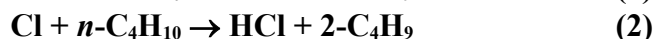
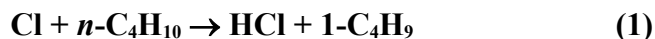


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X\_VOC8

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 updated: 3<sup>rd</sup> July 2005.



### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.15 \times 10^{-10} \exp[(12 \pm 26)/T]$	298-598	Lewis et al., 1980	DF-RF (a)
$(2.25 \pm 0.10) \times 10^{-10}$	298		
$(1.8 \pm 0.2) \times 10^{-10}$	298	Nesbitt and Leone, 1982	(b)
$(2.11 \pm 0.18) \times 10^{-10}$	298	Beichert et al., 1995	DF-RF (c)
$(2.15 \pm 0.15) \times 10^{-10}$	298	Tyndall et al., 1997	FP-RF (d)
$(1.91 \pm 0.10) \times 10^{-10}$	298	Qian et al., 2002	PLP-TDLS (e)
$(2.05 \pm 0.15) \times 10^{-10}$	298	Hitsuda et al., 2001	PLP-LIF (f)
<i>Branching Ratios</i>			
$k_1/k = 0.29 \pm 0.02$	298	Tyndall et al., 1997	GC
$k_2/k = 0.71 \pm 0.02$	298	Tyndall et al., 1997	GC
$k_1/k = 0.44 \exp[-(122 \pm 104)/T]$	295-469	Sarzynski and Sztuba, 2002	RR (g)
$k_1/k = (0.29 \pm 0.03)$	295		
$k_2/k = 0.59 \exp[(56 \pm 100)/T]$	295-469		
$k_2/k = (0.71 \pm 0.07)$	295		

### Comments

- Rate constant was measured at three temperatures: 298 K, 422 K and 598 K. Within experimental uncertainty, these three values were the same. Authors gave as an alternative rate expression the simple mean of the three values:  $k = (2.20 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- Laser photodissociation of  $\text{Cl}_2$  with time-resolved monitoring of infrared emission of HCl ( $\nu = 1$ ) product.
- Both relative and absolute rate studies of reactions of Cl atoms with  $\text{C}_1$  to  $\text{C}_4$  alkanes. Direct measurement of ratio  $k / k(\text{Cl} + \text{C}_2\text{H}_6)$  is in very good agreement with the ratio of the absolute values.
- Both relative and absolute rate studies of reactions of Cl atoms with  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $n\text{-C}_4\text{H}_{10}$ . Measurements of  $k / k(\text{Cl} + \text{C}_2\text{H}_6)$  over the temperature range 298 K to 540 K indicate essentially zero temperature dependence for  $k$ . GC measurements at 298 K show that the reaction  $\text{Cl} + n\text{-C}_4\text{H}_{10}$  yields  $(29 \pm 2)\%$  1-butyl radicals and  $(71 \pm 2)\%$  2-butyl radicals.
- 193 nm Laser photolysis of  $(\text{ClOC})_2$  to form Cl. Kinetics of reaction derived from HCl formation profiles, measured using infra red diode laser absorption spectroscopy.
- 193 nm photolysis of HCl as Cl source. Detection of both  $\text{Cl}(^2\text{P}_{1/2})$  and  $\text{Cl}(^2\text{P}_{3/2})$  using VUV-LIF. The rate constant for  $\text{Cl}(^2\text{P}_{1/2})$  was found to be  $\approx 30\%$  that of the  $\text{Cl}(^2\text{P}_{3/2})$  ground state.
- Photochlorination experiments with Cl atoms initially generated by the 420 nm photolysis of  $\text{Cl}_2$  in  $\text{N}_2$  at a total pressure of  $\approx 133$  mbar. Relative formation rates of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  (abstraction of

primary H) and  $\text{CH}_3\text{CHClCH}_2\text{CH}_3$  (abstraction of secondary H) were used to derive the branching ratios  $k_1/k$  and  $k_2/k$ .

### Preferred Values

$k = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 290-600 K.

$k_1/k = 0.44 \exp(-120/T)$

$k_2/k = 0.59 \exp(55/T)$

#### *Reliability*

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

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

#### *Comments on Preferred Values*

The preferred value at room temperature is the mean of the values reported by Beichert et al. (1995), Tyndall et al. (1997), Qian et al. (2002) and Hitsuda et al. (2001). The temperature independence is based on the results of Lewis et al. (1980) over the range 298 K to 598 K and is supported by the relative measurements of Tyndall et al. (1997) over the range 298 K to 540 K. Tyndall et al. (1997) studied the mechanism of the reaction at 298 K and reported the yield of 1-butyl radicals to be  $(29 \pm 2)\%$  and that of 2-butyl radicals to be  $(71 \pm 2)\%$ . This is in excellent agreement with the results of Sarzynski and Sztuba (2002), who also report a weak temperature dependence in the branching ratio.

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