IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx8

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$O(^1D) + CH_2FCF_3$(HFC-134a) $\rightarrow O(^3P) + CH_2FCF_3$ (1)
$\rightarrow$ HO + products (2)
$\rightarrow$ other products (3)

$\Delta H°(1) = -190$ kJ mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(4.85 \pm 0.25) \times 10^{-11}$	298	Warren et al., 1991	PLP-RF
$(4.9 \pm 0.5) \times 10^{-11}$	298	Kono and Matsumi, 2001	PLP-LIF (a)
Relative Rate Coefficients			
$k_2 + k_3 = (6.10 \pm 1.43) \times 10^{-11}$	298	Nilsson et al., 2012	RR (b)
Branching Ratios			
$k_1/k = 0.94 \left(^{+0.06}_{-0.10}\right)$	298	Warren et al., 1991	PLP-RF (c)
$k_1/k = 0.65 \pm 0.06$	298	Kono and Matsumi, 2001	PLP-LIF (d)
$k_2/k = 0.24 \pm 0.04$			(e)
$k_3/k = 0.11 \pm 0.07$			(f)

Comments

(a) Rate constant for the overall reaction ($k_1 + k_2 + k_3$) determined by using LIF (at 115.22 nm) to monitor the rate of loss of $O(^1D)$ atoms.

(b) $O(^1D)$ atoms were produced by the 254 nm photolysis of O_3 in the presence of CH_4 and CH_2FCF_3. The loss of CH_4 and CH_2FCF_3 was monitored using FTIR spectroscopy and chemical modeling was used to account for the secondary loss of CH_2FCF_3 via reaction with HO radicals produced in the system. A value of $k(O(^1D)+CH_4) = 1.7 \times 10^{-10}$ was used in the model which is larger than the IUPAC recommended value of $k(O(^1D)+CH_4) = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2004). Given the complexity in the model it is not possible to simply rescale the value of $k(O(^1D)+ CH_2FCF_3)$

(c) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CH_2FCF_3$ relative to that for $O(^1D) + N_2$.

(d) Branching ratio determined by monitoring the yield of $O(^3P)$ atoms (using LIF at 130.22 nm) from $O(^1D) + CH_3CHF_2$ relative to that for $O(^1D) + N_2$.

(e) Branching ratio determined by monitoring the yield of OH radicals (using LIF at 282 nm) from $O(^1D) + CH_3CHF_2$ relative to that for $O(^1D) + H_2O$.

(f) Inferred from $k_3/k = 1 - (k_1/k + k_2/k)$

Preferred Values

$k = 4.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.65$ at 298 K.
$k_2/k = 0.24$ at 298 K.
$k_3/k = 0.11$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(k_1/k) = \pm 0.15$ at 298 K.
$\Delta(k_2/k) = \pm 0.1$ at 298 K.
$\Delta(k_3/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The preferred value of k is based upon the results from the studies by Warren et al. (1991) and Kono and Matsumi (2001) which are in excellent agreement. Both studies find that quenching to O(^{3}P) is the dominant reaction pathway however the magnitude of the reported quenching branching ratio k_1/k is significantly different in the two studies. Based upon the study by Baasandorj et al. (2013) of analogous HFCs such as CHF_2CF_3 and CH_3CF_3 where a substantial fraction of the total reaction occurs via chemical reaction, the finding by Warren et al. (1991) that the reaction proceeds essentially exclusively via quenching appears implausible. The preferred values for the branching ratios are based on the work by Kono and Matsumi (2001). The value of $k_2 + k_3$ measured by Nilsson et al. (2012) is somewhat larger than expected from the preferred values given above and may reflect complications in the complex model used to extract the kinetic data.

References

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