IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A7.168 SOx4

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$Cl + C_2H_4 + M \rightarrow C_2H_4Cl + M$

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.4 ±0.2) x 10^{-29} (T/298)$^{-2.0}$ [N_2]	218-297	Maricq, Szente, and Kaiser, 1993[1]	(a)
(1.0 ± 0.2) x 10^{-29} [He]	293	Stutz, Ezell, and Finlayson-Pitts, 1997[2]	(b)
Relative Rate Coefficients			
(1.6 $^{+1}_{-0.3}$) x 10^{-29} [air]	295	Wallington *et al.*, 1990[3]	RR (a)
(1.7 ± 0.3) x 10^{-29}(T/298)$^{-3.28}$ [air]	297-383	Kaiser and Wallington, 1996[4]	(b)
(1.42 ± 0.05) x 10^{-29} [air]	297		
1.0 x 10^{-29} [He]	297	Kaiser and Wallington, 1998[5]	(d,e)
1.85 x 10^{-29} [N_2]			

Comments

(a) IR absorption measurements of C_2H_6 and HCl after laser photolysis of Cl_2 in $Cl_2/C_2H_4/O_2/N_2$ mixtures. Measurements at 39 mbar of N_2, here evaluated without falloff corrections. k also measured at 170 mbar and 297 K.

(b) Fast-flow discharge study detecting Cl by resonance fluorescence at 135 nm. Similar results by relative rate measurements.

(c) Measurements of k performed by a relative rate technique. Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_4, and C_2H_6 (or C_2H_5Cl). Decay of C_2H_4, C_2H_6 (or C_2H_5Cl) monitored by FTIR spectroscopy. Using a value of 5.7 x 10^{-11} cm^3 molecule^{-1} s^{-1} for the rate coefficient for the $Cl + C_2H_6 \rightarrow C_2H_5 + HCl$ reaction, the relative data were placed on an absolute basis. The reaction was studied over the pressure range 13 mbar to 4000 mbar and the measured rate coefficients fitted with $F_c = 0.6$.

(d) Mixtures of Cl_2, C_2H_4, CH_4, CH_3Cl, CCl_3H, 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_4 and the above reference compounds were determined by GC or FTIR techniques. The experiments were performed at total pressures of 0.26 mbar to 130 mbar. The following values were used for the reference abstraction reactions: 1.0 x 10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl + CH_4$), 4.9 x 10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl + CH_3Cl$), 1.1 x 10^{-13} cm^3 molecule^{-1} s^{-1} ($Cl + CCl_3H$), 5.7 x 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 conducted at 130 mbar to 4000 mbar of air3 and extrapolated with $F_c = 0.6$.

(e) Falloff extrapolation with $F_{cent} = 0.4$.

Preferred Values

$k_0 = 1.85 \times 10^{-29} (T/300)^{-3.3}$ [air] cm^3 molecule^{-1} s^{-1} over the temperature range 250 to 300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the most detailed results from refs. 4-5 which agree with the results from refs. 1 and 2 (only for the bath gas He, but not N_2). The given value of k_0 corresponds to a falloff extrapolation with $F_c = 0.4$.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(3.05^{+2}_{-0.4}) \times 10^{-10}$	295	Wallington *et al.*, 1990[3]	FP-FTIR (a)
$(3.2 \pm 0.15) \times 10^{-10}$	297	Kaiser and Wallington, 1996[4]	(b)
5.7×10^{-10}	297	Kaiser and Wallington, 1998[5]	(c)

Comments

(a) See comment (c) for k_0.

(b) See comment (d) for k_0.

(c) See comments (d) and (e) for k_0.

Preferred Values

$k = 1.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_\infty = 6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250-300 K.

Reliability

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

$\Delta n = \pm 1$.

Comments on Preferred Values

The falloff extrapolation of the data from ref. 3 is consistent with results in the intermediate falloff range from refs. 1, 6-10. Measurements of the reverse decomposition of C_2H_4Cl in the falloff range at 400-480 K have been reported in ref. 11.

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:

=((1.85e-29*(*T*/300)^-3.3)*M*(6e-10))/((1.85e-29*(*T*/300)^-3.3)*M+(6e-10))*10^(log10(0.4)/(1+(log10((1.85e-29*(*T*/300)^-3.3)*M/(6e-10))/(0.75-1.27*log10(0.4)))^2))

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

References

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