IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC20

This data sheet updated: 10th December 2007 (with no revision of the preferred values).

$NO_3 + CH_2=C(CH_3)C(O)OONO_2$ (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	RR (a)

Comments

(a) 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 (IUPAC, current recommendation). 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. (1999), 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 (Canosa-Mas et al., 1999). 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 (Atkinson, 1997; IUPAC, current recommendations), 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

Atkinson, R.: J. Phys. Chem. Ref. Data, 26, 215, 1997.
Canosa-Mas, C. E., King, M. D., Shallcross, D. E. and Wayne, R. P.: Phys. Chem. Chem. Phys., 1, 2411, 1999.
IUPAC: http://iupac.pole-ether.fr, 2013.