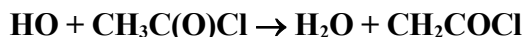


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx70

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This datasheet last evaluated: June 2015; last change in preferred values: November 2003.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.66 \pm 0.20) \times 10^{-14}$	298 ± 2	Nádasdi et al. (2006)	DF-RF
<i>Relative Rate Coefficients</i>			
6.8×10^{-14}	298 ± 3	Nelson et al., 1984, 1990	RR (a)

Comments

- (a) HO radicals were generated by the photolysis of CH_3ONO in $\text{CH}_3\text{ONO-NO-CH}_3\text{C}(\text{O})\text{Cl-CHCl}_3$ (the reference compound)-air mixtures at 987 mbar pressure. The concentrations of $\text{CH}_3\text{C}(\text{O})\text{Cl}$ and CHCl_3 were monitored during the experiments by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{Cl})/k(\text{HO} + \text{CHCl}_3) \sim 0.65$ is placed on an absolute basis using $k(\text{HO} + \text{CHCl}_3) = 1.05 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson et al., 2008).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.7×10^{-14}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the absolute rate coefficient of Nádasdi et al. (2006). The relative rate coefficient of Nelson et al. (1984) and Nelson et al. (1990) given in the table above was taken from the data presented in Table I and Figure 2 of Nelson et al. (1984) and in Figure 5 of Nelson et al. (1990), which are the same data-set. Note that Table I of Nelson et al. (1990) cites a rate coefficient a factor of 7 lower [$(9.1 \pm 3.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $298 \pm 3 \text{ K}$], inconsistent with the data presented in their Figure 5 and with the data presented in Nelson et al. (1984). The rate coefficient derived from the relative rate study of Nelson et al. (1984, 1990) is a factor of approximately 4 greater than that derived from the absolute rate study of Nádasdi et al. (2006). Nelson et al. (1984, 1990) used CH_3ONO as a

source of HO radicals. While photolysis of CH₃ONO is a convenient source of HO radicals, it is not well suited to the study of less reactive compounds because CH₃ONO itself reacts with HO at a moderate rate, approximately $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Tuazon et al., 1983; Nielsen et al., 1991), scavenges HO radicals, and makes loss of a less reactive compound (e.g., CH₃C(O)Cl) small and difficult to measure.

The loss of CH₃C(O)Cl observed by Nelson et al. (1984, 1990) was approximately 1-12%. The discrepancy between the relative rate study of Nelson et al. (1984, 1990) and the absolute rate study of Nádásdi et al. (2006) probably reflects the contribution of unwanted secondary losses of CH₃C(O)Cl in the relative rate experiments.

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