$NO_3 + C_3H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
4.74×10^{-13} exp[-(1171 ± 66)/T]	298-423	Canosa-Mas et al., 1991	DF-A
$(9.3 \pm 1.2) \times 10^{-15}$	298		
$(6.4 \pm 1.1) \times 10^{-15}$	295 ± 5	Picqet-Varrault et al., 2009	(a)
Relative Rate Coefficients			
$(5.2 \pm 1.3) \times 10^{-15}$	300	Morris and Niki, 1974	RR (b)
$(8.7 \pm 0.5) \times 10^{-15}$	300	Japar and Niki, 1975	RR (b)
$(6.1 \pm 1.3) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (b)
$(7.4 \pm 2.0) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (c)
$(9.45 \pm 0.47) \times 10^{-15}$	296 ± 2	Atkinson et al., 1988	RR (d)

Comments

(a) Experiments were carried out in a 977 L evacuable chamber. NO_3 radicals were generated from the thermal decomposition of N_2O_5. Concentrations of propene and NO_3 radicals were monitored during the experiments by FTIR spectroscopy and by absorption at 662 nm, respectively. The rate coefficients were obtained from a plot of $\triangle$[propene] against ([propene][NO_3]$\triangle$t), where the [propene] and [NO_3] concentrations were averaged over the time intervals considered and the data for 9 experiments carried out at 292 ± 2 K to 298 ± 2 K were combined.

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient K for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.75 \times 10^{-11}$ cm^3 molecule^{-1} at 298 K and 2.15×10^{-11} cm^3 molecule^{-1} at 300 K (IUPAC, current recommendation).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of propene and *trans*-2-butene were measured by GC, and a rate coefficient ratio of $k(NO_3 +$ propene)/$k(NO_3 + trans$-2-butene) = 0.019 ± 0.005 obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + trans$-2-butene) = 3.90×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

(d) 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, 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 $k(NO_3 +$ propene)/$k(NO_3 + trans$-2-butene) = 0.0243 ± 0.0012 at 296 ± 2 K was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + trans$-2-butene) = 3.89×10^{-13} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.6 \times 10^{-13}$ exp($-1155/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 290-430 K.

Reliability

Δlog $k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

The measured room temperature rate coefficients from absolute and relative rate studies range from 5.4×10^{-15} cm^3 molecule^{-1} s^{-1} to 9.5×10^{-15} cm^3 molecule^{-1} s^{-1}. The rate coefficients of Morris and Niki (1974), Japar and Niki (1975) and Atkinson et al. (1984) are relative to the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions which is subject to significant uncertainty, and are hence not used in the evaluation of k. The rate coefficient of Atkinson et al. (1984) measured relative to that for *trans*-2-butene also has a significant associated uncertainty because of the factor of ~40 difference in reactivity of propene and *trans*-2-butene towards NO$_3$ radicals. Of the remaining rate coefficients of Atkinson et al. (1988), Canosa-Mas et al. (1991) and Picquet-Varrault et al. (2009), those of Atkinson et al. (1988) and Canosa-Mas et al. (1991) are in excellent agreement at room temperature but are a factor of ~1.4-1.5 higher than that of Picquet-Varrault et al. (2009). Relative rate studies indicate that the rate coefficients of Atkinson et al. (1988) and Canosa-Mas et al. (1991) are more consistent with the available absolute rate data for NO$_3$ + 1-butene [see datasheet for NO$_3$ + 1-butene (IUPAC, current recommendation)], and hence the preferred values are derived using the room temperature relative rate coefficient of Atkinson et al. (1988) and the 298-423 K absolute rate coefficients of Canosa-Mas et al. (1991).

The NO$_3$ radical reaction with propene proceeds by initial addition, leading to the formation under simulated tropospheric conditions of HCHO, CH$_3$CHO and CH$_3$C(O)CH$_2$ONO$_2$ (Bandow et al., 1980; Shepson et al., 1985; Barnes et al., 1990; Hjorth et al., 1990).

References

Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984.

Atkinson, R., Aschmann, S. M. and Pitts Jr., J. N.: J. Phys. Chem., 92, 3454, 1988.

Bandow, H., Okuda, M. and Akimoto, H.: J. Phys. Chem., 84, 3604, 1980.

Barnes, I., Bastian, V., Becker, K. H. and Tong, Z.: J. Phys. Chem., 94, 2413, 1990.

Canosa-Mas, C. E., Smith, S. J., Waygood, S. J. and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 87, 3473, 1991.

Hjorth, J., Lohse, C., Nielsen, C. J., Skov, H. and Restelli, G.: J. Phys. Chem., 94, 7494, 1990.

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

Japar, S. M. and Niki, H.: J. Phys. Chem., 79, 1629, 1975.

Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 78, 1337, 1974.

Picquet-Varrault, B., Scarfogliero, M., Ait Helal, W. and Doussin, J.-F.: Int. J. Chem. Kinet., 41, 73, 2009.

Shepson, P. B., Edney, E. O., Kleindienst, T. E., Pittman, J. H., Namie, G. R. and Cupitt, L. T.: Environ. Sci. Technol., 19, 849, 1985.