IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx28

This data sheet last evaluated: May 2008 (with no changes to the preferred values).

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
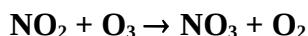
ΔH° = -102.2 kJ mol^{-1}

Rate coefficient data

k / cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
(3.2 ± 0.5) x 10^{-17}	298	Ghormley et al., 1973	FP (a)
9.76 x 10^{-14} exp$[-(2427 \pm 140)/T]$	260-343	Davis et al., 1974	(b)
(3.42 ± 0.27) x 10^{-17}	303		
1.34 x 10^{-13} exp$[-(2466 \pm 30)/T]$	231-298	Graham and Johnston, 1974	(c)
(3.49 ± 0.23) x 10^{-17}	298		
1.57 x 10^{-13} exp$[-(2509 \pm 76)/T]$	259-362	Huie and Herron, 1974	(d)
(3.78 ± 0.07) x 10^{-17}	297		
(3.45 ± 0.12) x 10^{-17}	296	Cox and Coker, 1983	(e)

Comments

(a) Flash photolysis system. [O$_3$] and [NO$_2$] were monitored by optical absorption.

(b) Stopped flow system with detection of O$_3$ by time-of-flight mass spectrometry. The exponential term given in the abstract is incorrect; the correct value is tabulated here (D. D. Davis, private communication).

(c) Long path static cell. [O$_3$] and [NO$_2$] monitored in separate experiments by UV absorption spectrometry. Stoichiometric ratio ($\Delta NO_2/\Delta O_3$) was measured to be 1.89 ± 0.08.

(d) Stopped flow system. [O$_3$] monitored by molecular-beam sampling mass spectrometry.

(e) Static system. Experiments performed with both NO$_2$ and O$_3$ in excess. Time resolved absorption spectroscopy was used to monitor [N$_2$O$_5$] with a diode laser infrared source, and [NO$_2$] and [O$_3$] were monitored at 350 nm and 255 nm, respectively, using conventional UV techniques. Total pressure 13 mbar (10 Torr) N$_2$. N$_2$O$_5$ was shown to be the only nitrogen containing product. Overall stoichiometry ($\Delta NO_2/\Delta O_3$) was determined to have the value 1.85 ± 0.09. Minor role for unsymmetrical NO$_3$ species were suggested to account for a stoichiometric factor less than 2.

Preferred Values

k = 3.5 x 10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.4 x 10^{-13} exp(-2470/T) cm^3 molecule^{-1} s^{-1} over the temperature range 230-360 K.

Reliability
  Δlog k = $\pm$ 0.06 at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The preferred value at 298 K is taken as the mean of the five values tabulated, corrected where necessary for the difference between the temperature of the measurement and 298 K. The temperature coefficient is taken as the mean of the values obtained by Davis et al. (1974), Graham and Johnston (1974), and Huie and Herron (1974), which are in excellent agreement. Verhees and Adema (1985) obtained a significantly higher temperature coefficient for k and a higher pre-exponential factor, but wall corrections were shown to be important in their work. There are also a number of other measurements of k at, or close to, 298 K, which have not been used in deriving the preferred values because of their substantial deviation from those listed above.

References

Cox, R. A. and Coker, G. B.: J. Atmos. Chem. 1, 53, 1983.

Davis, D. D., Prusazcyk, J., Dwyer, M., and Kim, P.: J. Phys. Chem. 78, 1775, 1974.

Ghormley, J. A., Ellsworth, R. L., and Hochenadel, C. J.: J. Phys. Chem. 77, 1341, 1973. Erratum 78, 2698 (1974).

Graham, R. A. and Johnston, H. S.: J. Chem. Phys. 60, 4628, 1974.

Huie, R. E. and Herron, J. T.: Chem. Phys. Lett. 27, 411, 1974.

Verhees, P. W. C. and Adema, E. H.: J. Atmos. Chem. 2, 387, 1985.