IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC7

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This data sheet updated: 29th October 2007 (with no revisions of the preferred values).

$NO_3 + n\text{-}C_4H_{10} \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$\leq 2 \times 10^{-17}$	298 ± 2	Wallington et al., 1986	FP-A (a)
$(4.5 \pm 0.6) \times 10^{-17}$	298	Bagley et al., 1990	DF-A
$(1.44 \pm 0.12) \times 10^{-16}$	333		
$(4.6 \pm 1.2) \times 10^{-16}$	373		
$(1.12 \pm 0.12) \times 10^{-15}$	423		
$(3.2 \pm 0.3) \times 10^{-15}$	473		
$(9.0 \pm 0.4) \times 10^{-15}$	523		
Relative Rate Coefficients			
$(6.6 \pm 1.7) \times 10^{-17}$	296 ± 2	Atkinson et al., 1984	RR (b)

Comments

(a) NO_3 radicals were generated by the flash photolysis of $ClONO_2$ at wavelengths >180 nm and monitored by optical absorption at 662 nm..

(b) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of *n*-butane and *n*-heptane (the reference organic) were measured by GC. A rate coefficient ratio of $k(NO_3 + n\text{-butane})/k(NO_3 + n\text{-heptane}) = 0.48 \pm 0.12$ was obtained and is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + n\text{-heptane}) = 1.37 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1991).

Preferred Values

$k = 4.6 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.8 \times 10^{-12} \exp(-3280/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta \log(E/R) = \pm 400$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298-423 K (at temperatures above 423 K the Arrhenius plot exhibits upward curvature, especially above 473 K). A least-squares analysis of the 298-423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The

preferred rate coefficient at 298 K is at least a factor of 2 higher than the upper limit reported by Wallington et al. (1986), but is in agreement within the measurement uncertainties with the relative rate coefficient of Atkinson et al. (1984). At room temperature and below the reaction proceeds mainly by H-atom abstraction from the CH_2 groups (Bagley et al., 1990; Atkinson, 1991).

References

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