IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A7.167 X_VOC3

This data sheet last evaluated: June 2003.

$Cl + C_2H_2 + M \rightarrow C_2H_2Cl + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.15 \pm 0.30) \times 10^{-21}\ T^{-3.5}$ [Ar]	210-361	Brunning and Stief, 1985[1]	FP-RF (a)
6.9×10^{-30} [Ar]	298		
Relative Rate Coefficients			
$(5.2 \pm 0.7) \times 10^{-30}$ [air]	295	Wallington *et al.*, 1990[2]	(b)
$5.4 \times 10^{-30}\ (T/300)^{-2.092}$ [air]	252-370	Kaiser, 1992[3]	(c)
$(6.1 \pm 0.2) \times 10^{-30}$ [air]	297	Kaiser and Wallington, 1996[4]	(d)

Comments

(a) The concentration of the bath gas Ar was varied over the range $(2.7 - 120) \times 10^{17}$ molecule cm^{-3}. Some experiments with N_2 were also conducted. Falloff extrapolations were made using $F_c = 0.6$.

(b) Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_2 and C_2H_6 (or C_2H_5Cl). The decays of C_2H_2, C_2H_6 (or C_2H_5Cl) were followed by FTIR spectroscopy. The measured rate coefficient ratios have been placed on an absolute basis using a rate coefficient of $k(Cl + C_2H_6) = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Measurements were conducted over the pressure range 0.013 mbar to 7.6 bar. Falloff extrapolations were made with $F_c = 0.6$.

(c) Mixtures of C_2H_2, C_2H_6, Cl_2 and diluent (air, N_2, or SF_6) were irradiated by a UV fluorescent lamp. C_2H_2 and C_2H_6 concentrations were determined by GC. The reaction was studied at pressures between 0.03 bar and 1.7 bar. The measured rate coefficient ratios are placed on an absolute basis using the rate coefficient $8.68 \times 10^{-11} \exp(-113/T)$ cm^3 molecule^{-1} s^{-1} for the reaction $Cl + C_2H_6 \rightarrow C_2H_5 + HCl$. Falloff extrapolations were made with a temperature independent $F_c = 0.6$.

(d) Mixtures of Cl_2, C_2H_2, CH_4, CH_3Cl, C_2H_6 and C_2H_5Cl and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation C_2H_2, CH_4 and CH_3Cl were monitored by GC (0.4 mbar to 13 mbar). CH_3Cl, C_2H_6 and C_2H_5Cl were determined by FTIR (13 mbar to 920 mbar). The following values were used for the reference abstraction reactions: 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl + CH_4$), 4.9×10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl + CH_3Cl$), 5.7×10^{-11} cm^3

molecule^{-1} s^{-1} (Cl + C_2H_6) and 8.05 x 10^{-12} cm^3 molecule^{-1} s^{-1} (Cl + C_2H_5Cl). The results were analyzed together with previous determinations performed between 0.13 bar and 7.9 bar and extrapolated with $F_c = 0.6$.[2]

Preferred Values

$k_0 = 6.1 \times 10^{-30} (T/300)^{-3}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the room temperature measurements of Kaiser and Wallington[4] which have been evaluated with $F_c = 0.6$. The temperature dependence is a compromise of the results from refs. 1 and 3.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.52 ± 0.15) x 10^{-4} $T^{-2.63}$	210-361	Brunning and Stief, 1985[1]	FP-RF (a)
4.7 x 10^{-11}	298		
Relative Rate Coefficients			
2.3 ± 0.7) x 10^{-10}	295	Wallington *et al.*, 1990[2]	(b)
2.13 x 10^{-10} (T/300)$^{-1.045}$	252-370	Kaiser, 1992[3]	(c)
(2.0 ± 0.1) x 10^{-10}	297	Kaiser and Wallington, 1996[4]	(d)

Comments

(a) to (d) See comments (a) to (d) for k_0.

Preferred Values

$k = 5.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200 to 400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data of Kaiser and Wallington[4] which cover the broadest pressure range (0.13 bar to 7.9 bar). They have been evaluated with $F_c = 0.6$. Relative rate coefficients near 1 bar from refs. 5 to 7 are in good agreement with the preferred

values. A branching ratio of 0.19 ± 0.05 for formation of *cis*- and *trans*-isomers of the adduct in ref. 8 was determined around 1 bar of N_2 and 295 K.

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*:

=((6.1e-30*(*T*/300)^-3)*M*(2.0e-10))/((6.1e-30*(*T*/300)^-3)*M+(2.0e-10))*10^(log10(0.6)/(1+(log10((6.1e-30*(*T*/300)^-3)*M/(2.0e-10))/(0.75-1.27*log10(0.6)))^2))

The molecular density, $M = 7.243\times10^{21}P(bar)/T(K)$

References

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