IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC12

This data sheet last evaluated June 2008 (with changes to the preferred values).

$Cl + CH_3C(O)CH_3 \rightarrow HCl + CH_3C(O)CH_2$

$\Delta H° = -20.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	***Reference***	Technique/ Comments
Absolute Rate Coefficients			
$(3.06 \pm 0.38) \times 10^{-12}$	298 ± 2	Notario et al., 2000	PLP-RF (a)
$(2.93 \pm 0.29) \times 10^{-12}$	298 ± 2	Albaladejo et al., 2003	PLP-RF (b)
$(2.20 \pm 0.14) \times 10^{-12}$	298	Martinez et al., 2004	DF-MS (c)
$(2.30 \pm 0.12) \times 10^{-12}$	295 ± 2	Takahashi et al., 2007	LP-LIF (d)
$1.53 \times 10^{-11} \exp[(-594 \pm 33)/T]$	210 - 440	Zhao et al., 2008	LP-RF (e)
$(2.07 \pm 0.31) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(2.3 \pm 0.2) \times 10^{-12}$	295 ± 2	Wallington et al., 1990	RR (f)
$(1.7 \pm 0.3) \times 10^{-12}$	294 ± 1	Olsson et al., 1997	RR (g)
$1.28 \times 10^{-11} \exp(-580 \pm 28)/T$	215 -298	Orlando et al., 2000	RR (h)
$(1.84 \pm 0.3) \times 10^{-12}$	298		
$(1.87 \pm 0.12) \times 10^{-12}$	296	Christensen et al., 2000	RR (i)
$(2.25 \pm 0.08) \times 10^{-12}$	296	Christensen et al., 2000	RR (j)
$(2.15 \pm 0.04) \times 10^{-12}$	296	Christensen et al., 2000	RR (k)
$(2.22 \pm 0.14) \times 10^{-12}$	296	Christensen et al., 2000	RR (l)
$(2.00 \pm 0.09) \times 10^{-12}$	298	Sellevåg and Nielsen, 2003	RR (m)
$(2.12 \pm 0.05) \times 10^{-12}$	298	Carr et al., 2003	RR (n)

Comments

(a) Experiments carried out at pressures of 15 or 60 Torr (20 or 80 mbar) He using the 355 nm photolysis of Cl_2 as Cl-atom source. Addition of 0.4 Torr (0.53 mbar) O_2 (to scavenge organic radicals and prevent secondary formation of Cl) resulted in similar rate coefficients.

(b) Experiments carried out at pressures of 26.7, 80 and 267 mbar He using the 308 nm photolysis of Cl_2 as Cl-atom source.

(c) Experiments at 1.33 mbar He

(d) Cl atoms ($^2P_{3/2}$) formed from Cl_2 / Ar photolysis at 351 nm and detected at 134.72 nm.

(e) Cl atoms generated in the 248 n photolysis of Cl_2CO. Experiments were conducted at pressures of ≈ 40-400 mbar N_2.

(f) Cl atoms were generated by the photolysis of Cl_2-air (or N_2)-$CH_3C(O)CH_3$-C_2H_5Cl mixtures. From the relative decays of CH_3COCH_3 and C_2H_5Cl, a rate coefficient ratio of $k(Cl + CH_3C(O)CH_3) / k(Cl + C_2H_5Cl) = 0.295 \pm 0.015$ was obtained. Absolute rate coefficient obtained using $k(Cl + C_2H_5Cl) = 7.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Wine et al, 1983 and Bryukov et al., 2003).

(g) Cl atoms were generated by pulsed laser photolysis of Cl_2 at 355 nm followed by competition between the reactions Cl + $CH_3C(O)CH_3$ and Cl + $ClONO_2 \rightarrow Cl_2 + NO_3$. The formation of NO_3 with and without acetone in the reaction mixture was monitored by TDLS at 661.8 nm. The value recommended in Yokelson et al. (1995) for the value of the rate constant of the reference reaction (Cl + $ClONO_2$) was used.

(h) Cl atoms were generated by the photolysis of Cl_2-$CH_3C(O)CH_3$-CH_2Cl_2 mixtures. From the relative decays of $CH_3C(O)CH_3$ and CH_2Cl_2, temperature dependent rate coefficient ratios of k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_2Cl_2) = 5.39 (298 K), 5.83 (267 K), 6.26 (251 K), 6.69 (240 K), 7.21 (225 K) and 7.72 (215 K) were derived. These ratios were placed on an absolute basis using k(Cl + CH_2Cl_2) = 5.9 x 10^{-12} exp(-850/T) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2008). The uncertainty given for E/R does not include uncertainty in the temperature dependence of k(Cl + CH_2Cl_2).

(i) Cl atoms were generated by the broad band photolysis of Cl_2 in O_2/N_2 at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to C_2H_5F to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + C_2H_5F) = 0.288 ± 0.017. Rate coefficient in table calculated using k(Cl + C_2H_5F) = 6.5 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2008).

(j) Cl atoms were generated by the broad band photolysis of Cl_2 in O_2/N_2 at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to CH_3Cl to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_3Cl) = 4.69 ± 0.16. Rate coefficient in table calculated using k(Cl + CH_3Cl) = 4.8 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2008).

(k) Cl atoms were generated by the broad band photolysis of Cl_2 in O_2/N_2 at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to CH_3F to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_3F) = 6.15 ± 0.26. Rate coefficient in table calculated using k(Cl + CH_3F) = 3.5 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2008).

(l) Cl atoms were generated by the broad band photolysis of Cl_2 in O_2/N_2 at 933 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to C_2H_5Cl to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + C_2H_5Cl) = 0.284 ± 0.018. Rate coefficient in table calculated using k(Cl + C_2H_5Cl) = 7.8 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Wine et al, 1983 and Bryukov et al., 2003).

(m) Broad band photolysis (370 nm) of Cl_2 in presence of $CH_3C(O)CH_3$ and CH_2ClCH_2Cl. Relative decay rates of $CH_3C(O)CH_3$ and CH_2ClCH_2Cl measured using FTIR. Value of k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_2ClCH_2Cl) = 1.54 ± 0.06 was placed on an absolute basis using k(Cl + CH_2ClCH_2Cl) = 1.3 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Wallington et al., 1996).

(n) Cl atoms were generated by the broad band photolysis of Cl_2 in air or N_2 at 973-1013 mbar. Consumption of $CH_3C(O)CH_3$ measured relative to CH_3Cl to derive k(Cl + $CH_3C(O)CH_3$) / k(Cl + CH_3Cl) = 4.42 ± 0.11. Rate coefficient in table calculated using k(Cl + CH_3Cl) = 4.8 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2005).

Preferred Values

$k = 2.10 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.50 \times 10^{-11} \exp(-590/T)$ cm^3 molecule^{-1} s^{-1}, over the temperature range 215-300 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
$\Delta(E/R) = \pm 150$

Comments on Preferred Values

There have been eleven studies of this reaction and, with the exception of Olsson et al. (1997), Albaladejo et al. (2003) and Notario et al. (2000), all suggest that the rate constant at room temperature is within 10 % of 2.1×10^{-12} cm^3 molecule^{-1} s^{-1}. Because of the potential for errors in the experimental technique of Olsson et al. (1997) (the assumption that Cl atoms only react with $ClONO_2$ and acetone, the need for absolute concentration measurements of acetone, and the experimental approach of sequential experiments in the presence and absence of acetone) these data are not considered when making the recommendation. The rate coefficients reported by Albaladejo et al. (2003) and Notario et al. (2000) are larger than all others, possibly due to secondary removal of Cl atoms with e.g. alkyl fragments or peroxy radicals.

For room temperature, the preferred value of k is an average of the results from Wallington et al. (1990), Orlando et al. (2000), Christensen et al. (2000), Sellevåg and Nielsen (2003), Carr et al. (2003), Martinez et al. (2004), Takahashi et al. (2007) and Zhao et al (2008).

The temperature dependent expression adopts the values of E/R from Zhao et al. (2008) and Orlando et al., (2000) with the pre-exponential factor adjusted to yield the recommended rate coefficient at 298 K.

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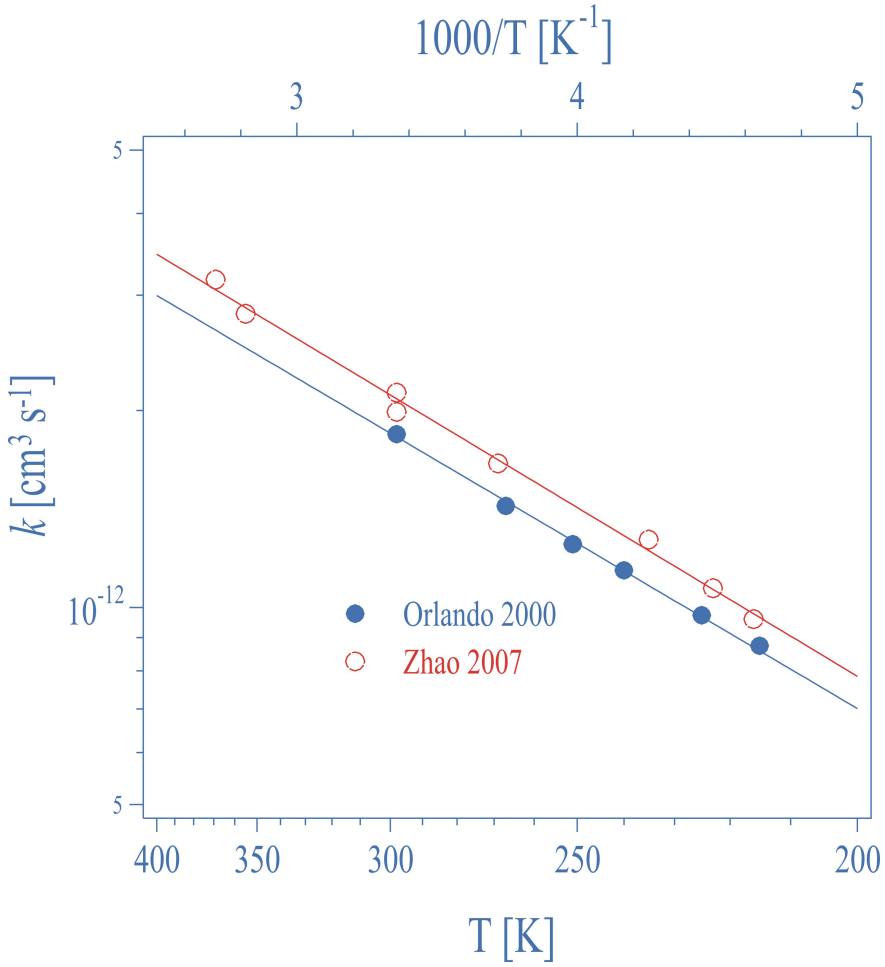
1000/T [K-1]
3
4
5
5
k [cm3 s-1]
10-12
5
Orlando 2000
Zhao 2007
400
350
300
250
200
T [K]