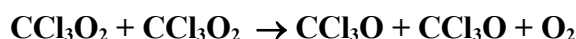


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet on $\text{CCl}_3\text{O}_2$

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: 27<sup>th</sup> January 2006.



## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.6 \times 10^{-12} (T/298)^{-(3.0 \pm 1.0)}$	253-333	Danis et al., 1991	FP-UVA (a,b)
$3.3 \times 10^{-13} \exp[(745 \pm 58)/T]$	273-460	Catoire et al., 1996	FP-UVA (a,c)
$(4.07 \pm 0.54) \times 10^{-12}$	298		

## Comments

- (a)  $k$  is defined by  $-\text{d}[\text{CCl}_3\text{O}_2]/\text{dt} = 2k[\text{CCl}_3\text{O}_2]^2$ .
- (b) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHCl}_3\text{-O}_2\text{-N}_2$  mixtures at 1013 mbar total pressure.  $k$  was determined from the formation of  $\text{C(O)Cl}_2$ , using UV absorption spectroscopy at 240 nm. Results were consistent with chain formation of  $\text{C(O)Cl}_2$ , resulting from thermal decomposition of  $\text{CCl}_3\text{O}$  to generate  $\text{C(O)Cl}_2$  and regenerate  $\text{Cl}$ .
- (c) Flash photolysis of  $\text{Cl}_2$  in the presence of  $\text{CHCl}_3\text{-O}_2\text{-N}_2$  mixtures at 1013 mbar total pressure.  $k$  was determined from time-resolved UV absorption at 230nm, 240nm and 250nm, which was dominated by formation of  $\text{C(O)Cl}_2$  as part of an efficient chain mechanism. Results were consistent with a chain length of ca. 100. FTIR product studies of the photolysis of  $\text{Cl}_2\text{-CHCl}_3\text{-O}_2\text{-N}_2$  mixtures and  $\text{F}_2\text{-CHCl}_3\text{-O}_2\text{-N}_2$  mixtures also demonstrated 100% formation of  $\text{C(O)Cl}_2$ .

## Preferred Values

$k = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.3 \times 10^{-13} \exp(740/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 270-460 K.

### Reliability

$\Delta \log k = \pm 0.3$  at 298 K.

$\Delta(E/R) = \pm 300$  K.

### Comments on Preferred Values

The reported formation of  $\text{C(O)Cl}_2$  with 100% yield from  $\text{CHCl}_3$  oxidation in a number of product studies (Jayanty et al., 1975; Ohta and Mizoguchi, 1980; Catoire et al., 1996) has established that the self-reaction of  $\text{CCl}_3\text{O}_2$  proceeds exclusively via formation of  $\text{CCl}_3\text{O}$  radicals, which decompose by elimination of  $\text{Cl}$ . This is also supported by kinetics study of Catoire et al. (1996), involving flash photolysis-UV absorption of  $\text{Cl}_2$  in the presence of  $\text{CHCl}_3$  and  $\text{O}_2$ . The results demonstrate essentially quantitative regeneration of  $\text{Cl}$  atoms in the system, the chain length for conversion of  $\text{CHCl}_3$  into  $\text{C(O)Cl}_2$  being ca. 100

The preferred values are based on the results of Catoire et al. (1996), which supersede those of Danis et al. (1991) (also cited in Russell et al., 1990) performed in the same laboratory. Catoire et al. (1996) demonstrated that the smaller formation rate of  $\text{C(O)Cl}_2$  and shorter chain lengths observed in the earlier study (Danis et al., 1991) resulted from traces of ethanol which are

invariably present in commercial samples of the reagent  $\text{CHCl}_3$ . Ethanol is three orders of magnitudes more reactive than  $\text{CHCl}_3$  towards  $\text{Cl}$ , and can therefore scavenge a proportion of  $\text{Cl}$  atoms when present in trace amounts.

### References

- Catoire, V., Lesclaux, R., Schneider, W. F. and Wallington, T. J.: *J. Phys. Chem.*, 100, 14356, 1996.
- Danis, F., Caralp, F., Rayez, M.-T. and Lesclaux, R.: *J. Phys. Chem.*, 97, 7300, 1991.
- Jayanty, R. K. M., Simonaitis, R. and Heicklen, J.: *J. Photochem.*, 4, 203, 1975.
- Melius, C. F. and Senkan, S. M.: *J. Phys. Chem.*, 94, 3277, 1990.
- Ohta, T. and Mizoguchi, I.: *Int. J. Chem. Kinet.*, 12, 717, 1980.
- Russell, J. J., Seetula, J. A., Gutman, D., Danis, F., Caralp, F., Lightfoot, P. D., Lesclaux, R., Melius, C. F. and Senkan, S. M.: *J. Phys. Chem.*, 94, 3277, 1990.