IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC17

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

$Cl + CH_3CH(OH)CH_3 \rightarrow CH_3C(OH)CH_3 + HCl$ (1)

$\rightarrow CH_3CH(OH)CH_2 + HCl$ (2)

Rate coefficient data, $k = k_1 + k_2$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(9.11 \pm 0.60) \times 10^{-11}$	295	Taketani et al., 2005	LP-LIF (a)
Relative Rate Coefficients			
$(8.80 \pm 0.35) \times 10^{-11}$	298 ± 2	Nelson et al., 1990	RR (b)
$(7.85 \pm 0.39) \times 10^{-11}$	295	Wu et al., 2003	RR (c)
$(8.77 \pm 0.78) \times 10^{-11}$	295	Wu et al., 2003	RR (d)
$(8.14 \pm 0.51) \times 10^{-11}$	296	Yamanaka et al., 2007	RR (e)
$(9.37 \pm 0.72) \times 10^{-11}$	296	Yamanaka et al., 2007	RR (f)
Branching Ratios			
$k_1 / k = (0.85 \pm 0.07)$	296	Yamanaka et al., 2007	(g)
$k_2 / k = (0.15 \pm 0.07)$			

Comments

(a) 193 nm photolysis of HCl to generate both excited $Cl(^2P_{1/2})$ and ground state $Cl(^2P_{3/2})$, which were detected using VUV LIF at 135.2 and 134.7 nm, respectively. $Cl(^2P_{3/2})$ decays were monitored in presence of CF_4 to ensure removal of $Cl(^2P_{1/2})$. The rate coefficient for excited Cl atoms was determined as $(8.5 \pm 2.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(b) Cl atoms were generated by the photolysis of Cl_2 or $C(O)Cl_2$ in isopropyl alcohol-cyclohexane-O_2 (or N_2) mixtures at 1 bar pressure. The decay rates of isopropyl alcohol and cyclohexane were measured, and rate coefficient ratio placed on an absolute basis by use of k(Cl + cyclohexane) / k(Cl + n-butane) = 1.59 (Aschmann and Atkinson, 1995) and k(Cl + n-butane) = 2.05×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2008).

(c) Photolysis of Cl_2 in presence of i-C_3H_7OH using propane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio k(Cl + i-C_3H_7OH) / k(Cl + C_3H_8) = (0.561 ± 0.028) was put on an absolute basis using k(Cl + C_3H_8) = 1.4×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2008).

(d) Photolysis of Cl_2 in presence of i-C_3H_7OH using cyclohexane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio k(Cl + i-C_3H_7OH) / k(Cl + cyclohexane) = (0.269 ± 0.024) was put on an absolute basis using k(Cl + cyclohexane) = 3.26×10^{-10} cm^3 molecule^{-1} s^{-1} which was derived using k(Cl + cyclohexane) / k(Cl + n-butane) = 1.59 (Aschmann and Atkinson, 1995) and k(Cl + n-butane) = 2.05×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2008).

(e) Photolysis of Cl_2 in presence of i-C_3H_7OH using C_2H_2 as reference reactant and 933 mbar N_2 as bath gas. $k(i\text{-}C_3H_7OH) / k(C_2H_2) = (1.60 \pm 0.10)$ was obtained and placed on an absolute basis using $k(C_2H_2) = 5.09 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2008).

(f) Photolysis of Cl_2 in presence of i-C_3H_7OH using C_2H_4 as reference reactant and 933 mbar N_2 as bath gas. $k(i\text{-}C_3H_7OH) / k(C_2H_4) = (0.91 \pm 0.07)$ was obtained and placed on an absolute basis using $k(C_2H_4) = 1.03 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2008).

(g) Branching ratios obtained by measuring products resulting from reaction of the primary radicals $CH_3C(OH)CH_3$ and $CH_3CH(OH)CH_2$ with Cl_2 and their decomposition products.

Preferred Values

$k = 8.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 7.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 1.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.06$ at 298 K.
$\Delta\log k_1 = \pm 0.10$ at 298 K.
$\Delta\log k_2 = \pm 0.10$ at 298 K.

Comments on Preferred Values

The six, room temperature, studies of this reaction are in good agreement and the preferred value of k is an unweighted average. The preferred values for k_1 and k_2 are based on the only measurements of the branching ratios available (Yamanaka et al., 2007).

References

Aschmann, S. M. and Atkinson, R.: Int. J. Chem. Kinet. 27, 613, 1995.
IUPAC: http://iupac.pole-ether.fr, 2013.
Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O. J.: Int. J. Chem. Kinet. 22, 1111, 1990.
Taketani, F., Takahashi, K., Matsumi, Y. and Wallington, T. J.: J. Phys. Chem. A 109, 3955, 2005.
Wu, H., Mu, Y., Zhang, X. and Jiang, G.: Int. J. Chem. Kinet. 35, 81, 2003.
Yamanaka, T., Kawasaki, M., Hurley, M. D., Wallington, T. J., Schneider, W. F. and Bruce, J.: Phys. Chem. Chem. Phys. 9, 4211, 2007.