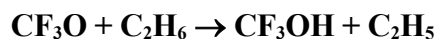


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FO_x44

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: 29th March 2005.



$$\Delta H^\circ = -32.2 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.2) \times 10^{-12}$	298	Saathoff and Zellner, 1993	(a)
$4.84 \times 10^{-12} \exp[-(400 \pm 70)/T]$	233-360	Barone et al., 1994	(b)
$(1.30 \pm 0.11) \times 10^{-12}$	298		
$1.13 \times 10^{-11} \exp[-(642 \pm 113)/T]$	295-573	Bourbon et al, 1995	(c)
$(1.31 \pm 0.13) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(1.1 \pm 0.6) \times 10^{-12}$	297	Chen et al., 1992	(d)

Comments

- Laser photolysis/laser induced fluorescence technique. CF₃O radicals were generated by the photolysis of CF₃OF at 248 nm.
- Pulsed laser photolysis/pulsed laser induced fluorescence technique. CF₃O radicals were generated by the photolysis of CF₃OOCF₃ at 193 nm.
- Fast flow tube (~1.3 mb pressure)/laser induced fluorescence. CF₃O radicals were generated by the pyrolysis of CF₃OOCF₃ at 193 nm.
- Long path FTIR-based product study of visible photolysis of CF₃NO-NO-C₂H₆ mixtures in 700 Torr air. The upper limit of k given in table is derived from measured ratio $k/k(\text{CF}_3\text{O}+\text{NO}) = 0.02 \pm 0.006$ and the value of $k(\text{CF}_3\text{O}+\text{NO})$ (IUPAC, current recommendation).

Preferred Values

$$k = 1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.9 \times 10^{-12} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 230\text{-}360 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

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) and Bourbon et al. (1995). Results of these direct studies are in excellent agreement. The temperature dependence is based on the 233-360 K data of Barone 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 measurement of Chen et al. (1992) is in good agreement with the preferred value. Kelly et al. (1993) used a relative rate

method with FTIR detection to determine the rate of CF_3O reaction with a number of hydrocarbons relative to the rate of the reaction of CF_3O with C_2H_6 . They reported $k(\text{CF}_3\text{O} + \text{CH}_4)/k = 0.010 \pm 0.001$ at 298 K and 1 bar pressure (Kelly et al., 1993). This is nearly a factor of 2 lower than the ratio of the preferred values given in this evaluation (0.017). Wallington and Ball (1995) reported $k(\text{CF}_3\text{O} + \text{CH}_4)/k = 0.0152 \pm 0.0023$ at 296 K in good agreement with the recommended rate coefficients.

References

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