IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC18
Website: http://www.iupac-kinetic.ch.cam.ac.uk/. See website for latest evaluated data.
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$NO_3 + CH_2=C(CH_3)C(O)OONO_2$ (MPAN) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients $(1.6 \pm 0.6) \times 10^{-16}$	296 ± 2	Canosa-Mas *et al*., 1999[1]	RR (a)

Comments

(a) Relative rate method carried out at one atmosphere of air. $CH_2=CH(CH_3)C(O)OONO_2$ (MPAN) was prepared *in situ* from the reaction of NO_3 radicals (generated from the thermal decomposition of N_2O_5) with methacrolein. After complete consumption of N_2O_5 and methacrolein, ethene (the reference compound) was added and several additions of N_2O_5 were made to the collapsible 56 L chamber. The concentrations of MPAN and ethene were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratio of $k(NO_3 + MPAN)/k(NO_3 + ethene) = 0.79 \pm 0.28$ (two standard deviations) is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + ethene) = 2.0 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K.[2] Dark decays of MPAN and dilution due to successive additions of N_2O_5 to the chamber were taken into account in the data analysis.

Preferred Values

$k = 1.6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Canosa-Mas *et al*.,[1] with large uncertainty limits because of the difficult nature of the experiments and the need for large dilution corrections (cited as being up to 40%). The reaction of NO_3 radicals with MPAN proceeds by initial addition of the NO_3 radical to the C=C bond.[1] On the basis of the recommended rate coefficients for the reactions of MPAN with HO radicals and O_3 and those for the reactions of ethene, propene and 2-methylpropene with HO and NO_3 radicals and O_3,[2,3] the rate coefficient for the reaction of NO_3 radicals with MPAN may be expected to be significantly higher than the measured value (*i.e.*, ~10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K).

References

[1] C. E. Canosa-Mas, M. D. King, D. E. Shallcross, and R. P. Wayne, Phys. Chem. Chem. Phys. **1**, 2411 (1999).

[2] IUPAC, http://iupac-kinetic.ch.cam.ac.uk/ (2002).

[3] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).