**Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.88**

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This data sheet last evaluated: June 2014; last change in preferred values: December 2007.

**Cl + HC(O)Cl  HCl + ClCO**

**Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1  | Temp./K | Reference | Technique/ Comments |
| *Relative Rate Coefficients* |  |  |  |
| 7.4 x 10-13 | 305 | Sanhueza and Heicklen, 1975 | RR (a) |
| (7.7  1.0) x 10-13 | 298  2 | Niki et al., 1980 | RR (b) |
| 8.2 x 10-12 exp(-705/*T*) | 266-321 | Libuda et al., 1990 | RR (c) |
| 7.7 x 10-13 | 298 |  |  |
| (6.7  1.0) x 10-13 | 295 | Wallington et al., 1996 | RR (d) |
| (6.8  0.7) x 10-13 | 295 | Catoire et al., 1996 | RR (e) |
| 8.3 x 10-12 exp (-745/*T*) | 222-296 | Orlando, 1999 | RR (f) |
| 6.8 x 10-13 | 298 |  |  |

# Comments

(a) Rate coefficient ratios of *k*(Cl + HC(O)Cl)/*k*(Cl + CH3Cl) = 1.85  0.43 and *k*(Cl + HC(O)Cl)/*k*(Cl + CH2Cl2) = 1.66  0.15 derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH2Cl2 and CH3Cl. This was placed on an absolute basis using *k*(Cl + CH3Cl) = 4.8 x 10-13 cm3 molecule-1 s-1 and *k*(Cl + CH2Cl2) = 3.6 x 10-13 cm3 molecule-1 s-1 (Atkinson et al., 2008). The rate coefficient cited in the table is the average of the two values obtained, which however differ significantly.

(b) Rate coefficient ratio of *k*(Cl + HC(O)Cl)/*k*(Cl + CH3Cl) = 1.6  0.2 determined using FTIR absorption spectroscopy in irradiated Cl2-CH3Cl-O2-N2 mixtures at 933 mbar total pressure. The rate coefficient ratio was placed on an absolute basis using *k*(Cl + CH3Cl) = 4.8 x 10-13 cm3 molecule-1 s-1 (Atkinson et al., 2008).

1. Relative rate study. Cl atoms generated by the photolysis of Cl2 in Cl2-HC(O)Cl-CH4-N2 mixtures at 1000 mbar total pressure. The concentrations of HC(O)Cl and CH4 were measured by FTIR absorption spectroscopy (HC(O)Cl) and/or gas chromatography (CH4). Rate coefficient ratios were determined over the temperature range 265.8-321.3 K, and placed on an absolute basis using *k*(Cl + CH4) = 6.6 x 10-12 exp(-1240/*T*) cm3 molecule-1 s-1 (Atkinson et al., 2006).
2. Relative rate study. Cl atoms generated by the photolysis of Cl2 in Cl2-CH3Cl-air mixtures at 933 mbar total pressure. The concentrations of HC(O)Cl and CH3Cl were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio *k*(Cl + HC(O)Cl)/*k*(Cl + CH3Cl) = 1.4  0.2 is placed on an absolute basis using *k*(Cl + CH3Cl) = 4.8 x 10-13 cm3 molecule-1 s-1 (Atkinson et al., 2008).
3. Relative rate study. Cl atoms generated by the photolysis of Cl2 in Cl2-CH2Cl2-air mixtures at 933 mbar total pressure. The concentrations of HC(O)Cl and CH2Cl2 were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio *k*(Cl + HC(O)Cl)/*k*(Cl + CH2Cl2) = 2.0  0.2 is placed on an absolute basis using *k*(Cl + CH2Cl2) = 3.4 x 10-13 cm3 molecule-1 s-1 (Atkinson et al., 2008).
4. Temperature dependent rate coefficient ratios of *k*(Cl + HC(O)Cl)/*k*(Cl + CH2Cl2) were derived from the kinetic analysis of HC(O)Cl in Cl atom-sensitized oxidation of CH2Cl2. Placed on an absolute basis by use of *k*(Cl + CH2Cl2) = 5.9 x 10-12 exp (-850/*T*) cm3 molecule-1 s-1 (Atkinson et al., 2008). The value of *k* at 298 K was taken from the Arrhenius expression presented.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* /cm3 molecule-1 s-1 | 7.5 x 10-13 | 298 |
| *k* /cm3 molecule-1 s-1 | 1.12 x 10-12 exp(-805 /*T*) | 220-330 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.08 | 298 |
| Δ(*E*/*R*) |  150 |  |

**Preferred Values**

 *k* = 7.5 x 10-13 cm3 molecule-1 s-1 at 298 K.

 *k* = 1.12 x 10-12 exp(-805 /*T*) cm3 molecule-1 s-1 over the temperature range 220-330 K.

*Reliability*

 log *k* =  0.08 at 298 K.

 (*E/R*) =  150 K.

*Comments on Preferred Values*

At 298 K, the rate coefficients of Sanhueza and Heicklen (1975), Niki et al. (1980), Libuda et al. (1990), Wallington et al. (1996), Catoire et al. (1996), and Orlando (1999) are in good agreement. The temperature dependence reported by Liduda et al. (1990) and Orlando et al. (1999) are in good agreement. A fit of the Arrhenius expression to the combined data set gives the recommended value of *k*(Cl+HC(O)Cl) = 1.12 x 10-12 exp(-805 /*T*) cm3 molecule-1 s-1.

**References**

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, [http://iupac.pole-ether.fr](http://iupac.pole-ether.fr/)

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