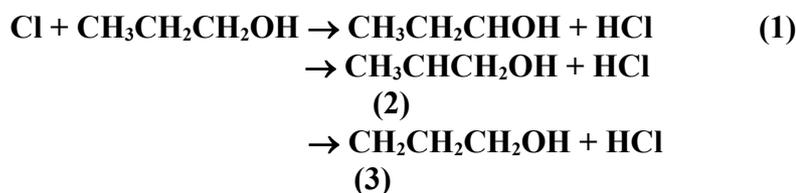


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC16

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> | | | |
| $(1.71 \pm 0.11) \times 10^{-10}$ | 295 | Taketani et al., 2005 | LP-LIF (a) |
| $(1.53 \pm 0.12) \times 10^{-10}$ | 298 | Garzón et al., 2006 | LP-RF (b) |
| $2.63 \times 10^{-11} \exp[(525 \pm 51)/T]$ | 266-381 | | |
| <i>Relative Rate Coefficients</i> | | | |
| $(1.49 \pm 0.12) \times 10^{-10}$ | 295 ± 2 | Wallington et al., 1988 | RR (c) |
| $(1.53 \pm 0.07) \times 10^{-10}$ | 298 ± 2 | Nelson et al., 1990 | RR (d) |
| $2.68 \times 10^{-10} \exp[-(128 \pm 20)/T]$ | 273-342 | Cheema et al., 2001 | RR (e) |
| $(1.69 \pm 0.20) \times 10^{-10}$ | 298 | | |
| $(1.64 \pm 0.14) \times 10^{-10}$ | 295 | Wu et al., 2003 | RR (f) |
| $(1.56 \pm 0.12) \times 10^{-10}$ | 295 | Wu et al., 2003 | RR (g) |
| $(1.93 \pm 0.13) \times 10^{-10}$ | 296 | Yamanaka et al., 2007 | RR (h) |
| $(1.52 \pm 0.09) \times 10^{-10}$ | 296 | Yamanaka et al., 2007 | RR (i) |
| <i>Branching ratios</i> | | | |
| $k_1 / k = 0.56$ | 298 | Cheema et al., 2001 | (e) |
| $k_2 / k = 0.30$ | 298 | | |
| $k_3 / k = 0.14$ | 298 | | |
| $k_1 / k = 0.60 \pm 0.05$ | 296 | Yamanaka et al., 2007 | (j) |
| $k_2 / k = 0.25 \pm 0.08$ | 296 | | |
| $k_3 / k = 0.15 \pm 0.03$ | 296 | | |

Comments

- (a) 193 nm photolysis of HCl to generate both excited $\text{Cl}(^2\text{P}_{1/2})$ and ground state $\text{Cl}(^2\text{P}_{3/2})$, which were detected using VUV LIF at 135.2 and 134.7 nm, respectively. $\text{Cl}(^2\text{P}_{3/2})$ decays were monitored in presence of CF_4 to ensure removal of $\text{Cl}(^2\text{P}_{1/2})$. The rate coefficient for excited Cl atoms was determined as $(8.5 \pm 2.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (b) Cl atoms generated by Cl_2 photolysis at 308 nm and detected by RF at ≈ 135 nm. All experiments in He bath gas (26.7-266.7 mbar) with traces of O_2 to scavenge organic radicals. k was independent of pressure.
- (c) Cl atoms were generated by photolysis of Cl_2 in Cl_2 - n - $\text{C}_3\text{H}_7\text{OH}$ - C_2H_6 -air (or N_2) mixtures at 990 mbar (740 Torr) total pressure. n - $\text{C}_3\text{H}_7\text{OH}$ and C_2H_6 were monitored by GC and a rate coefficient

ratio $k(\text{Cl} + n\text{-C}_3\text{H}_7\text{OH}) / k(\text{Cl} + \text{C}_2\text{H}_6) = 2.518 \pm 0.202$ determined. Placed on an absolute basis by use of $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).

- (d) Cl atoms were generated by the photolysis of Cl_2 or COCl_2 in Cl_2 (or COCl_2)- N_2 (or O_2)- n -propanol-cyclohexane mixtures at 1 bar pressure. Decay rates of n -propanol and cyclohexane were measured by GC, and the rate coefficient ratio placed on an absolute basis by use of $k(\text{Cl} + \text{cyclohexane}) / k(\text{Cl} + n\text{-butane}) = 1.59$ (Aschmann and Atkinson, 1995) and $k(\text{Cl} + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (e) The reaction was initiated in 100, 250 or 1000 cm^3 Pyrex vessels by photolysis of Cl_2 in presence of O_2 , NO , $n\text{-C}_3\text{H}_7\text{OH}-\text{C}_2\text{H}_6$ and N_2 mixtures at 700 Torr total pressure. $n\text{-C}_3\text{H}_7\text{OH}$ and C_2H_6 were monitored by GC and rate coefficient ratios $k(\text{Cl} + n\text{-C}_3\text{H}_7\text{OH}) / k(\text{Cl} + \text{C}_2\text{H}_6)$ determined at temperatures between 273 and 342 K. Placed on an absolute basis by use of $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.3 \times 10^{-11} \exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008). Product analysis in separate FTIR experiments combined with an assumed reaction scheme to give branching ratios.
- (f) Photolysis of Cl_2 in presence of $n\text{-C}_3\text{H}_7\text{OH}$ using propane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio $k(\text{Cl} + n\text{-C}_3\text{H}_7\text{OH}) / k(\text{Cl} + \text{C}_3\text{H}_8) = (1.168 \pm 0.099)$ was put 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).
- (g) Photolysis of Cl_2 in presence of n -propanol using cyclohexane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio $k(\text{Cl} + n\text{-C}_3\text{H}_7\text{OH}) / k(\text{Cl} + \text{cyclohexane}) = (0.479 \pm 0.036)$ was put on an absolute basis using $k(\text{Cl} + \text{cyclohexane}) = 3.26 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which was derived using $k(\text{Cl} + \text{cyclohexane}) / k(\text{Cl} + n\text{-butane}) = 1.59$ (Aschmann and Atkinson, 1995) and $k(\text{Cl} + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (h) Photolysis of Cl_2 in presence of $n\text{-C}_3\text{H}_7\text{OH}$ using C_2H_4 as reference reactant and 933 mbar N_2 as bath gas. $k(n\text{-C}_3\text{H}_7\text{OH}) / k(\text{C}_2\text{H}_4) = (1.84 \pm 0.13)$ was obtained and placed on an absolute basis using $k(\text{C}_2\text{H}_4) = 1.03 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (i) Photolysis of Cl_2 in presence of $n\text{-C}_3\text{H}_7\text{OH}$ using C_3H_6 as reference reactant and 933 mbar N_2 as bath gas. $k(n\text{-C}_3\text{H}_7\text{OH}) / k(\text{C}_3\text{H}_6) = (0.66 \pm 0.04)$ was obtained and placed on an absolute basis using $k(\text{C}_3\text{H}_6) = 2.30 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (j) Steady state UV irradiation of $n\text{-C}_3\text{H}_7\text{OH}/\text{Cl}_2$ mixtures in 933 mbar of N_2 diluent. FTIR spectroscopy was used to observe and quantify the formation of the chlorides $\text{CH}_3\text{CH}_2\text{CHClOH}$ and $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{OH}$. The difference between unity and sum of the yields of $\text{CH}_3\text{CH}_2\text{CHClOH}$ and $\text{CH}_2\text{ClCH}_2\text{CH}_2\text{OH}$ was ascribed to the yield of $\text{CH}_3\text{CHClCH}_2\text{OH}$.

Preferred Values

$k = 1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(525/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270 K to 350 K.

$k_1 / k = 0.60$ at 298 K

$k_2 / k = 0.25$ at 298 K

$k_3 / k = 0.15$ at 298 K

Reliability

$\Delta \log k = \pm 0.07$ at 298 K.

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

$\Delta \log (k_1 / k) = 0.07$ at 298 K

$\Delta \log (k_2 / k) = 0.15$ at 298 K

$\Delta \log (k_3 / k) = 0.12$ at 298 K

Comments on Preferred Values

The preferred 298 K rate coefficient is an un-weighted average of all absolute and relative studies, which are in good agreement. We note the difference in activation energies reported by Cheema et al. (2001) and Garzón et al. (2006) and have adopted the temperature dependence from the absolute study (Garzón et al., 2006). The branching ratios near 298 K reported by Cheema et al. (2001) and Yamanaka et al. (2008) are in good agreement. We adopt the branching ratios from Yamanaka et al. (2008) which were obtained in a more direct fashion. The branching ratios are expected to be approximately independent of temperature over the atmospheric temperature range, but until this is confirmed, we make no recommendation of the temperature dependence.

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