))

The molecular density, M = 7.243×10^{21}P(bar)/T(K)

References

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