IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oFOx43

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$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$

$\Delta H° = -16.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.2) \times 10^{-14}$	298	Saathoff and Zellner, 1993	LP/LIF(a)
$1.92 \times 10^{-12} \exp[-(1370 \pm 85)/T]$	247-360	Barone et al., 1994	PLP/LIF (b)
$(1.93 \pm 0.11) \times 10^{-14}$	298		
$3.1 \times 10^{-12} \exp[-(1470 \pm 250)/T]$	231-385	Jensen et al., 1994	FT/CIMS(c)
$(2.2 \pm 0.4) \times 10^{-14}$	298		
$4.49 \times 10^{-12} \exp[-(1606 \pm 84)/T]$	296-573	Bourbon et al., 1995	FT/LIF(d)
$(2.05 \pm 0.20) \times 10^{-12}$	298		
$3.3 \times 10^{-12} \exp[-(1430 \pm 150)/T]$	235--401	Bednarek et al., 1995	LP/LIF (e)
2.5×10^{-14}	298		
Relative Rate Coefficients			
$<5 \times 10^{-15}$	297	Chen et al., 1992	(f)
$(1.2 \pm 0.1) \times 10^{-14}$	298	Kelly et al., 1993	(g)

Comments

(a) CF_3O radicals were generated by photolysis of CF_3OF at 248 nm.
(b) CF_3O radicals were generated by photolysis of CF_3OOCF_3 at 193 nm.
(c) CF_3O radicals were generated by pyrolysis of CF_3OOCF_3.
(d) CF_3O radicals were generated by the pyrolysis of CF_3OOCF_3.
(e) CF_3O radicals were generated by photolysis of CF_3OF at 248 nm.
(f) Long path FTIR-based product study of visible photolysis of CF_3NO-NO-CH_4 mixtures in 700 torr air. Searched for CH_2O product from oxidation of CH_4 initiated by reaction of CF_3O radicals with CH_4. Upper limit of k given in table is derived from the measured ratio $k/k(CF_3O+NO) < 10^{-4}$ and the value of $k(CF_3O+NO)$ given in this evaluation.
(g) Long-path FTIR-based study. CF_3O radicals were generated by photolysis of CF_3OOCF_3. The decay of the reactant hydrocarbon was compared with the decay of the reference hydrocarbon. The value of k given in table is derived from the measured ratio $k/k(CF_3O+C_2H_6) = 0.010 \pm 0.001$ and the value of $k(CF_3O+C_2H_6)$ (IUPAC, current evaluation).

Preferred Values

$k = 2.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.6 \times 10^{-12} \exp(-1420/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230-380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred value at room temperature is the average of the values reported by Saathoff and Zellner (1993), Barone et al. (1994), Jensen et al. (1994), Bourbon et al. (1995) and Bednarek et al. (1994). Results of these direct studies are in excellent agreement at room temperature. The temperature dependence is based on the 247-360 K data of Barone et al. (1994) the 231-385 K data of Jensen et al. (1994) and the 235-401 K data of Bednarek et al. (1994). The temperature dependence of Bourbon et al. (1995) is thought to be high due to possible influence of wall reaction at high temperature. The relative rate measurements of Chen et al. (1992) and Kelly et al. (1993) are factors of 4 and 2, respectively, lower than the preferred value. Wallington and Ball (1995) reported $k/k(CF_3O + C_2H_6) = 0.0152 \pm 0.0023$ at 296 K in good agreement with the recommended rate coefficients. Jensen et al. (1994) detected the product CF_3OH by chemical ionization mass spectrometer (CIMS) and observed its formation to correlate with the loss of the CF_3O reactant. The CF_3OH product of this reaction was also observed by Bevilacqua et al. (1993) and also by Bednareck et al. (1994), who used FTIR spectroscopy to show that CF_3OH is converted slowly to CF_2O.

References

Barone, S. B., Turnipseed, A. A. and Ravishankara, A. R.: J. Phys. Chem., 98, 4602, 1994.
Bednarek, G., Kohlmann, J. P., Saathoff, H. and Zellner, R.: Z. Phys. Chem., 188, 1, 1995.
Bevilacqua, T. J., Hanson, D. R. and Howard, C. J.: J. Phys. Chem. 97, 3750, 1993.
Bourbon, C., Fittschen, C., Sawersyn, J. P. and Devolder, P.: J. Phys. Chem., 99, 15102, 1995.
Chen, J., Zhu, T., Niki, H. and Mains, G. J.: Geophys. Res. Lett., 19, 2215, 1992.
Jensen, N. R., Hanson, D. R. and Howard, C. J.: J. Phys. Chem., 98, 8574, 1994.
Kelly, C., Treacy, J., Sidebottom, H. W. and Nielsen, O. J.: Chem. Phys. Lett., 207, 498, 1993.
Saathoff , H. and Zellner, R.: Chem. Phys. Lett., 206, 349, 1993.
Wallington, T. J., and Ball, J. C.: J. Phys. Chem., 99, 3201, 1995.