IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx69

$$CHF_2CF_2O_2 + CHF_2CF_2O_2 \rightarrow CHF_2CF_2O + CHF_2CF_2O + O_2$$
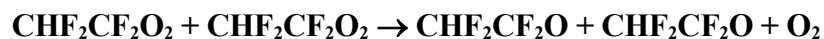
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients $k_{obs} = (2.7 \pm 0.6)$ x 10^{-12}	298	Nielsen et al., 1992a	PR-UVA (a)

Comments

(a) Pulse radiolysis study of CHF_2CHF_2-O_2-SF_6 mixtures at a total pressure of 1000 mbar. $CHF_2CF_2O_2$ radicals were monitored by UV absorption with $\sigma_{230} = (3.2 \pm 0.5)$ x 10^{-18} cm^2 molecule^{-1}. k_{obs} is based on the measured overall second-order decay in absorption at 230 nm, which was defined as -d[$CHF_2CF_2O_2$]/dt = $2k_{obs}$[$CHF_2CF_2O_2$]^2. Products studies were also performed on the steady-state photolysis of Cl_2 in the presence of CHF_2CHF_2-air mixtures at 933 mbar total pressure. The decay of CHF_2CHF_2 and the formation of COF_2, the only carbon-containing product observed, were monitored by FTIR spectroscopy. The yield of COF_2 was 98 $\pm$ 2% relative to the decay of CHF_2CHF_2.

Preferred Values

No recommendation

Comments

Although the value of k_{obs} reported by Nielsen et al. (1992a) is likely to be indicative of the magnitude of the self-reaction rate coefficient for $CHF_2CF_2O_2$, the probable formation of CHF_2O_2 and HO_2 radicals from the subsequent chemistry (see below) is expected to lead to secondary removal of $CHF_2CF_2O_2$, but also interferences in the absorption traces at 230 nm, because the spectra for all three peroxy radicals are similar. 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 product study of Nielsen et al. (1992a) demonstrated approximately 100% formation of COF_2 from the oxidation of CHF_2CHF_2, consistent with exclusive formation of CHF_2CF_2O from the self-reaction of $CHF_2CF_2O_2$, followed by decomposition to form COF_2 and CHF_2. The CHF_2 radicals form CHF_2O_2 radicals, which are known (Nielsen et al., 1992b) to interact *via* their self-reaction, resulting in the formation of COF_2 and HO_2 from the subsequent reaction of CHF_2O with O_2. However, it is probable that CHF_2O_2 is also converted to CHF_2O *via* reaction with $CHF_2CF_2O_2$ in the system. HO_2 radicals, generated from $CHF_2O + O_2$, potentially also react with both $CHF_2CF_2O_2$ and CHF_2O_2, in competition with their self-reaction. The absence of the products $CHF_2CF_2O_2H$ and CHF_2O_2H, which might be formed in these reactions, raises several possibilities: the reactions of HO_2 with $CHF_2CF_2O_2$ and CHF_2O_2 may be too slow to compete with the self-reaction, or they may proceed by alternative pathways leading to COF_2 formation. 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. and Wallington, T. J.: J. Phys. Chem. 96, 10875, 1992a.
Nielsen, O. J., Ellermann, T., Bartkiewicz, E., Wallington, T. J. and Hurley, M. D.: Chem. Phys. Lett. 192, 82, 1992b.