IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC34

This datasheet last evaluated: June 2018; last change in preferred values: 2018

$Cl + i\text{-}C_4H_9OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.95 \pm 0.04) \times 10^{-10}$	295	Wu et al., 2003	RR (a)
$(2.11 \pm 0.12) \times 10^{-10}$	295	Wu et al., 2003	RR (b)
$(2.31 \pm 0.16) \times 10^{-10}$	296	Andersen et al., 2010	RR (c)
$(1.99 \pm 0.23) \times 10^{-10}$			RR (d)

Comments

(a) Photolysis of Cl_2 in presence of i-C_4H_9OH using propane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio $k(Cl + i\text{-}C_4H_9OH) / k(Cl + C_3H_8) = (1.39 \pm 0.03)$ was put on an absolute basis using $k(Cl + C_3H_8) = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(b) Photolysis of Cl_2 in presence of i-C_4H_9OH using cyclohexane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio $k(Cl + i\text{-}C_4H_9OH) / k(Cl +$ cyclohexane$) = (0.648 \pm 0.036)$ was put on an absolute basis using $k(Cl +$ cyclohexane$) = 3.26 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} which was derived from $k(Cl +$ cyclohexane$) / k(Cl +$ i-butane$) = 1.59$ (Aschmann and Atkinson, 1995) and $k(Cl +$ i-butane$) = 2.05 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(c) Cl was generated by the photolysis of Cl_2. Experiments were conducted in 700 Torr air with reactant concentrations monitored by FTIR. Using C_2H_4 as reference reactant, the rate coefficient ratio $k(Cl + i\text{-}C_4H_9OH) / k(Cl + C_2H_4) = (2.24 \pm 0.16)$ was obtained. This was placed on an absolute basis using $k(Cl + C_2H_4) = 1.03 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(d) See note (e). Using cyclohexane as reference reactant, the rate coefficient ratio $k(Cl + i\text{-}C_4H_9OH) / k(Cl +$ cyclohexane$) = (0.61 \pm 0.07)$ was obtained. This was placed on an absolute basis using $k(Cl +$ cyclohexane$) = 3.26 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} which was derived from $k(Cl +$ cyclohexane$) / k(Cl +$ i-butane$) = 1.59$ (Aschmann and Atkinson, 1995) and $k(Cl +$ i-butane$) = 2.05 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

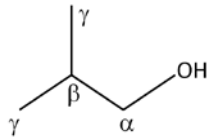
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.1 x 10^{-10}	298
Reliability		
$\Delta \log k$	± 0.07	298

Comments on Preferred Values

The preferred room temperature rate coefficient is an average value from the four relative-rate studies of this reaction, which are in good agreement.

The products formed following reaction of Cl with *i*-butanol in air depend on the site (α, β, γ) at which the Cl-atom abstracts an H-atom, with *i*-butyraldehyde formed following H-abstraction at the α position, acetone and HCHO following H-abstraction at the β-site and acetaldehyde following H-abstraction at the γ-site.



Modelling of time dependent concentration profiles of *i*-butanol, *i*-butyraldehyde, acetone, HCHO and HCHO enabled McGillen et al (2016) to derive fractional reactivities of each site of 0.48 ± 0.04 (α), 0.35 ± 0.04 (β) and 0.17 ± 0.04 (γ), which are consistent with the molar yields of *i*-butyraldehyde (0.46 ± 0.03) and acetone (0.35 ± 0.03) reported by Andersen et al., (2010).

References

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