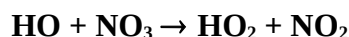


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO_x14

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).



$$\Delta H^\circ = -63.1 \text{ kJ mol}^{-1}$$

Rate coefficient data

k/cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.6 \pm 0.6) \times 10^{-11}$	298	Mellouki et al., 1988	DF-EPR (a)
$(2.0 \pm 0.6) \times 10^{-11}$	298	Boodaghians et al., 1988	DF-RF (b)
$(1.22 \pm 0.35) \times 10^{-11}$	298	Becker et al., 1992	DF-RF/MS (c)
$(2.1 \pm 1.0) \times 10^{-11}$	297	Mellouki et al., 1993	DF-LMR (d)

Comments

- Both [HO] and [HO₂] (after conversion of HO₂ to HO) were monitored in the presence of excess NO₃ radicals. [NO₃] was measured by titration with NO or 2,3-dimethyl-2-butene. A complex kinetic analysis accounting for secondary chemistry was required to extract values of *k*.
- The measured rate coefficient, *k*, was corrected for the effects of secondary reactions which accelerate the removal of HO radicals.
- [HO] was monitored by RF, and [NO₃] and [HO₂] were monitored by MS. Identical values of *k* were obtained from HO produced *in situ* by the H + NO₂ reaction or by injection of HO radicals produced from the H + NO₂ or F + H₂O reactions. A complex analysis accounting for the secondary chemistry was required to extract values of *k*.
- [HO], [HO₂], and [NO₂] were monitored by LMR in an excess of NO₃ radicals.

Preferred Values

$$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3.$$

Comments on Preferred Values

In all of the studies listed it proved necessary to make extensive corrections for the secondary reactions. The values of *k* obtained by Mellouki et al. (1988, 1993) and Boodaghians et al. (1988) are in good agreement, although the error limits quoted are large. The value reported by Becker et al., (1992) is substantially lower, but still overlapping within the combined uncertainties, which were reported. The preferred value of *k* is thus a simple average of all of the reported values, with extended

uncertainty to reflect the scatter within the individual measurements and the complexity of the chemical systems used.

No measurements have been made of the temperature dependence of k but a small negative value is expected by analogy with similar reactions. The reaction has been suggested (Jitariu and Hirst, 1999) to proceed on a singlet surface via formation of an association complex similar in structure to pernitric acid (HO_2NO_2).

References

- Becker, E., Rahman, M. M., and Schindler, R. N.: Ber. Bunsenges. Phys. Chem. 96, 776, 1992.
Boodaghians, R. B., Canosa-Mas, C. E., Carpenter, P. J., and Wayne, R. P.: J. Chem. Soc. Faraday Trans. 2 84, 931, 1988.
Jitariu, L. C. and Hirst, D. M.: J. Phys. Chem. A 103, 6673, 1999.
Mellouki, A., Le Bras, 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.