

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRCIOx51

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Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (4.36 \pm 0.64) \times 10^{-12}$	298	Wallington and Nielsen, 1991	PR-UVA (a,b)
<i>Branching Ratios</i>			
$k_2/k \approx 1.0$	298	Tuazon and Atkinson, 1994	UV-P-FTIR (e)

Comments

- (a) k_{obs} is based on the measured overall second-order decay of $\text{CFCl}_2\text{CH}_2\text{O}_2$, defined by $-\text{d}[\text{CFCl}_2\text{CH}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CFCl}_2\text{CH}_2\text{O}_2]^2$. As described in detail by Lesclaux (1997), HO_2 radicals formed from the subsequent chemistry of $\text{CFCl}_2\text{CH}_2\text{O}$ (formed from channel (2)) are expected to lead to secondary removal of $\text{CFCl}_2\text{CH}_2\text{O}_2$. The true value of k is expected to fall in the range $k_{\text{obs}}/(1+\alpha) < k < k_{\text{obs}}$, where $\alpha = k_2/k$.
- (b) Pulse radiolysis study of $\text{CF}_2\text{ClCH}_3\text{-O}_2\text{-SF}_6$ mixtures over the pressure range 152-1013 mbar. $\text{CF}_2\text{ClCH}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{250 \text{ nm}} = (3.38 \pm 0.68) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (c) Photolysis of Cl_2 in the presence of $\text{CFCl}_2\text{CH}_3\text{-air}$ mixtures at 987 mbar pressure. In situ monitoring of reactants and products by FTIR spectroscopy was consistent with formation of CFCl_2CHO with a yield ca. 100%, once corrections were made for secondary removal.

Preferred Values

$k = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 1.0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

$\Delta(k_2/k) = {}^{+0.0}_{-0.2}$ at 298 K.

Comments on Preferred Values

The observed formation of CFCl_2CHO in ca. 100% yield from CFCl_2CH_3 oxidation in the product study of Tuazon and Atkinson (1994) is consistent with the reaction proceeding predominantly *via* the radical-forming channel (2), followed by reaction of $\text{CFCl}_2\text{CH}_2\text{O}$ with O_2 to form CFCl_2CHO and HO_2 . This also indicates that secondary removal of $\text{CFCl}_2\text{CH}_2\text{O}_2$ by reaction with HO_2 must generate CFCl_2CHO as the major carbon-containing product, in a similar fashion to the observed dominant formation of HCOCl from the reaction of HO_2 with CH_2ClO_2 (Wallington et al., 1996).

The preferred value of k at 298 K is derived from the k_{obs} value reported by Wallington and Nielsen (1991). Similar to a procedure adopted by Lesclaux (1997) for peroxy radicals for which the self reaction rate coefficients are \geq ca. $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, k is estimated to be $k_{\text{obs}}/(1+0.5(k_2/k))$, with this approximation assuming that the secondary reaction of HO_2 with $\text{CFCl}_2\text{CH}_2\text{O}_2$ competes equally with its removal via $\text{HO}_2 + \text{HO}_2$. The reliability range reflects that k has been derived by this approximate procedure. Confirmatory kinetics and product studies are required.

References

- Lesclaux, R.: Combination of peroxy radicals in the gas phase. In 'Peroxy Radicals', edited by Z.B. Alfassi. John Wiley and Sons, 1997.
- Tuazon, E.C. and Atkinson, R.: Environ. Sci. Technol. 28, 2306, 1994.
- Wallington, T. J. and Nielsen, O. J.: Int. J. Chem. Kinet. 23, 785, 1991.
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