**Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.89**

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This data sheet last evaluated: June 2014; last change in preferred values: November 2003.

**Cl + CH3OCl  Cl2 + CH3O (1)**

** HCl + CH2OCl (2)**

*H*°(1) = -39.7 kJ·mol-1

*H*°(2) = -14.2 kJ·mol-1

**Rate coefficient data (*k* = *k*1 + *k*2)**

|  |  |  |  |
| --- | --- | --- | --- |
| k/cm3 molecule-1 s-1 | Temp./K | Reference | Technique/ Comments |
| *Absolute Rate Coefficients* |  |  |  |
| (6.0  0.2) x 10-11 | 300 | Kukui et al., 1997 | DF-MS/LIF (a) |
| *Relative Rate Coefficients* |  |  |  |
| (6.3  0.1) x 10-11 | 295 | Carl et al., 1996 | RR (b) |
| *Branching ratios* |  |  |  |
| *k*1/*k* = 0.8  0.2 | 295 | Carl et al., 1996 | FTIR /UV (c) |
| *k*2/*k* = 0.2  0.1 | 295 |  |  |
| *k*1/*k* = 0.85  0.06 | 300 | Kukui et al., 1997 | DF-MS/LIF (a) |

**Comments**

1. Flow tube operated at 2.5 – 3.5 mbar of He. Cl and Cl2 monitored as their parent ions, CH3O was monitored by LIF, but not quantified. The relative sensitivity of the MS to Cl and Cl2 was determined by titration of Cl to Cl2 via reaction with NOCl. Rate coefficients were obtained from the Cl decay in excess CH3OCl, and the branching ratio, *k*1/*k*, was derived by numerical modeling of Cl loss and Cl2 production processes both in the desired reaction and secondary processes.
2. Relative rates of removal of CH3OCl and C2H6 (reference reactant) monitored by FTIR in air and N2 bath gas at total pressure of 133 to 988 mbar. The value *k*/*k*(Cl + C2H6) = 1.07  0.02 was combined with *k*(Cl + C2H6) = 5.9  10-11 cm3 molecule-1 s‑1 (Atkinson et al., 2006) to yield the value for *k* listed in the table.
3. Branching ratios determined by quantitative analysis of CH3OCl loss combined with HCl formation (FTIR experiments) and also by CH3OCl loss combined with Cl2 formation (UV experiments). The chemistry was initiated by photolysis of Cl2 or CH3OCl itself. The HCl formation was modeled to assess the effects of secondary reactions such as Cl + HCHO.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | ***T*/K** |
|  |  |  |
| *k* /cm3 molecule-1 s-1 | 6.1 x 10-11 | 298 |
| *k*1/*k* | 0.85 | 298 |
| *k*2/*k* | 0.15 | 298 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.1 | 298 |
| Δ(*k*1/*k*) |  0.1 | 298 |
| Δ(*k*2/*k*) |  0.1 | 298 |

*Comments on Preferred Values*

The preferred values of *k*(298 K) is an average of the absolute and relative rate experiments, which are in excellent agreement. A consistent result for the branching ratios also emerges from these studies, and the value obtained by Kukui et al. (1997) for *k*1/*k* is adopted. The product analysis of Carl et al. (1996) provides confirmation of this result, and that channel (2) provides the rest of the product formation. Theoretical work confirms the existence of these two reaction channels, and suggests comparable effciencies at room temperature and dominance of hydrogen abstraction at higher temperatures (He et al., 2005).

**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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