IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx3

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$O(^1D) + CH_2F_2(HFC\text{-}32) \rightarrow O(^3P) + CH_2F_2$ (1)
$\rightarrow$ other products (2)

$\Delta H°(1) = -190$ kJ mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.13 \pm 0.33) \times 10^{-11}$	298	Schmoltner et al., 1993	PLP-RF
Branching Ratios			
$k_1/k = 0.70 \pm 0.11$	298	Schmoltner et al., 1993	PLP-RF (a)
Relative Rate Coefficients			
$k_2 = (4.6 \pm 2.3) \times 10^{-11}$	297	Green and Wayne, 1976	RR (b)
$k_2 = (4.78 \pm 1.03) \times 10^{-11}$	298	Nilsson et al., 2012	RR (c)

Comments

(a) Branching ratio was determined from the ratio of the $O(^3P)$ yield from $O(^1D) + CH_2F_2$ relative to that for $O(^1D) + N_2$.

(b) $O(^1D)$ produced by photolysis of NO_2 at 229 nm. $\Delta(CH_2F_2)/\Delta(N_2O)$ monitored by IR absorption spectroscopy. Measured rate coefficient ratio of $k_2/k(O(^1D) + N_2O) = 0.4 \pm 0.2$ is placed on an absolute basis by use of $k(O(^1D) + N_2O) = 1.16 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2004). The cited rate coefficient refers to chemical reaction only and does not include physical quenching.

(c) $O(^1D)$ atoms were produced by the 254 nm photolysis of O_3 in the presence of CH_4 and CH_2F_2. The loss of CH_4 and CH_2F_2 was monitored using FTIR spectroscopy and chemical modeling was used to account for the secondary loss of CH_2F_2 via reaction with HO radicals produced in the system.

Preferred Values

$k = 5.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1/k = 0.7$ at 298 K.

Reliability

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

Comments on Preferred Values

The preferred value of k and the preferred value of the branching ratio k_1/k are based on the results of Schmoltner et al. (1993). In these experiments, only $O(^3P)$ was monitored and therefore no direct information relating to the products of the chemical reaction of $O(^1D) + CH_2F_2$ was obtained. Burks and Lin (1981) have observed the appearance of stimulated emissions from vibrationally excited HF. The results from the relative rate study by Green and Wayne (1976) and Nilsson et al. (2012) are consistent with the preferred values.

References

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