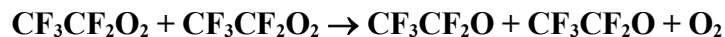


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx71

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 24th 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>			
$k_{\text{obs}} = (2.10 \pm 0.38) \times 10^{-12}$	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.