IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC29

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NO_3 + *cis*-2-Butene → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.75 \pm 0.24) \times 10^{-13}$	298	Benter et al., 1992	DF-MS
$(3.3 \pm 0.8) \times 10^{-13}$	298	Wille et al., 1992	DF-MS
Relative Rate Coefficients			
$(2.97 \pm 0.33) \times 10^{-13}$	300	Japar and Niki, 1975	RR (b)
$(3.47 \pm 0.01) \times 10^{-13}$	298 ± 1	Atkinson et al., 1984	RR (c)

Comments

(a) NO_3 radicals generated by the thermal decomposition of N_2O_5.

(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 $K = 2.15 \times 10^{-11}$ 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 *cis*-2-butene and *trans*-2-butene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3 + cis\text{-2-butene})/k(NO_3 + trans\text{-2-butene}) = 0.897 \pm 0.003$ (Atkinson et al., 1984) obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + trans\text{-2-butene}) = 3.87 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 3.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

Rate coefficients are only available at room temperature, and the absolute and relative rate coefficients of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992) are in good agreement. While the rate coefficient of Japar and Niki (1975) is in good agreement with those of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992), it is not used in the rate coefficient evaluation because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow$

$NO_3 + NO_2$ reactions. The preferred value is obtained from an average of the rate coefficients of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992).
The NO_3 radical reaction with *cis*-2-butene proceeds by initial addition,

$$NO_3 + \textit{cis}\text{-}CH_3CH{=}CHCH_3 \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3^{*}$$

with the chemically-activated nitrooxyalkyl radicals decomposing to *cis*- or *trans*-2,3-epoxybutane + NO_2 in competition with collisional stabilization.

$$CH_3C^{\bullet}HCH(ONO_2)CH_3^{*} \rightarrow \text{2,3-epoxybutane} + NO_2$$
$$CH_3C^{\bullet}HCH(ONO_2)CH_3^{*} + M \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3 + M$$

Under atmospheric conditions the thermalized nitrooxybutyl radical reacts with O_2 to form the peroxy radical $CH_3CH(OO^{\bullet})CH(ONO_2)CH_3$. At atmospheric pressure of air, the observed products and their molar formation yields are: CH_3CHO, 34 ± 12% (Hjorth et al., 1990); $CH_3C(O)CH(ONO_2)CH_3$, 41 ± 13% (Hjorth et al., 1990); $CH_3CH(OH)CH(ONO_2)CH_3$, 15 ± 5% (Hjorth et al., 1990); and 2,3-epoxybutane, ≤1% (Skov et al., 1994).

References

Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 1210, 1984.
Benter, Th., Becker, E., Wille, U., Rahman, M. M. and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 769, 1992.
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.
Skov, H., Benter, Th., Schindler, R. N., Hjorth, J. and Restelli, G.: Atmos. Environ., 28, 1583, 1994.
Wille, U., Rahman, M. M. and Schindler, R. N.: Ber. Bunsenges. Phys. Chem., 96, 833, 1992.