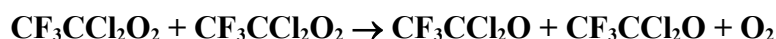


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRCIOx52

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This data sheet updated: 27th January 2006.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (3.33 \pm 0.53) \times 10^{-12}$	295	Wallington et al., 1994	PR-UVA (a,b)
$(3.6 \pm 0.5) \times 10^{-12}$	298	Hayman et al., 1994	LP-UVA (c)

Comments

- (a) k_{obs} is based on the measured overall second-order decay of $\text{CF}_3\text{CCl}_2\text{O}_2$, defined by $-\text{d}[\text{CF}_3\text{CCl}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CF}_3\text{CCl}_2\text{O}_2]^2$.
- (b) Pulse radiolysis study of $\text{CF}_3\text{CHCl}_2\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 1013 mbar. $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{250 \text{ nm}} = (1.70 \pm 0.26) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The derived value of k was determined from the measured overall second-order decay of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals.
- (c) $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals were generated by 193 nm laser flash photolysis of $\text{CF}_3\text{CCl}_3\text{-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures and $\text{CF}_3\text{CCl}_3\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at a total pressure of 1013 mbar. $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals were monitored by UV absorption in the range 230-270nm, with $\sigma_{250 \text{ nm}} = (1.79 \pm 0.18) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. k determined from global simulation of two sets of transient decays observed at 230, 240, 250, 260 and 270 nm using a 15 reaction mechanism. Rate coefficients for the reactions $\text{CF}_3\text{CCl}_2\text{O}_2$ with HO_2 and $\text{C}_2\text{H}_5\text{O}_2$ were determined simultaneously.

Preferred Values

$k = 3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The reported formation of $\text{CF}_3\text{C(O)Cl}$ with approximately 100% yield from CF_3CHCl_2 oxidation in a number of product studies (Edney et al., 1991; Tuazon and Atkinson, 1993; Hayman et al., 1994) has established that the self-reaction of $\text{CF}_3\text{CCl}_2\text{O}_2$ proceeds essentially exclusively via formation of $\text{CF}_3\text{CCl}_2\text{O}$ radicals, which decompose by elimination of Cl. This is also supported by the UV spectral study of $\text{CF}_3\text{CCl}_2\text{O}_2$ by Jemi-Alade et al. (1991), involving flash photolysis-UV absorption of Cl_2 in the presence of CF_3CHCl_2 and O_2 . In that study, no decay in the absorption due to $\text{CF}_3\text{CCl}_2\text{O}_2$ was observed over a 40 ms time scale, demonstrating near-quantitative regeneration of Cl atoms, and therefore $\text{CF}_3\text{CCl}_2\text{O}_2$, in the system.

The kinetics studies of Wallington et al. (1994) and Hayman et al. (1994) reported UV absorption spectra for $\text{CF}_3\text{CCl}_2\text{O}_2$ which are in excellent agreement in both shape and magnitude with that reported by Jemi-Alade et al. (1991). The values of k reported by

Wallington et al. (1994) and Hayman et al. (1994) are also in close agreement, even though only the methodology of Hayman et al. was designed to preclude the regeneration of $\text{CF}_3\text{CCl}_2\text{O}_2$, and to extract the true value of k . It is noted that Wallington et al. (1994) made use of concentrations of $\text{CF}_3\text{CCl}_2\text{O}_2$ radicals which were an order of magnitude higher than those in the experiments of Hayman et al. (1994) (and Jemi-Alade et al. (1991)), such that other secondary reactions of $\text{CF}_3\text{CCl}_2\text{O}$ and/or Cl might partially preclude regeneration of $\text{CF}_3\text{CCl}_2\text{O}_2$, or lead to secondary removal of $\text{CF}_3\text{CCl}_2\text{O}_2$. The agreement with the study of Hayman et al. (1994) is therefore likely to be fortuitous. The preferred value at 298 K is based on the rate coefficient reported by Hayman et al. (1994), with the reliability range reflecting the requirement to simulate a comparatively complex system to extract k . Further kinetics studies are required to allow k to be defined more accurately.

References

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