IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC21

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

$NO_3 + CH_3OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$\leq 6 \times 10^{-16}$	298 ± 2	Wallington et al., 1987	FP-A
$1.25 \times 10^{-12} \exp[-(2562 \pm 241)/T]$	294-473	Canosa-Mas et al., 1989	DF-A
$(2.1 \pm 1.1) \times 10^{-16}$	294		
$1.06 \times 10^{-12} \exp[-(2093 \pm 803)/T]$	258-367	Langer and Ljungström, 1995	DF-A (a)
$(1.32 \pm 0.24) \times 10^{-16}$	295		

Comments

(a) The cited Arrhenius expression leads to a rate coefficient at 295 K of 8.8×10^{-16} cm^3 molecule^{-1} s^{-1}, clearly in disagreement with the measured value. A unit-weighted least-squares analysis of the rate coefficients measured by Langer and Ljungström (1995) (Table 3 of Langer and Ljungström, 1995) leads to $k = 9.36 \times 10^{-13} \exp[-(2652 \pm 312)/T]$ cm^3 molecule^{-1} s^{-1}, where the indicated error is one standard deviation.

Preferred Values

$k = 1.3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 9.4 \times 10^{-13} \exp(-2650/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 700$ K.

Comments on Preferred Values

The reported rate coefficients of Canosa-Mas et al. (1987) are higher by factors of 1.6-2.1 than those of Langer and Ljungström (1995) over the temperature range common to both studies (294-373 K). Clearly there are systematic errors in one or both of these studies. Based on the observation that for the NO_3 radical reaction with 2-propanol the data of Langer and Ljungström (1995) may still be an upper limit to the rate coefficient (see datasheet for $NO_3 + CH_3CH(OH)CH_3$), the preferred values were derived from the data of Langer and Ljungström (1995) using the Arrhenius parameters given in Comment (a). The preferred 298 K rate coefficient is calculated from the resulting Arrhenius expression. It is possible that the preferred values are still high because of the potential for secondary reactions in slowly reacting systems using absolute rate methods.

References

Canosa-Mas, C. E., Smith, S. J., Toby, S. and Wayne, R. P.: J. Chem. Soc. Faraday Trans. 2, 85, 709, 1989.
Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.
Wallington, T. J., Atkinson, R., Winer, A. M. and Pitts Jr., J. N.: Int. J. Chem. Kinet., 19, 243, 1987.