**Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx23**

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This data sheet last evaluated: June 2014; last change in preferred values: June 2011.

**Cl + CHCl3  HCl + CCl3**

*H* = -39.2 kJ mol-1

**Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | Technique/ Comments |
| *Absolute Rate Coefficients* |  |  |  |
| 1.45 x 10-11 exp[-(1379  44)/*T*] | 297-652 | Clyne and Walker, 1973 | DF-MS |
| (1.47  0.35) x 10-13 | 297 |  |  |
| (9.9  0.9) x 10-14 | 298 | Watson et al. (1976) | FP-RF |
| (3.7  1.0) x 10-14 | 298 | Jeoung et al., 1991 | (a) |
| (1.1  0.1) x 10-13 | 298 | Beichert et al., 1995 | DF-RF |
| 8.0 x 10-12 exp [-(1390  80)/*T*] | 298-430 | Talhaoui et al., 1996 | DF-MS |
| (7.6  1.3) x 10-14 | 298 |  |  |
| 1.19 x 10-16 T1.51 exp (-571 /T) | 297-854 | Bryukov et al., 2002 | DF-RF |
| (8.9  0.9) x 10-14 | 297 |  |  |
| *Relative Rate Coefficients* |  |  |  |
| 1.9 x 10-12 exp(-980/*T*) | 286-593 | Knox, 1962 | RR (b,c) |
| 6.9 x 10-14 | 298 |  |  |
| 6.0 x 10-12 exp(-1280/*T*) | 240-593 | Knox, 1962 | RR (b,d) |
| 8.4 x 10-14 | 298 |  |  |
| (1.13  0.07) x 10-13 | 298 | Beichert et al., 1995 | RR (e) |
| (1.19  0.13) x 10-13 | 298 | Brahan et al., 1996 | RR (f) |
| (1.1  0.1) x 10-13 | 298 | Catoire et al., 1996 | RR (g) |
| 2.9 x 10-12 exp (-950/*T*) | 222-298 | Orlando, 1999 | RR (h) |
| 1.18 x 10-13 | 298 |  |  |
| 4.8 x 10-12 exp (-1160/*T*) | 297.3-526.9 | Gola et al., 2009 | RR (i) |
| 1.04 x 10-13 | 297.3 |  |  |
| (3.770.32)x10-12exp[-(101124)/*T*] | 253-313 | Nilsson et al., 2010 | RR (j) |
| (1.21  0.05) x 10-13 | 298 |  |  |

# Comments

(a) Very low pressure reactor with chemiluminescence and mass spectrometric detection. The reaction of Cl with CHCl3 was studied as part of a complex chemical system.

(b) Cl atoms were generated by photolysis of Cl2 in Cl2-CHCl3-CH4 or Cl2-CHCl3-CH3Cl mixtures. Organic reactants and products monitored by GC.

(c) Rate coefficient ratio of *k*(Cl + CHCl3)/*k*(Cl + CH4) = 0.286 exp(259/*T*) was obtained 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).

(d) Rate coefficient ratio of *k*(Cl + CHCl3)/*k*(Cl + CH3Cl) = 0.26 exp(-133/*T*) obtained, and placed on an absolute basis using *k*(Cl + CH3Cl) = 2.3 x 10-11 exp(-1150/*T*) cm3 molecule-1 s-1 (Atkinson et al., 2008).

(e) Cl atoms were generated from the photolysis of Cl2 in Cl2-CHCl3-CH4 mixtures at atmospheric pressure of N2, air or Ar. The concentrations of CHCl3 and CH4 were monitored by GC and a rate coefficient ratio *k*(Cl + CHCl3)/*k*(Cl+CH4) = 1.13  0.07 was determined. This was placed on an absolute basis using *k*(Cl + CH4) = 1.0 x 10-13 cm3 molecule-1 s-1 (Atkinson et al., 2006).

(f) Cl atoms were generated by photolysis of Cl2 in Cl2-CHCl3-CH4 or Cl2-CHCl3-CH3Cl mixtures in an air or N2 bath gas at 1023 mbar total pressure and 298 K. Rate coefficient ratios *k*(Cl + CHCl3)/*k*(Cl+CH4) = 1.26 ± 0.07 and *k*(Cl + CHCl3)/*k*(Cl+CH3Cl) = 0.243 ± 0.028 were placed on an absolute basis using *k*(Cl + CH4) = 1.0 x 10-13 cm3 molecule-1 s-1 and *k*(Cl + CH3Cl) = 4.8 x 10-13 cm3 molecule‑1 s-1 (Atkinson et al., 2006; Atkinson et al., 2008). The value presented in the table is the average of experiments using both CH4 and CH3Cl as reference reactants. The uncertainty quoted in the table encompasses the uncertainties associated with the two individual determinations (neglecting uncertainties in the reference rate coefficients).

(g) Cl atoms were generated from the photolysis of Cl2 in Cl2-CHCl3-CH4 mixtures at 930 mbar total pressure of air. The relative removal rates of CH2Cl2 and CH4 were measured by FTIR. A rate coefficient ratio *k*(Cl + CHCl3)/*k*(Cl+CH4) = 1.1  0.1 was obtained and placed on an absolute basis using *k*(Cl + CH4) = 1.0 x 10-13 cm3 molecule-1 s-1 (Atkinson et al., 2006).

(h) Cl atoms were generated from the photolysis of Cl2 in Cl2-CHCl3-CH4 mixtures at 930 mbar total pressure of O2-N2. The concentrations of CHCl3 and CH4 were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio *k*(Cl + CHCl3)/*k*(Cl+CH4) = 0.436 exp (290/T) was determined. This was 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).

(i) Cl atoms were generated from the photolysis of Cl2 in Cl2-CHCl3-CH3Br mixtures int 133 mbar total pressure of N2. The concentrations of CHCl3 and CH3Br were monitored by thermal conductivity GC. Rate coefficient ratios *k*(Cl + CHCl3)/*k*(Cl+CH3Br) were placed on an absolute basis using *k*(Cl+CH3Br) = 3.32 x 10-12 (T/298)1.42 exp(-605/T) cm3 molecule-1 s-1 (Piety et al., 1998).

# (j) Cl atoms were generated from the photolysis of Cl2 in Cl2-CHCl3-CH4 and Cl2-CHCl3-CH2F2 mixtures int 930 mbar total pressure of N2. The concentrations of CHCl3, CH4, and CH2F2 were monitored by FTIR spectroscopy. Rate coefficient ratios *k*(Cl + CHCl3)/*k*(Cl+CH4) and *k*(Cl + CHCl3)/*k*(Cl+CH2F2) were placed on an absolute basis using *k*(Cl+CH4) = 6.6 x 10-12 exp (-1240/*T*) and *k*(Cl+CH2F2) = 6.93 x 10-12 exp (-1591/*T*) cm3 molecule-1 s-1 (Atkinson et al., 2006; Atkinson et al., 2008).

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* /cm3 molecule-1 s-1 | 1.1 x 10-13 | 298 |
| *k* /cm3 molecule-1 s-1 | 2.14 x 10-12 exp(-884/*T*) | 220-400 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.06 | 298 |
|  E/R | ± 200 |  |

*Comments on Preferred Values*

The absolute rate constants of Watson et al. (1976), Beichert et al. (1995), and Bryukov et al. (2002), and the relative rate constants of Beichert et al. (1995), Brahan et al. (1996), Catoire et al. (1996), Orlando (1999), Gola et al. (2009), and Nilsson et al. (2010) are in good agreement. The value at 298 K reported by Knox et al. (1962) is for reasons which are unclear lower than the other studies. The 298 K recommendation is an average result from these studies. Fitting the Arrhenius expression to the data reported in these studies at temperatures below 400 K and adjusting the A factor for consistency with the recommended rate coefficient at 298 K gives the recommended expression given above. Fitting the three-parameter equation *k* = *CT*2 exp(-*D/T*) to the data from Beichert et al. (1995) and Bryukov et al. (2002), Beichert et al. (1995), Brahan et al. (1996), Catoire et al. (1996) and Orlando (1999), Gola et al. (2009), and Nilsson et al. (2010) gives *k* = 3.27 x 10-18 *T*2 exp(-287/*T*) cm3 molecule-1 s-1 which can be used for temperatures up to 855 K.

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