IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.105 oClOx31

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$Cl + CH_3CCl_3 \rightarrow HCl + CH_2CCl_3$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$<2.40 \times 10^{-14}$	259	Wine et al., 1982	PLP-RF
$<3.68 \times 10^{-14}$	298		
$<7.74 \times 10^{-14}$	356		
$2.8 \times 10^{-12} \exp[-(1790 \pm 320)/T]$	298-418	Talhaoui et al., 1996	DF-MS
$(7.1 \pm 1.1) \times 10^{-15}$	298		
Relative Rate Coefficients			
$1.63 \times 10^{-12} \exp -(1300/T)$	323-423	Cillien et al., 1967	RR (a)
$6.7 \times 10^{-12} \exp -(1780/T)$	280-368	Tschuikow-Roux et al, 1985	RR (b)
1.7×10^{-14}	298		
$(9.9 \pm 2.0) \times 10^{-15}$	296	Platz et al., 1995	RR (c)
$2.41 \times 10^{-12} \exp(-1630/T)$	253-313	Nilsson et al., 2009	RR (d)
$(1.01 \pm 0.08) \times 10^{-14}$	298		

Comments

(a) Photolysis of Cl_2 in Cl_2-CH_3CCl_3-CH_3Cl mixtures at 200 – 2720 mbar total pressure with the formation of chlorinated products measured by GC. The rate coefficient ratio $k(Cl+CH_3CCl_3)/k(Cl+CH_3Cl) = 0.0708 \exp(-151/T)$ was obtained and was placed on an absolute basis using $k(Cl+CH_3Cl) = 2.3 \times 10^{-11} \exp(-1150/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(b) Photolysis of Cl_2 in Cl_2-CH_3CCl_3-CH_4 mixtures at about 28 mbar total pressure with the formation of chlorinated products measured by GC. The rate coefficient ratio $k(Cl+CH_3CCl_3)/k(Cl+CH_4) = 1.015 \exp(-541/T)$ was obtained and was 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).

(c) Photolysis of Cl_2-CH_3CCl_3-CD_4 mixtures in air or N_2 at 930 mbar total pressure, with the loss of reactants monitored by FTIR. A value of $k(Cl + CH_3CCl_3)/k(Cl + CD_4) = (1.62 \pm 0.05)$ was obtained and placed on an absolute basis using $k(Cl + CD_4) = 6.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (Wallington and Hurley, 1992).

(d) Photolysis of Cl_2 in presence of Cl_2-CH_3CCl_3-CH_2F_2 and Cl_2-CH_2F_2-CH_4 mixtures in 930 mbar of N_2 diluent was used to measure $k(CH_3CCl_3)/k(CH_2F_2)$ and $k(CH_2F_2)/k(CH_4)$ and hence $k(CH_3CCl_3)/k(CH_4)$ rate coefficient ratios at 253 – 313 K. The values of $k(CH_3CCl_3)/k(CH_4)$ obtained at < 300 K were 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). The value of

$k(CH_3CCl_3)/k(CH_4)$ obtained at 313 K was placed on an absolute basis using $k(Cl+CH_4)$ = $5.69 \times 10^{-19}\ T^{2.49} \exp(-609/T)$ cm^3 $molecule^{-1}$ s^{-1} from Bryukov et al. (2002).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 $molecule^{-1}$ s^{-1}	9.0×10^{-15}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$1.09 \times 10^{-12} \exp(-1430/T)$	250-430
Reliability		
$\Delta \log k$	± 0.06	298
$\Delta(E/R)$	± 300	250-430

Comments on Preferred Values

The preferred value of k at 298 K is an average of the room temperature determinations by Platz et al. (1995), Talhaoui et al. (1996), and Nilsson et al. (2009) which is consistent with the upper limit of Wine et al. (1982). Fitting the Arrhenius expression to the data reported by Platz et al. (1995), Talhaoui et al. (1996), and Nilsson et al. (2009) and adjusting the A factor for consistency with the recommended rate coefficient at 298 K gives the recommended expression given above. Dalmasso et al. (2006) measured the rate coefficient ratio $k(Cl + CHF_2OCH_2CF_3)/k(Cl + CH_3CCl_3)$ = 1.15 ± 0.02 at room temperature. Using the absolute rate measurement of $k(Cl + CHF_2OCH_2CF_3) = 1.1 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} by Beach et al. (2001), the rate coefficient ratio measured by Dalmasso et al. (2006) gives a value of $k(Cl + CH_3CCl_3) = 9.6 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} which is consistent with the preferred value above. The relative rate studies by Cillien et al. (1967) and Tschuikow-Roux et al. (1985) have temperature dependencies which are consistent with the preferred value but have absolute values which are a factor of approximately 1.5-2.0 larger than the preferred values.

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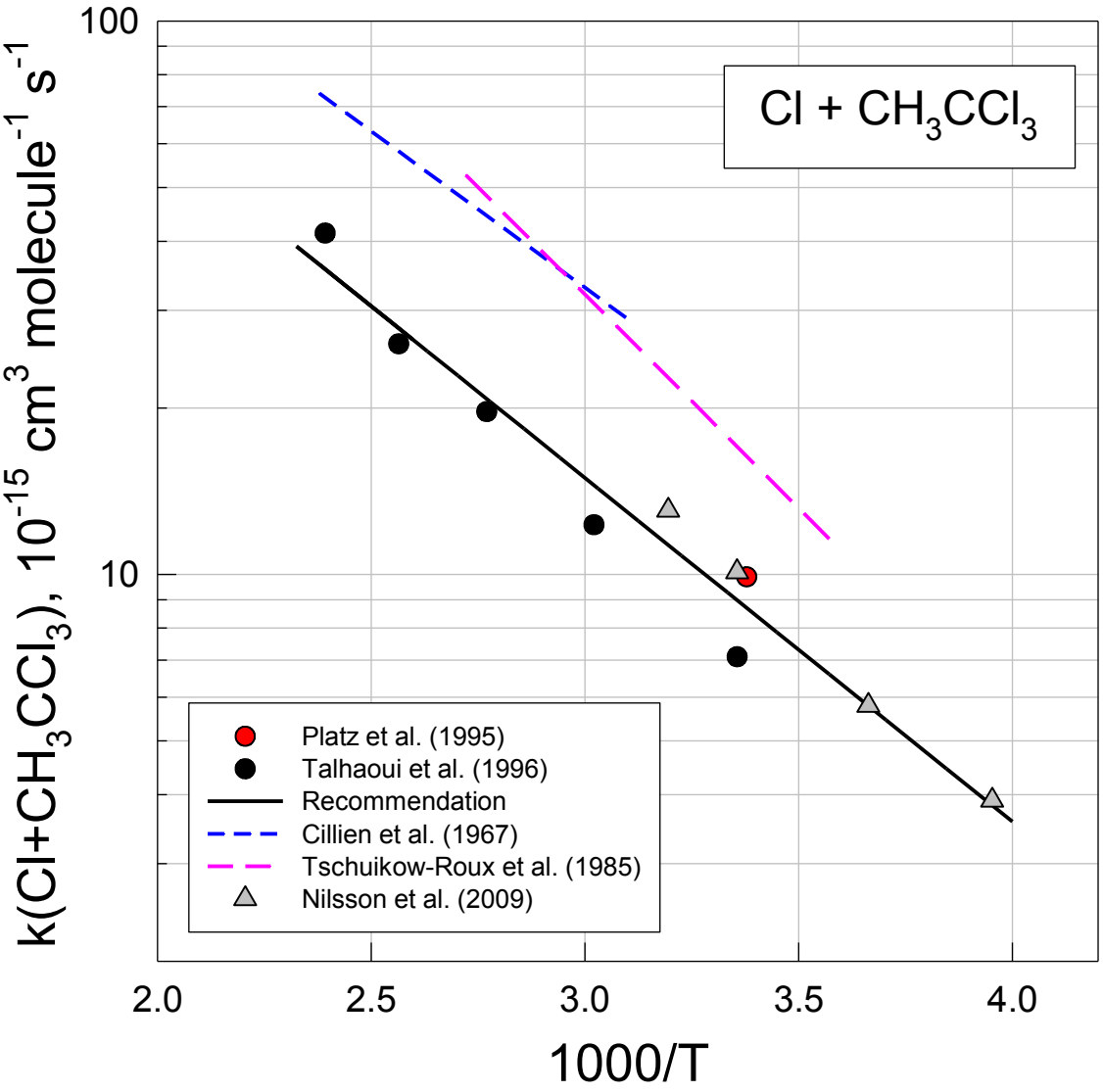
Cl + CH3CCl3
k(Cl+CH3CCl3), 10-15 cm3 molecule-1 s-1
100
10
2.0
2.5
3.0
3.5
4.0
1000/T
Platz et al. (1995)
Talhaoui et al. (1996)
Recommendation
Cillien et al. (1967)
Tschuikow-Roux et al. (1985)
Nilsson et al. (2009)