IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.88 oClOx14

This data sheet last evaluated: June 2015; last change in preferred values: December 2007.

$Cl + HC(O)Cl \rightarrow HCl + ClCO$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
7.4×10^{-13}	305	Sanhueza and Heicklen, 1975	RR (a)
$(7.7 \pm 1.0) \times 10^{-13}$	298 ± 2	Niki et al., 1980	RR (b)
$8.2 \times 10^{-12} \exp(-705/T)$	266-321	Libuda et al., 1990	RR (c)
7.7×10^{-13}	298		
$(6.7 \pm 1.0) \times 10^{-13}$	295	Wallington et al., 1996	RR (d)
$(6.8 \pm 0.7) \times 10^{-13}$	295	Catoire et al., 1996	RR (e)
$8.3 \times 10^{-12} \exp(-745/T)$	222-296	Orlando, 1999	RR (f)
6.8×10^{-13}	298		

Comments

(a) Rate coefficient ratios of $k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.85 \pm 0.43$ and $k(Cl + HC(O)Cl)/k(Cl + CH_2Cl_2) = 1.66 \pm 0.15$ derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH_2Cl_2 and CH_3Cl. This was placed on an absolute basis using $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $k(Cl + CH_2Cl_2) = 3.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008). The rate coefficient cited in the table is the average of the two values obtained, which however differ significantly.

(b) Rate coefficient ratio of $k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.6 \pm 0.2$ determined using FTIR absorption spectroscopy in irradiated Cl_2-CH_3Cl-O_2-N_2 mixtures at 933 mbar total pressure. The rate coefficient ratio was placed on an absolute basis using $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

(c) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2-HC(O)Cl-CH_4-N_2 mixtures at 1000 mbar total pressure. The concentrations of HC(O)Cl and CH_4 were measured by FTIR absorption spectroscopy (HC(O)Cl) and/or gas chromatography (CH_4). Rate coefficient ratios were determined over the temperature range 265.8-321.3 K, and placed on an absolute basis using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(d) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2-CH_3Cl-air mixtures at 933 mbar total pressure. The concentrations of HC(O)Cl and CH_3Cl were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio $k(Cl + HC(O)Cl)/k(Cl + CH_3Cl) = 1.4 \pm 0.2$ is placed on an absolute basis using $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

(e) Relative rate study. Cl atoms generated by the photolysis of Cl_2 in Cl_2-CH_2Cl_2-air mixtures at 933 mbar total pressure. The concentrations of HC(O)Cl and CH_2Cl_2 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio $k(Cl + HC(O)Cl)/k(Cl + CH_2Cl_2)$

= 2.0 ± 0.2 is placed on an absolute basis using $k(Cl + CH_2Cl_2) = 3.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008).

(f) Temperature dependent rate coefficient ratios of $k(Cl + HC(O)Cl)/k(Cl + CH_2Cl_2)$ were derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH_2Cl_2. Placed on an absolute basis by use of $k(Cl + CH_2Cl_2) = 5.9 \times 10^{-12} \exp(-850/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2008). The value of k at 298 K was taken from the Arrhenius expression presented.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	7.5×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$1.12 \times 10^{-12} \exp(-805/T)$	220-330
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta(E/R)$	± 150	

Preferred Values

$k = 7.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.12 \times 10^{-12} \exp(-805/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-330 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

At 298 K, the rate coefficients of Sanhueza and Heicklen (1975), Niki et al. (1980), Libuda et al. (1990), Wallington et al. (1996), Catoire et al. (1996), and Orlando (1999) are in good agreement. The temperature dependence reported by Liduda et al. (1990) and Orlando et al. (1999) are in good agreement. A fit of the Arrhenius expression to the combined data set gives the recommended value of $k(Cl+HC(O)Cl) = 1.12 \times 10^{-12} \exp(-805/T)$ cm^3 molecule^{-1} s^{-1}.

References

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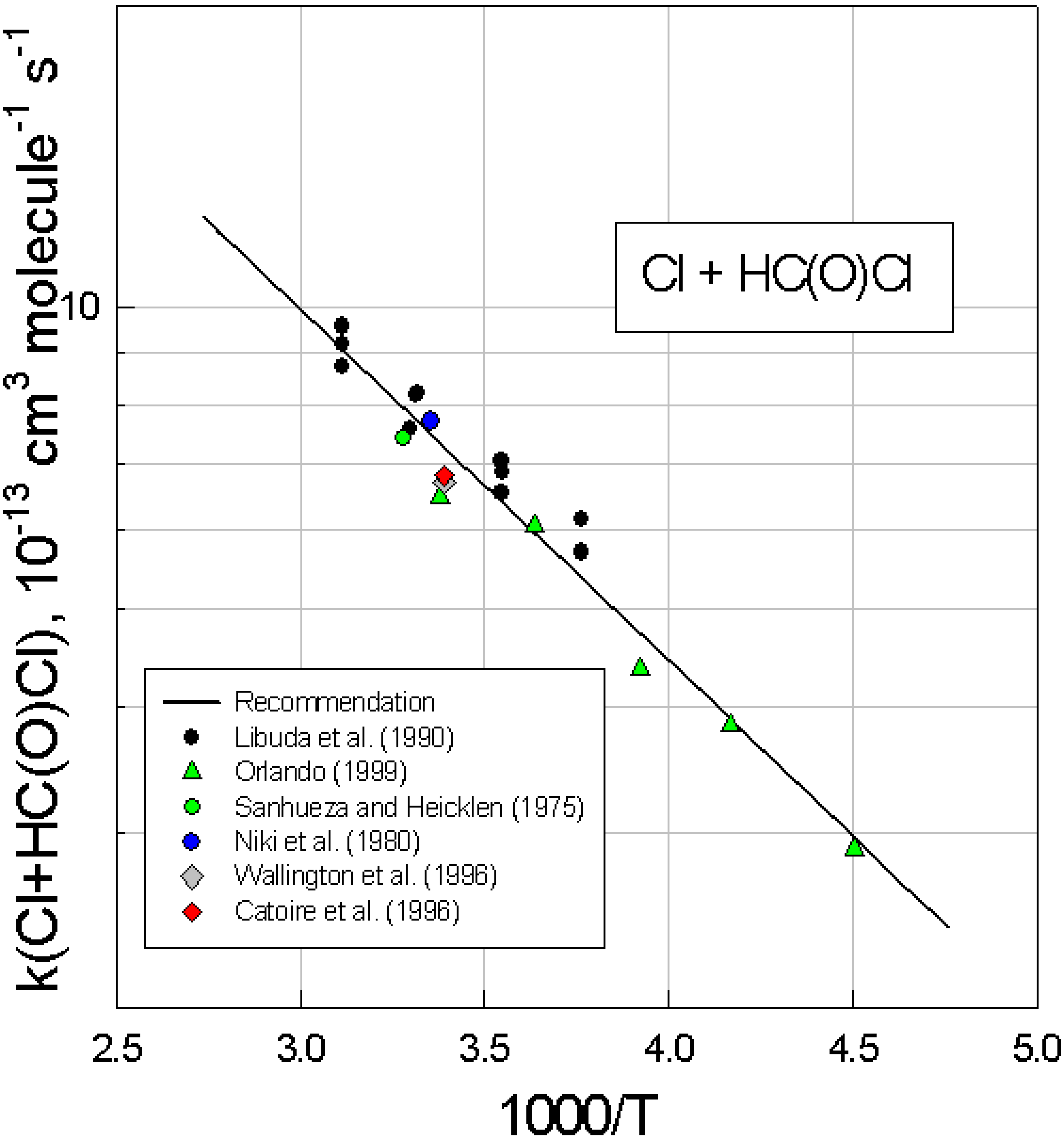
Cl + HC(O)Cl
k(Cl+HC(O)Cl), 10^-13 cm^3 molecule^-1 s^-1
10
2.5
3.0
3.5
4.0
4.5
5.0
1000/T
Recommendation
Libuda et al. (1990)
Orlando (1999)
Sanhueza and Heicklen (1975)
Niki et al. (1980)
Wallington et al. (1996)
Catoire et al. (1996)