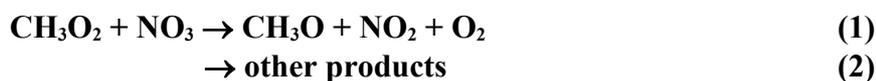


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_19

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated: May 2008 (with changes to the preferred values).



$$\Delta H^\circ(1) = -32.3 \text{ kJ mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 0.7) \times 10^{-12}$	298	Crowley et al., 1990	MMS-AS (a)
$(1.0 \pm 0.6) \times 10^{-12}$	298	Biggs et al., 1994	DF-LIF/AS (b)
$(1.2 \pm 0.6) \times 10^{-12}$	298	Daële et al., 1995	DF-LIF/MS (c)
$(1.3 \pm 0.2) \times 10^{-12}$	298	Helleis et al., 1996	DF-MS (d)
$(1.1 \pm 0.5) \times 10^{-12}$	295 ± 4	Vaughan et al., 2006	DF (e)
<i>Branching Ratios</i>			
$k_1/k > 0.9$	298	Kukui et al., 1995	DF-LIF/MS (f)

Comments

- Computer simulation of NO_3 absorption profiles formed in the modulated photolysis of HNO_3 in the presence of CH_4 and O_2 .
- CH_3O product of reaction (1) measured by LIF; NO_3 by visible absorption spectroscopy. Pressure = 3.5 mbar. Modelling of CH_3O time-dependence gave $k / k(\text{CH}_3\text{O} + \text{NO}_3) = 0.43 \pm 0.09$. k calculated with $k(\text{CH}_3\text{O} + \text{NO}_3) = (2.3 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained in a similar study in the same apparatus.
- CH_3O measured by LIF; NO_3 by titration with 2,3-dimethylbutene. The rate coefficient was extracted by numerical simulation from the $\text{CH}_3\text{O} + \text{NO}_3$ reactant system.
- CD_3O_2 decay measured directly in excess NO_3 . Numerical simulation to take into account the re-formation of CD_3O_2 from $\text{CD}_3\text{O} + \text{NO}_3$.
- Flow tube at ≈ 6.7 mbar. NO_3 ($0.3\text{-}8 \times 10^{11} \text{ molecule cm}^{-3}$) was formed in the reaction of F atoms with HNO_3 and detected by cavity enhanced absorption spectroscopy (CEAS) at 663 nm. CH_3O_2 (excess reactant with $0.9\text{-}50 \times 10^{11} \text{ molecule cm}^{-3}$) was formed in the reaction of F atoms with CH_4 / O_2 and detected as NO_2 (by CEAS at 404 nm) following titration with NO . Derivation of the CH_3O_2 concentration required numerical modelling. Time dependent decays of NO_3 were not observed, but the analysis was based on NO_3 changes for a fixed reaction time when the CH_3O_2 was modulated on and off.
- Based on observations of DCDO formation from the $\text{CD}_3\text{O} + \text{NO}_3$ reaction and the relative rates of reactions of CD_3O and CD_3O_2 with NO_3 .

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2/k = 0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

None of the experimental studies for this reaction can be described as definitive or direct. In the flow tube measurements with NO_3 in excess, a quasi-equilibrium between CH_3O_2 and CH_3O radicals is established and concentrations and decay kinetics are influenced by reactions of both radicals. The ratio k_1/k ($\text{CH}_3\text{O} + \text{NO}_3$) should be well determined but values of 0.43,² 0.66,³ and 0.30⁴ were obtained. The quasi-equilibrium was avoided by using O_2 to scavenge CH_3O in the work of Crowley et al. (1990) but the need to simulate a complex reaction system, and the possible influence of a dark reaction (Crowley et al., 1993) that generated NO_3 , reduce the reliability of these experiments. Vaughan used CH_3O_2 as the excess reactant, the concentration of which is limited due to its self-reaction so that only small changes in the NO_3 concentrations were detected.

Given the complex analyses conducted, the results of the flow tube studies are in good agreement. The preferred value is an average of the four flow tube studies (Biggs et al., 1994; Däele et al., 1995; Helleis et al., 1996; Vaughan et al., 2006). The value of k reported by Kukui et al. (1995) differs substantially from the other studies and was not included in the evaluation of the rate coefficient. Their work suggests, however, that channel (1) is the predominant pathway, with $k_2/k < 0.10$.

References

- Biggs, P., Canosa-Mas, C. E., Fracheboud, J.-M., Shallcross, D. E., and Wayne, R. P.: J. Chem. Soc. Faraday Trans. 90, 1205, 1994.
- Biggs, P., Canosa-Mas, C. E., Fracheboud, J.-M., Shallcross, D. E., and Wayne, R. P.: J. Chem. Soc. Faraday Trans. 90, 1197, 1994.
- Crowley, J.N. Burrows, J. P., Moortgat, G. K., Poulet, G. and LeBras, G.: Int. J. Chem. Kin. 22, 673, 1990.
- Crowley, J. N., Burrows, J. P., Moortgat, G. K., Poulet, G., and Le Bras, G.: Int. J. Chem. Kinet. 25, 795, 1993.
- Däele, V., Laverdet, G., Le Bras, G., and Poulet, G.: J. Phys. Chem. 99, 1470, 1995.
- Helleis, F., Moortgat, G. K., and Crowley, J. N.: J. Phys. Chem. 100, 17846, 1996.
- Kukui, A. S., Jungkamp, T. P. W., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem. 99, 1565, 1995.
- Vaughan, S., Canosa-Mas, C. E., Pfrang, C., Shallcross, D. E., Watson, L., and Wayne, R. P.: Phys. Chem. Chem. Phys. 8, 3749, 2006.