IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC26

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NO_3 + 2-methylpropane, $(CH_3)_3CH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.2) \times 10^{-16}$	298	Bagley et al., 1990	DF-A
$(4.5 \pm 1.6) \times 10^{-16}$	348		
$(8.0 \pm 0.8) \times 10^{-16}$	373		
$(2.3 \pm 0.4) \times 10^{-15}$	423		
$(5.4 \pm 1.2) \times 10^{-15}$	473		
$(1.30 \pm 0.24) \times 10^{-14}$	523		
$\leq(6 \pm 1) \times 10^{-16}$	298	Boyd et al., 1991	(a)
Relative Rate Coefficients			
$(9.8 \pm 2.1) \times 10^{-17}$	296 ± 2	Atkinson et al., 1984	RR (b)
$(1.18 \pm 0.25) \times 10^{-16}$	298 ± 2	Barnes et al., 1990	RR (c)

Comments

(a) Stopped-flow technique with optical absorption of NO_3 radicals at 662 nm. Secondary reactions were expected to be significant, with a stoichiometry factor of ≥2. The cited upper limit to the rate coefficient includes a stoichiometry factor of 2.0.

(b) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of 2-methylpropane and 2,3-dimethylbutane (the reference organic) were measured by GC. A rate coefficient ratio of $k(NO_3 + \text{2-methylpropane})/k(NO_3 + \text{2,3-dimethylbutane}) = 0.24 \pm 0.05$ was obtained and is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{2,3-dimethylbutane}) = 4.08 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1991).

(c) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of 2-methylpropane and ethene were measured by GC. A rate coefficient ratio of $k(NO_3 + \text{ethene})/k(NO_3 + \text{2-methylpropane}) = 1.78 \pm 0.37$ was obtained and is placed on an absolute basis by use of a rate coefficient of $k(NO_3 + \text{ethene}) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.0 \times 10^{-12} \exp(-3050/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-430 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta \log(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298-423 K (at temperatures above 423 K the Arrhenius plot exhibits upward curvature). A least-squares analysis of the 298-423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The preferred room temperature rate coefficient is in excellent agreement with the relative rate coefficients of Atkinson et al. (1984) and Barnes et al. (1990). At room temperature and below the reaction proceeds almost totally by H-atom abstraction from the tertiary CH group (Bagley et al., 1990; Atkinson, 1991).

References

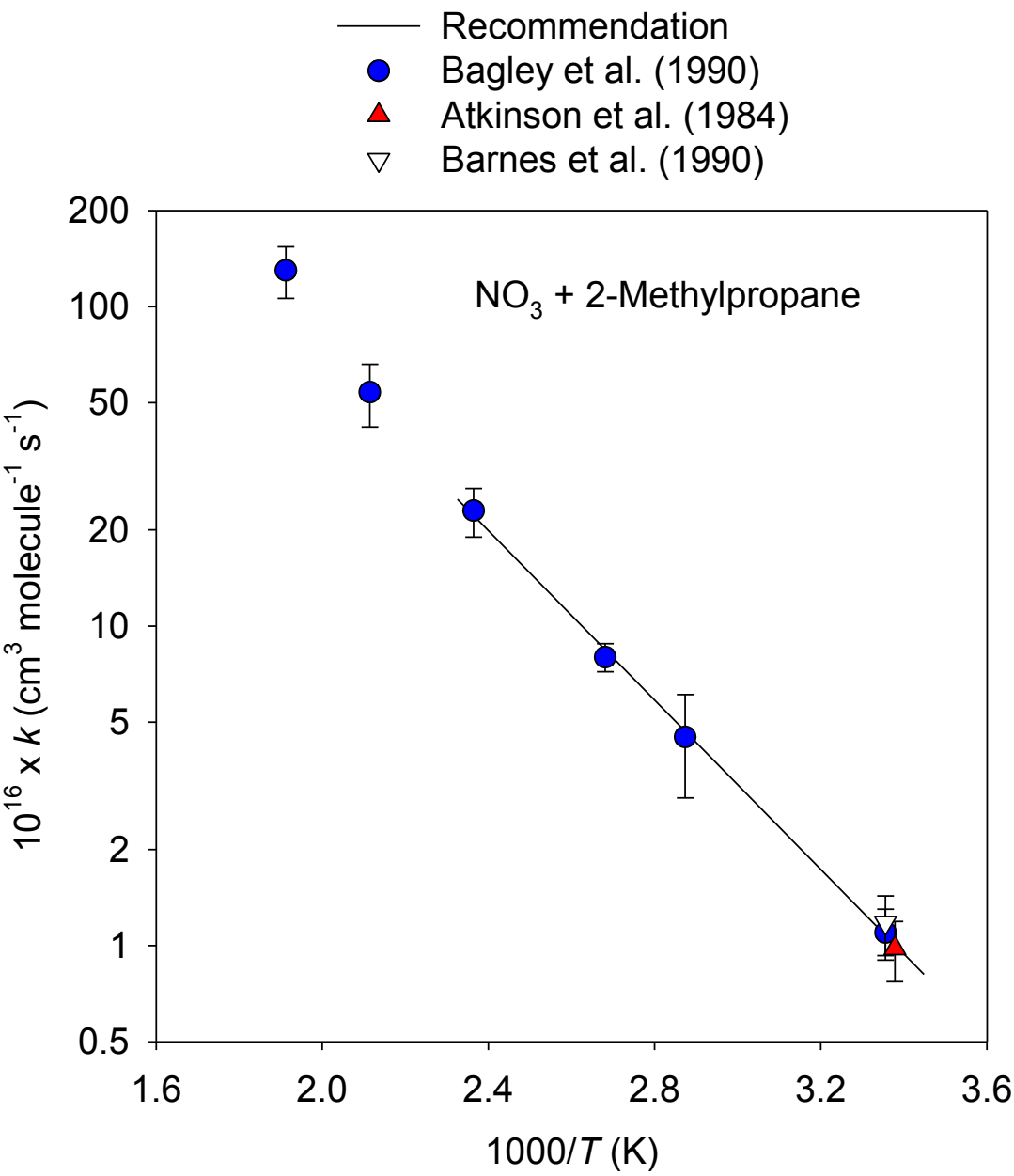
Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.

Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: J. Phys. Chem., 88, 2361, 1984.

Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J. and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.

Boyd, A. A., Canosa-Mas, C. E., King, A. D., Wayne, R. P. and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.

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


Recommendation
Bagley et al. (1990)
Atkinson et al. (1984)
Barnes et al. (1990)
NO3 + 2-Methylpropane
200
100
50
20
10
5
2
1
0.5
10^16 x k (cm^3 molecule^-1 s^-1)
1.6
2.0
2.4
2.8
3.2
3.6
1000/T (K)