IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC1

$$NO_3 + CH_4 \rightarrow HNO_3 + CH_3$$
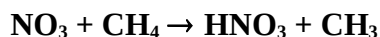
$\Delta H^\circ = 12.4 \text{ kJ·mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$<4 \times 10^{-16}$	298	Burrows et al., 1985	(a)
$\leq 2 \times 10^{-17}$	298 ± 2	Wallington et al., 1986	FP-A (b)
$\leq 8 \times 10^{-19}$	302	Boyd et al., 1991	(c)
Relative Rate Coefficients			
$<5 \times 10^{-21}$	~298	Cantrell et al., 1987	RR (d)

Comments

(a) NO$_3$ radicals were generated by the modulated photolysis of Cl$_2$-ClONO$_2$-N$_2$ or F$_2$-HNO$_3$-N$_2$ mixtures, and monitored by optical absorption at 662 nm.

(b) NO$_3$ radicals were generated by the flash photolysis of ClONO$_2$-He mixtures, and detected by optical absorption at 662 nm.

(c) Stopped-flow system with optical absorption detection of NO$_3$ radicals at 662 nm. The occurrence of secondary reactions was expected to lead to a stoichiometry factor of ≥ 2, resulting in the upper limit to the rate coefficient cited in the table.

(d) Upper limit to the rate coefficient was derived from the absence of observed CO and CO$_2$ formation after addition of CH$_4$ to N$_2$O$_5$-NO$_3$-NO$_2$-N$_2$ mixtures. An equilibrium constant for the NO$_2$ + NO$_3$ $\leftrightarrow$ N$_2$O$_5$ reactions of 2.75×10^{-11} cm^3 molecule^{-1} at 298 K (IUPAC, current recommendation) has been used to derive the cited rate coefficient.

Preferred Values

$k <1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred value is based on the upper limits to the rate coefficients obtained by Cantrell et al. (1987) and Boyd et al. (1991), and is consistent with the higher upper limits reported by Burrows et al. (1985) and Wallington et al. (1986).

References

Boyd, A. A., Canosa-Mas, C. E., King, A. D., Wayne, R. P. and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.

Burrows, J. P., Tyndall, G. S. and Moortgat, G. K.: J. Phys. Chem., 89, 4848, 1985.

Cantrell, C. A., Davidson, J. A., Shetter, R. E., Anderson, B. A. and Calvert, J. G.: J. Phys. Chem., 91, 6017, 1987.

IUPAC,: http://iupac.pole-ether.fr, 2013.

Wallington, T. J., Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 90, 4640, 1986.