IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx85

This datasheet updated: 5th July 2005.

$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M$

$\Delta H° = -92$ 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			
$(5.8 \pm 0.6) \times 10^{-31}$ [He]	295	Ryan and Plumb, 1984	DF-MS (a)
$(1.6 \pm 0.3) \times 10^{-30} (T/298)^{-6.3}$ [N_2]	233-333	Danis et al., 1991	PLP-MS/UVA (b)
$(6.5 \pm 0.2) \times 10^{-31} (T/300)^{-6.1}$ [N_2]	298-333	Fenter et al., 1993	PLP-MS/UVA (c)
$(2.7 \pm 0.2) \times 10^{-31} (T/300)^{-8.7}$ [He]	286-332	Nottingham et al., 1994	F-MS (d)
$(1.1 \pm 0.3) \times 10^{-30} (T/300)^{-6.3}$ [N_2]	260-346	Luther, Oum and Troe, 2001	PLP-UVA (e)
$(4.2 \pm 0.7) \times 10^{-31} (T/298)^{-6.9}$ [He]			

Comments

(a) Microwave discharge flow-quadrupole MS study. CCl_3 radicals generated by the reaction F + $CHCl_3 \rightarrow CCl_3$ + HF. Falloff curve studied between 2.3 and 7 mbar of He and extrapolated with $F_c = 0.25$.

(b) Laser photolysis of CCl_4 with MS detection at lower and UV absorption detection at higher pressures. Measurements between 1 and 16 mbar as well as at 930 mbar of N_2. Evaluation with $F_c = \exp(-T/255)$, i. e., $F_c = 0.31$ at 300 K, and $k_\infty = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

(c) Photolysis of CCl_3Br at 248 nm with detection of CCl_3 by MS or UV absorption at 215 nm. Measurements at 1.3-16 mbar (MS detection) and 27-930 mbar (UV absorption detection). Falloff curve represented with $F_c = 0.6$ and $k_\infty = 2.6 \times 10^{-12} (T/300)^{-1.1}$ cm^3 molecule^{-1} s^{-1}.

(d) Flow tube using dissociative election attachment for radical production and MS for radical detection. Pressures of He below 4 mbar. Measurements evaluated with $F_c = 0.33$ and $k_\infty = 2.74 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 286 K.

(e) Photolysis of CCl_3Br at 248 nm and detection of CCl_3 at 223.5 nm. Measurements at 200, 300, and 346 K over the pressure range 2-900 bar in He and N_2. Data represented with $F_c(N_2) = 0.35 (T/300)^{-0.35}$ and $k_\infty = 5.2 \times 10^{-12} (T/300)^{-1.4}$ cm^3 molecule^{-1} s^{-1}.

Preferred Values

$k_0 = 1.1 \times 10^{-30} (T/300)^{-6.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 230-350 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are the average of the data from Danis et al. (1991) and Fenter et al.

(1993) which are consistent with the falloff extrapolation from Luther et al. (2001). As the experiments were conducted to sufficiently low pressures, the different F_c-values used are of no relevance for the determination of k_0.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
5.1×10^{-12}	300	Cooper et al., 1980	PR-UVA (a)
2.5×10^{-12}	295	Ryan and Plumb, 1984	DF-MS(b)
$(3.2 \pm 0.7) \times 10^{-12} (T/298)^{-1.2}$	233-333	Danis et al., 1991	PLP-MS/UVA(c)
$(2.5 \pm 0.2) \times 10^{-12} (T/298)^{-1.1}$	298-333	Fenter et al., 1993	PLP-MS/UVA (d)
$(5.2 \pm 0.2) \times 10^{-12} (T/300)^{-1.4}$	260-346	Luther, Oum and Troe, 2001	PLP-UVA (e)

Comments

(a) Pulse radiolysis of CCl_4 at 930 mbar of He. CCl_3O_2 radicals detected by UV absorption.
(b) See comment (a) for k_0.
(c) See comment (b) for k_0.
(d) See comment (c) for k_0.
(e) See comment (d) for k_0.

Preferred Values

$k_\infty = 5.2 \times 10^{-12} (T/300)^{-1.4}$ cm^3 molecule^{-1} s^{-1} over the temperature range 260-350 K.

Reliability

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

Comments on Preferred Values

The combined data by Danis et al. (1991), Fenter et al. (1993) and Luther et al. (2001) at 300 K are well represented by a falloff curve with $F_c = 0.35$. Since the falloff curve has been measured up to very high pressures, the derived values from Luther et al. (2001) for k_∞ are preferred. The small temperature dependence of F_c employed by Luther et al. (2001) may be neglected.

References

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