**Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet IV.A2.92**

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This datasheet last evaluated: June 20141; last change in preferred values: June 2011.

**Cl + CH2F2 (HFC-32)  HCl + CHF2**

*H* = 0.5 kJ mol-1

**Rate coefficient data**

|  |  |  |  |
| --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1  | Temp./K | Reference | Technique/ Comments |
| *Relative Rate Coefficients* |  |  |  |
| 1.0 x 10-11 exp(-1470/*T*) | 281-368 | Tschuikow-Roux et al., 1985 | RR (a) |
| 7.3 x 10-14 | 298 |  |  |
| (3.2  0.2) x 10-14 | 295 | Nielsen et al., 1992 | RR (b) |
| 1.19 x 10-17 T2 exp(-1023/*T*) | 253-553 | Nilsson et al., 2009 | RR (c) |
| (3.34  0.16) x 10-14 | 298 |  |  |

**Comments**

(a) Cl atoms were generated by the photolysis of Cl2. Product yield ratios were measured by GC. Kinetic data were derived by measuring the formation of CHF2Cl and CH3Cl following irradiation at 424 nm of CH4-CH2F2-Cl2 mixtures at a total pressure of about 27 mbar. Derived values of *A*/*A*CH4 = (1.51  0.06) and (*E*-*E*CH4)/R = (228  12) K were 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).

1. Photolysis of Cl2 in presence of CH2F2 and CH4 in 920 mbar air or N2 bath gas. The value obtained, *k*(CH2F2)/*k*(CH4) = 0.32  0.02 was placed on an absolute value using *k*(CH4) = 1.0  10-13 cm3 molecule-1 s‑1 (Atkinson et al., 2006).
2. Photolysis of Cl2 in presence of CH2F2 and CH4 in 930-1200 mbar of N2 diluent at 253 – 553 K. The values of *k*(CH2F2)/*k*(CH4) obtained at 200-300 K were 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). The values of *k*(CH2F2)/*k*(CH4) obtained at > 300 K were placed on an absolute basis using *k*(Cl+CH4) = 5.69 x 10-19 T2.49 exp(-609/T) cm3 molecule-1 s-1 from
Bryukov et al. (2002).

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* /cm3 molecule-1 s-1 | 3.3 x 10-14 | 298 |
| *k* /cm3 molecule-1 s-1 | 6.93 x 10-12 exp(-1591/*T*) | 250-300 |

*Reliability*

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

*Comments on Preferred Values*

 In the relative rate studies by Nielsen et al. (1992) and Nilsson et al. (2009) the rate coefficient ratio *k*(Cl+CH2F2)/*k*(Cl+CH4) was measured by monitoring the loss of CH2F2 and CH4 following UV irradiation of CH2F2–CH4–Cl2–N2 mixtures. The loss of CH2F2 and CH4 were monitored directly using in-situ FTIR spectroscopy or GC-FID. In the relative rate study by Tschuikow-Roux et al. (1985) the rate constant ratio *k*(Cl+CH2F2)/*k*(Cl+CH4) was measured by monitoring the formation of CHF2Cl and CH3Cl following UV irradiation of CH2F2–CH4–Cl2 mixtures. The formation of CHF2Cl and CH3Cl were measured by GC-FID and used to infer the loss of CH2F2 and CH4. Tschuikow-Roux et al. (1985) found it necessary to to apply an "unexpectly large" correction factor of 5.838 to account for the response of the GC-FID to CHF2Cl. The results from Nielsen et al. (1992) and Nilsson et al. (2009) are in excellent agreement and are preferred.

 Fitting the three-parameter equation *k* = *CT*2 exp(-*D/T*) to the data from Nielsen et al. (1992) and Nilsson et al. (2009) gives *k* = 1.24 x 10-17 *T*2 exp(-1041/*T*) cm3 molecule-1 s-1 over the temperature range 253-553 K. The preferred Arrhenius expression, *k* = *A* exp(-*B/T*), is centered at 275 K and is derived from the three parameter equation with *A* = *C* e2 *T*2 and *B* = *D* + 2*T*

**References**

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