IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC3

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

$NO_3 + C_2H_4 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$6.29 \times 10^{-12} \exp[-(3103 \pm 145)/T]$	295-523	Canosa-Mas et al., 1988a,b	DF-A
$(1.85 \pm 0.24) \times 10^{-16}$	295 ± 2		
$(1.7 \pm 0.5) \times 10^{-16}$	300	Biggs et al., 1991; Boyd et al., 1991	(a)
Relative Rate Coefficients			
$(2.16 \pm 0.20) \times 10^{-16}$	296 ± 2	Atkinson et al., 1988	RR (b)

Comments

(a) Stopped-flow technique with optical absorption of the NO_3 radical at 662 nm. The influence of the reaction $NO_2 + NO_3 + He \rightarrow N_2O_5 + He$ was taken into account by numerical modeling, leading to a stoichiometry factor for NO_3 radical decays of ~1.9 and the cited rate coefficient for the elementary NO_3 + ethene reaction.

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5. A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on rate coefficient ratios for the sets of organic compounds ethene *vs*. 2,3-dimethylbutane, 2,3-dimethylbutane *vs*. tetrahydrofuran, tetrahydrofuran *vs*. propene, propene *vs*. thiophene, thiophene *vs*. bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene *vs*. *trans*-2-butene, a rate coefficient ratio of $k(NO_3 + \text{ethene})/k(NO_3 + \textit{trans}\text{-2-butene}) = 0.000554 \pm 0.000050$ was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1997).

Preferred Values

$k = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.3 \times 10^{-12} \exp(-2880/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270-340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas et al. (1988a,b) and the relative rate coefficient of Atkinson et al. (1988). These data were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.88 \times 10^{-18} T^2 \exp(-2282/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 295-523 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$.

The preferred rate coefficient is in agreement with the 300 K rate coefficient of Biggs et al. (1991) and Boyd et al. (1991).

References

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