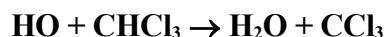


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx42

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. The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: Atmos. Chem. Phys., 9, 4141, 2008; IUPAC Task Group on Atmospheric Kinetic Data Evaluation, <http://iupac.pole-ether.fr>. This datasheet last evaluated: June 2015; last change in preferred values: November 2003.



$$\Delta H^\circ = -104.6 \text{ kJ mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.01 \pm 0.15) \times 10^{-13}$	296 ± 2	Howard and Evenson, 1976	DF-LMR
$4.69 \times 10^{-12} \exp[-(1134 \pm 108)/T]$	245-375	Davis et al., 1976	FP-RF
$(1.14 \pm 0.07) \times 10^{-13}$	298		
$6.91 \times 10^{-20} T^{2.65} \exp[-(262 \pm 398)/T]$	249-487	Jeong and Kaufman, 1982;	DF-RF
$(1.01 \pm 0.065) \times 10^{-13}$	298	Jeong et al., 1984	
$4.65 \times 10^{-17} T^{1.52} \exp[-(261 \pm 42)/T]$	295-775	Taylor et al., 1993	PLP-LIF (a)
$(1.12 \pm 0.10) \times 10^{-13}$	295		
<i>Relative Rate Coefficients</i>			
$1.53 \times 10^{-13}$	298	Cox et al., 1976	RR (b)
$1.46 \times 10^{-18} T^2 \exp[-(85 \pm 64)/T]$	288-357	Hsu and DeMore, 1994	RR (c)
$9.75 \times 10^{-14}$	298		

### Comments

- (a) These data supersede the earlier data from this group (Taylor et al., 1989).
- (b) HO radicals were generated by the photolysis of HONO-air mixtures at 1013 mbar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of CHCl<sub>3</sub> on NO formation and a rate coefficient for the reaction of HO radicals with CH<sub>4</sub> of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson et al., 2006), the rate coefficient cited in the table is obtained.
- (c) HO radicals were generated by the UV photolysis of O<sub>3</sub> in the presence of water vapor. The concentrations of CHCl<sub>3</sub> and CH<sub>3</sub>CHF<sub>2</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHCl}_3)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.52 \pm 0.11) \exp[(495 \pm 64)/T]$  is placed on an absolute base using  $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson et al., 2008).

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.05 \times 10^{-13}$	298

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.8 \times 10^{-12} \exp(-850/T)$	240-300
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.10$	298
$\Delta(E/R)$	$\pm 300$	240-300

#### *Comments on Preferred Values*

The room temperature rate coefficients of Howard and Evenson (1976), Davis et al. (1976), Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994) are in good agreement, ranging from  $9.75 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to  $1.14 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, the temperature dependencies obtained by Davis et al. (1976), Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994) differ significantly, with Davis et al. (1976) and Jeong and Kaufman (1982) determining larger temperature dependencies than obtained by Taylor et al. (1992) and Hsu and DeMore (1994). Note that only two rate coefficients have been measured at temperatures  $<288 \text{ K}$ , one by Davis et al. (1976) at  $245 \text{ K}$  and the other by Jeong and Kaufman (1982) at  $249 \text{ K}$ .

The  $298 \text{ K}$  preferred value is an average of the room temperature rate coefficients of Howard and Evenson (1976), Davis et al. (1976), Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994). The temperature dependence for the temperature range  $240\text{-}300 \text{ K}$  is obtained by averaging the Arrhenius activation energies centered at  $265 \text{ K}$ , with those of Jeong and Kaufman (1982), Taylor et al. (1993) and Hsu and DeMore (1994) being derived from the three parameter expressions cited in the table with  $B = D + nT$  (the Arrhenius activation energies being  $1134 \text{ K}$  for the Davis et al. (1976) study,  $964 \text{ K}$  for the Jeong and Kaufman (1982) study,  $664 \text{ K}$  for the Taylor et al. (1993) study and  $615 \text{ K}$  for the Hsu and DeMore (1994) study, all centered at  $265 \text{ K}$ ). The preferred Arrhenius expression, which should not be used outside of the temperature range  $240\text{-}300 \text{ K}$ , leads to rate coefficients at  $245 \text{ K}$  and  $249 \text{ K}$  which are  $28\%$  and  $8\%$  higher than those measured by Davis et al. (1976) and Jeong and Kaufman et al. (1982), respectively (note that the recommended Arrhenius expression for the temperature range  $240\text{-}300 \text{ K}$  is equivalent to the three parameter equation  $k = 3.47 \times 10^{-18} T^2 \exp(-320/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Clearly, additional studies of this reaction covering the temperature range  $\sim 200\text{-}400 \text{ K}$  are needed.

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