

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx71

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_{\text{obs}} = (2.10 \pm 0.38) \times 10^{-12}$	295	Sehested et al., 1993	PR-UVA (a)

Comments

- (a) Pulse radiolysis study of $\text{CF}_3\text{CHF}_2\text{-O}_2\text{-SF}_6$ mixtures at a total pressure of 1000 mbar. $\text{CHF}_2\text{CF}_2\text{O}_2$ radicals were monitored by UV absorption with $\sigma_{230 \text{ nm}} = (2.74 \pm 0.46) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. k_{obs} is based on the measured overall second-order decay in absorption at 230 nm, which was defined as $-\text{d}[\text{CF}_3\text{CF}_2\text{O}_2]/\text{dt} = 2k_{\text{obs}}[\text{CF}_3\text{CF}_2\text{O}_2]^2$. Products studies were also performed on the steady-state photolysis of Cl_2 in the presence of $\text{CF}_3\text{CHF}_2\text{-air}$ mixtures at 933 mbar total pressure. The decay of CF_3CHF_2 and the formation of products were monitored by FTIR spectroscopy. The observed products were C(O)F_2 , $\text{CF}_3\text{O}_3\text{CF}_3$ and $\text{CF}_3\text{O}_3\text{C}_2\text{F}_5$, and accounted for 100% of the $\text{CF}_3\text{CF}_2\text{H}$ loss.

Preferred Values

No recommendation

Comments

Although the value of k_{obs} reported by Sehested et al. (1993) is likely to be indicative of the magnitude of the self-reaction rate coefficient for $\text{CF}_3\text{CF}_2\text{O}_2$, the formation of CF_3O_2 and CF_3O radicals from the subsequent chemistry (see below) leads to secondary removal of $\text{CF}_3\text{CF}_2\text{O}_2$, but also interferences in the absorption traces at 230 nm, because the spectra for $\text{CF}_3\text{CF}_2\text{O}_2$ and CF_3O_2 are almost identical. These two factors have opposing influences on k_{obs} , and it is not possible to derive k without a detailed understanding of the rates and mechanisms of the secondary processes and appropriate simulations of the system. No firm recommendation for k can currently be made.

The quantitative formation of C(O)F_2 observed in the product study of Sehested et al. (1993) is consistent with exclusive formation of $\text{CF}_3\text{CF}_2\text{O}$ from the self-reaction of $\text{CF}_3\text{CF}_2\text{O}_2$, followed by decomposition to form C(O)F_2 and CF_3 . The CF_3 radicals form CF_3O_2 radicals, which are known (Nielsen et al., 1992) to interact *via* their self-reaction, resulting in the formation of CF_3O . However, it is probable that CF_3O_2 is also converted to CF_3O *via* reaction with $\text{CF}_3\text{CF}_2\text{O}_2$ in the system. Further removal of both $\text{CF}_3\text{CF}_2\text{O}_2$ and CF_3O_2 occurs *via* their reactions with CF_3O , which lead to the observed products $\text{CF}_3\text{O}_3\text{C}_2\text{F}_5$ and $\text{CF}_3\text{O}_3\text{CF}_3$ (Sehested et al., 1993). More information is therefore needed on the kinetics and mechanism of the secondary reactions, in addition to further kinetics studies of the title reaction, to allow k to be defined more accurately.

References

Nielsen, O. J., Ellermann, T., Sehested, J., Bartkiewicz, E., Wallington, T. J. and Hurley, M. D.: *Int. J. Chem. Kinet.*, 24, 1009, 1992.

Sehested, J., Ellermann, T., Nielsen, O. J., Wallington, T. J. and Hurley, M. D.: *Int. J. Chem. Kinet.* 25, 701, 1993.