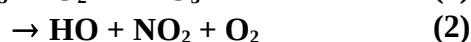


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx18

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 no changes to the preferred values).



$$\Delta H^\circ(1) = -223.4 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -17.9 \text{ kJ mol}^{-1}$$

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>			
$k_1 = (9.2 \pm 4.8) \times 10^{-13}$	298	Mellouki et al., 1988	DF-EPR (a)
$k_2 = (3.6 \pm 0.9) \times 10^{-12}$	298		
$2.3 \times 10^{-12} \exp[(170 \pm 270)/T]$	263-338	Hall et al., 1988	MM-UV/VIS (b)
$(4.1 \pm 0.8) \times 10^{-12}$	298		
$k_1 = (1.9 \pm 0.8) \times 10^{-12}$	298	Becker et al., 1992	DF-RF/MS (c)
$k_2 = (2.5 \pm 0.7) \times 10^{-12}$	298		
$(3.0 \pm 0.7) \times 10^{-12}$	297 ± 2	Mellouki et al., 1993	DF-LMR (d)

Comments

- [HO] and [NO₃] were monitored in excess NO₃. Kinetics of a complex mechanism were analysed to extract values of rate coefficients. Values of $k(\text{HO} + \text{NO}_3)$ were also obtained (see the HO + NO₃ data sheet).
- [HO₂] and [NO₃] were monitored by visible and UV spectroscopy. The kinetics of a complex mechanism were simulated to extract values of rate coefficients. An upper limit of $k_2/k < 0.6$ was obtained from measurements of [HO] by modulated resonance absorption.
- [HO] monitored by RF, and [NO₃] and [HO₂] monitored by MS. A quasi-steady state of [HO₂] and [HO] is produced by reaction of HO with NO₃, in excess, to reform HO₂ radicals. k_1 was inferred from the extra loss of HO₂ following the establishment of the quasi-steady state.
- [HO], [HO₂], and [NO₂] were all monitored by LMR, NO₃ concentrations determined by chemical titration (with NO) to NO₂. Three different methods for generation of NO₃ were used. k could be obtained under pseudo-first-order conditions by using an excess of NO₃ and adding C₂F₃Cl to scavenge HO radicals. A value of the branching ratio was obtained by simulation of the time dependences of [HO] and [HO₂] using a simple mechanism.

Preferred Values

$$k = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2.$$

Comments on Preferred Values

Although the 1993 study of Mellouki et al. gives a value of k at 298 K some 30% lower than obtained in the earlier studies, (Hall et al., 1988; Becker et al. 1992; Mellouki et al. 1988) all of the values are within the reported error limits, which are substantial. The preferred value is a mean of the data from all four studies. Measurements of the branching ratio k_2/k at 298 K range from < 0.6 (Hall et al., 1988) to unity (Mellouki et al., 1993). The 1993 study of Mellouki et al., in which HO yields were measured, appears to be the most direct, and suggests that the reaction proceeds almost entirely through the second channel, but at this stage no recommendation is made for the branching ratio because of the experimental uncertainties. Similarly, data on the temperature dependence is considered to be too uncertain to make a recommendation.

References

- Becker, E., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem. 96, 776, 1992.
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Mellouki, A., LeBras, G., and Poulet, G.: J. Phys. Chem. 92, 2229, 1988.
Mellouki, A., Talukdar, R. K., Bopegedera, A. M. R. P., and Howard, C. J.: Int. J. Chem. Kinet. 25, 25, 1993.