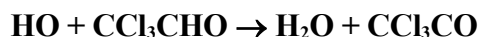


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx69

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This data sheet 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>			
$1.25 \times 10^{-11} \exp[-(600 \pm 90)/T]$	298-520	Dóbbé et al., 1989	DF-RF/LIF
$(1.56 \pm 0.34) \times 10^{-12}$	298		
$(8.7 \pm 1.7) \times 10^{-13}$	298	Balestra-Garcia et al., 1992	PLP-RF
$(1.28 \pm 0.25) \times 10^{-12}$	298 ± 2	Barry et al., 1994	DF-RF
$(8.9 \pm 1.5) \times 10^{-13}$	298 ± 2	Barry et al., 1994	DF-EPR
$1.79 \times 10^{-12} \exp[-(240 \pm 60)/T]$	233-415	Talukdar et al., 2001	PLP-LIF
$(8.3 \pm 0.8) \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
$(1.63 \pm 0.29) \times 10^{-12}$	298 ± 3	Nelson et al., 1990	RR (a)
$(1.5 \pm 0.2) \times 10^{-12}$	298 ± 2	Scollard et al., 1993	RR (b)
$(9.5 \pm 0.3) \times 10^{-13}$	298 ± 2	Barry et al., 1994	RR (c)

Comments

- (a) HO radicals were generated by the photolysis of CH₃ONO in CH₃ONO-CCl₃CHO-ethyl acetate (the reference compound)-air mixtures at 987 mbar pressure, and NO and ethene were added to the reactant mixtures to scavenge Cl atoms formed from the photolysis of CCl₃CHO. The concentrations of CCl₃CHO and ethyl acetate were measured by GC and/or FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CCl}_3\text{CHO})/k(\text{HO} + \text{ethyl acetate})$ is placed on an absolute basis using $k(\text{HO} + \text{ethyl acetate}) = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1989).
- (b) HO radicals were generated by the photolysis of CH₃ONO or C₂H₅ONO in CH₃ONO (or C₂H₅ONO)-CCl₃CHO-toluene-air mixtures at 987 ± 13 mbar pressure. The concentrations of CCl₃CHO and toluene were measured by GC and/or FTIR spectroscopy. Scollard et al. (1993) did not report a value for the rate coefficient ratio $k(\text{HO} + \text{CCl}_3\text{CHO})/k(\text{HO} + \text{toluene})$. Dividing the reported value of $k(\text{HO} + \text{CCl}_3\text{CHO})$ by the value of $k(\text{HO} + \text{toluene})$ used by Scollard et al. (1993) gives $k(\text{HO} + \text{CCl}_3\text{CHO})/k(\text{HO} + \text{toluene}) = 0.268 \pm 0.034$ which is placed on an absolute basis in the table above using a rate coefficient of $k(\text{HO} + \text{toluene}) = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Calvert et al., 2002).
- (c) HO radicals were generated by the photolysis of O₃ in the presence of water vapor in O₃-H₂O-CCl₃CHO-2-methylpropane-air mixtures at ~1 bar pressure. The concentrations of CCl₃CHO and 2-methylpropane were measured by GC. The measured rate coefficient ratio $k(\text{HO} + \text{CCl}_3\text{CHO})/k(\text{HO} + \text{2-methylpropane}) = 0.45 \pm 0.01$ is placed on an absolute basis using $k(\text{HO} + \text{2-methylpropane}) = 2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	8.0×10^{-13}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.8 \times 10^{-12} \exp(-240/T)$	230-420
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta(E/R)$	± 200	230-420

Comments on Preferred Values

The absolute and relative rate study of Barry et al. (1994) supersedes the earlier studies of Nelson et al. (1990), Balestra-Garcia et al. (1992) and Scollard et al. (1993). The three independent determinations of the rate coefficient by Barry et al. (1994) are all lower than the absolute 298 K rate coefficient of Dóbé et al. (1989), as is the most recent absolute room temperature rate coefficient of Talukdar et al. (2001). The most recent and extensive study of Talukdar et al. (2001) obtains a room temperature rate coefficient which agrees with the lowest of the previously reported 298 K rate coefficients, these being the PLP-RF rate coefficient of Balestra-Garcia et al. (1992) and the DF-EPR rate coefficient of Barry et al. (1994). The temperature dependence of the rate coefficient measured by Talukdar et al. (2001) is also significantly smaller than that reported by Dóbé et al. (1989). The potential exists for erroneously high measured rate coefficients because of secondary reactions involving Cl atoms generated from the photolysis of CCl_3CHO , as well as for erroneously low measured rate coefficients because of wall adsorption losses of CCl_3CHO . The concentrations of CCl_3CHO were measured by UV absorption at 213.9 nm before and after the reaction cell in the Talukdar et al. (2001) study, and losses were shown to be of no importance (<2%). The preferred values are therefore based on the absolute rate coefficients of Talukdar et al. (2001).

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