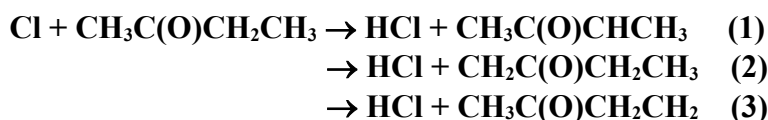


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC13

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

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



Rate coefficient data, $k = k_1 + k_2 + k_3$

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.24 \pm 0.38) \times 10^{-11}$	298 ± 2	Notario et al., 2000	LP-RF (a)
$(3.30 \pm 0.20) \times 10^{-11}$	298 ± 2	Albaladejo et al., 2003	LP-RF (b)
$7.30 \times 10^{-11} \exp[(-239 \pm 108)/T]$	270-380	Cuevas et al., 2004	LP-RF (c)
$(3.23 \pm 0.42) \times 10^{-11}$	298 ± 2		
$(4.08 \pm 0.21) \times 10^{-11}$	295 ± 2	Takahashi et al., 2007	LP-LIF (d)
$2.77 \times 10^{-11} \exp[(76 \pm 33)/T]$	210 - 440	Zhao et al., 2008	LP-RF (e)
$(3.66 \pm 0.55) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(4.28 \pm 0.59) \times 10^{-11}$	295 ± 2	Wallington et al., 1990	RR (f)
$(3.98 \pm 0.28) \times 10^{-11}$	296	Taketani et al., 2006	RR (g)
$(4.09 \pm 0.28) \times 10^{-11}$	296	Taketani et al., 2006	RR (h)
$(3.8 \pm 0.3) \times 10^{-11}$	296 ± 1	Kaiser and Wallington, 2007	RR (i)
<i>Branching Ratios</i>			
$k_1/k = 0.73 \pm 0.09$	296	Iwasaki et al., 2007	(j)

Comments

- 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.
- Cl generated from the 308 nm photolysis of Cl_2 .
- Cl (initially $3\text{-}5 \times 10^{11} \text{ cm}^{-3}$) generated from the 308 nm photolysis of Cl_2 .
- Cl atoms ($^2\text{P}_{3/2}$) at $\approx 3\text{-}10 \times 10^{10} \text{ molecule cm}^{-3}$ were formed from Cl_2 / Ar photolysis at 351 nm and detected at 134.72 nm.
- Cl atoms generated in the 248 nm photolysis of Cl_2CO . Experiments were conducted at pressures of $\approx 40\text{-}400 \text{ mbar N}_2$.
- Relative rate method in 931 mbar N_2 with Cl atoms generated from broad-band, CW photolysis of Cl_2 . Relative concentrations of $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ and the reference reactant (C_2H_6) monitored by FTIR to return $k(\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5) / k(\text{Cl} + \text{C}_2\text{H}_6) = 0.725 \pm 0.100$. This was placed on an absolute basis using $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- Relative rate method in 931 mbar N_2 with Cl atoms generated from broad-band, CW photolysis of Cl_2 . Relative concentrations of $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ and the reference reactant ($\text{C}_2\text{H}_5\text{Cl}$) monitored by FTIR. A rate constant ratio of $k(\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5) / k(\text{Cl} + \text{C}_2\text{H}_5\text{Cl}) = 4.95 \pm 0.35$ was obtained

and placed on an absolute basis using $k(\text{Cl} + \text{C}_2\text{H}_5\text{Cl}) = 8.04 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wine and Semmes, 1983).

- (h) as (g) but using C_2H_4 as reference. $k(\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5) / k(\text{Cl} + \text{C}_2\text{H}_4) = 0.44 \pm 0.03$ was obtained and placed on an absolute basis using $k(\text{Cl} + \text{C}_2\text{H}_4) = 9.29 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured in the same apparatus (Wallington et al., 1990a).
- (i) Relative rate method in 1067-1267 mbar N_2 with Cl atoms generated from broad-band, CW photolysis of Cl_2 . Relative concentrations of $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ and the reference reactants monitored by GC. Rate constant ratios of $k(\text{Cl} + \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5) / k(\text{Cl} + \text{C}_3\text{H}_8) = 0.27$ was placed on an absolute basis using $k(\text{Cl} + \text{C}_3\text{H}_8) = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (j) Broad-band, CW photolysis of Cl_2 in the presence of $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ in N_2 . Yields of $\text{CH}_3\text{C}(\text{O})\text{CHClCH}_3$ and $\text{CH}_3\text{C}(\text{O})\text{Cl}$ were used to derive the branching ratio to channel (1).

Preferred Values

$k = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296-298 K.

$k = 3.05 \times 10^{-11} \exp(80/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 200-450 K.

$k_1/k = 0.79$ at 296 K

Reliability

$\Delta \log k = \pm 0.08$

$\Delta(E/R) = \pm 100 \text{ K}$.

$\Delta \log(k_2/k) = 0.15$

Comments on Preferred Values

The reaction of Cl atoms with ketones proceeds almost exclusively via H abstraction. The absolute studies of Notario et al. (2000), Albaladejo et al. (2003) and Cuevas et al. (2004) may have suffered from secondary regeneration of Cl atoms from reaction of organic fragments with Cl_2 , resulting in an underestimation of k . This effect was reduced by Takahashi et al. (2007) by using lower Cl_2 concentrations and higher butanone concentrations, thus decoupling the time scales for primary loss and regeneration of Cl atoms. The use of phosgene as Cl source (Zhao et al., 2008) also avoids this problem. The results of Takahashi et al. (2007) and Zhao et al. (2008) are in good agreement with all the relative rate studies which, when combined, form the basis of the recommendation for $k(298 \text{ K})$.

The temperature dependence of k has been studied by Cuevas et al. (2004) and Zhao et al. (2008). The preferred value is that of Zhao et al. (2008), whose data are expected to be impacted less by secondary Cl formation (see above).

The branching ratio (at room temperature only) is taken from the single study of this parameter by Iwasaki et al. (2007).

References

- Albaladejo, J., Notario, A., Cuevas, C. A., Ballesteros, B. Martínez, E.: *J. Atmos. Chem.* 45, 35, 2003.
- Cuevas, C. A., Notario, A., Martínez, J., Albaladejo, J.: *Phys. Chem. Chem. Phys.* 6, 2230, 2004.
- IUPAC, 2013, <http://iupac.pole-ether.fr>.
- Iwasaki, E., Taketani, F., Takahashi, K., Matsumi, Y., Wallington, T. J., and Hurley, M. D.: *Chem. Phys. Lett.* 439, 274, 2007.
- Kaiser E. W., Wallington, T. J.: *J. Phys Chem.* 111, 10669, 2007
- Notario, A., Mellouki, A., and Le Bras, G.: *Int. J. Chem. Kinet.* 32, 62, 2000.
- Takahashi, K., Iwasaki, E., Matsumi, Y., and Wallington, T. J.: *J. Phys. Chem. A* 111, 1271, 2007. (Erratum: *J. Phys. Chem. A* 111, 8044, 2007).

Taketani, F., Matsumi, Y., Wallington, T. J., and Hurley, M. D.: Chem. Phys. Lett. 431, 257, 2006.
Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem. 10, 301, 1990
Wallington, T. J., Andino, J., Lorkovic, A. M., Kaiser, E.W., Marston, G.: J. Phys. Chem. 94, 3644, 1990a.
Wine, P. H. and Semmes, D.H.: J. Phys. Chem. 87, 4572, 1983.
Zhao, Z., Huskey, D. T., Nicovich, M., and Wine, P. H.: Int. J. Chem. Kin. 40, 259, 2008.