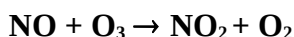


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO<sub>x</sub>24

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. The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 4, 1461, 2004; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



$$\Delta H^\circ = -199.8 \text{ kJ mol}^{-1}$$

### Rate coefficient data

k / cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
2.34 x 10 <sup>-12</sup> exp[-(1450 ± 50)/T]	203-361	Birks et al., 1976	(a)
(1.73 ± 0.09) x 10 <sup>-14</sup>	297		
4.3 x 10 <sup>-12</sup> exp[-(1598 ± 50)/T]	283-443	Lippmann et al., 1980	(b)
(2.14 ± 0.11) x 10 <sup>-14</sup>	304		
3.16 x 10 <sup>-12</sup> exp[-(1556 ± 40)/T]	212-422	Ray and Watson, 1981	DF-MS
(1.80 ± 0.04) x 10 <sup>-14</sup>	299		
2.6 x 10 <sup>-12</sup> exp[-(1435 ± 64)/T]	195-369	Michael et al., 1981	(c)
(2.0 ± 0.2) x 10 <sup>-14</sup>	298		
8.9 x 10 <sup>-19</sup> T <sup>2.2</sup> exp(-765/T)	204-353	Borders and Birks, 1982	(d)
(1.72 ± 0.04) x 10 <sup>-14</sup>	298		
5.1 x 10 <sup>-12</sup> exp[-(1670 ± 100)/T]	263-328	Moonen et al., 1998	(e)
(1.90 ± 0.19) x 10 <sup>-14</sup>	298		

### Comments

- (a) Fast flow system with NO in excess and with [O<sub>3</sub>] monitored by mass spectrometry.
- (b) First order decay of [O<sub>3</sub>] in the presence of excess NO in a 220 m<sup>3</sup> stainless steel spherical vessel at pressures below 0.13 mbar (0.1 Torr). Chemiluminescence was monitored under stopped flow conditions
- (c) Three independent low pressure fast-flow studies were carried out. The extent of reaction was monitored by NO<sub>2</sub> chemiluminescence under conditions of excess NO or excess O<sub>3</sub>. In other experiments the decay of [NO] in excess O<sub>3</sub> was monitored by RF. The results from all of the studies were in good agreement. An Arrhenius plot of the data showed significant curvature with *E/R* varying from 1258 K over the temperature range 195-260 K, to 1656 K over the temperature range 260-369 K.
- (d) Dual flow tube technique with NO<sub>2</sub> chemiluminescence used to monitor the reaction progress. The authors claim that this technique gives accurate values of *E/R* over temperature intervals as small as 10 K. Nonlinear Arrhenius behaviour was observed with *E/R* increasing from a value of 1200 K at the lowest temperature studied to 1470 K at the highest temperature.
- (e) A novel flow technique was used in which the reaction chamber consisted of PTFE tubing immersed in a thermostat. Different reaction times were achieved by varying the tube length. The carrier gas was artificial air at atmospheric pressure into which small concentrations (~

$10^{-12}$  molecule  $\text{cm}^3$ ) of NO and  $\text{O}_3$  were introduced in comparable amounts so that the reaction occurred under second order conditions. Concentrations at the outlet of the reactor were measured by means of an NO/ $\text{NO}_x$  chemiluminescence analyser. Some experiments were carried out at 200 K but are not included in the derivation of the Arrhenius expression because of their uncertain reliability.

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.9 \times 10^{-14}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.07 \times 10^{-12} \exp(-1400/T)$	195-310
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.07$	298
$\Delta(E/R)$	$\pm 200$	195-310

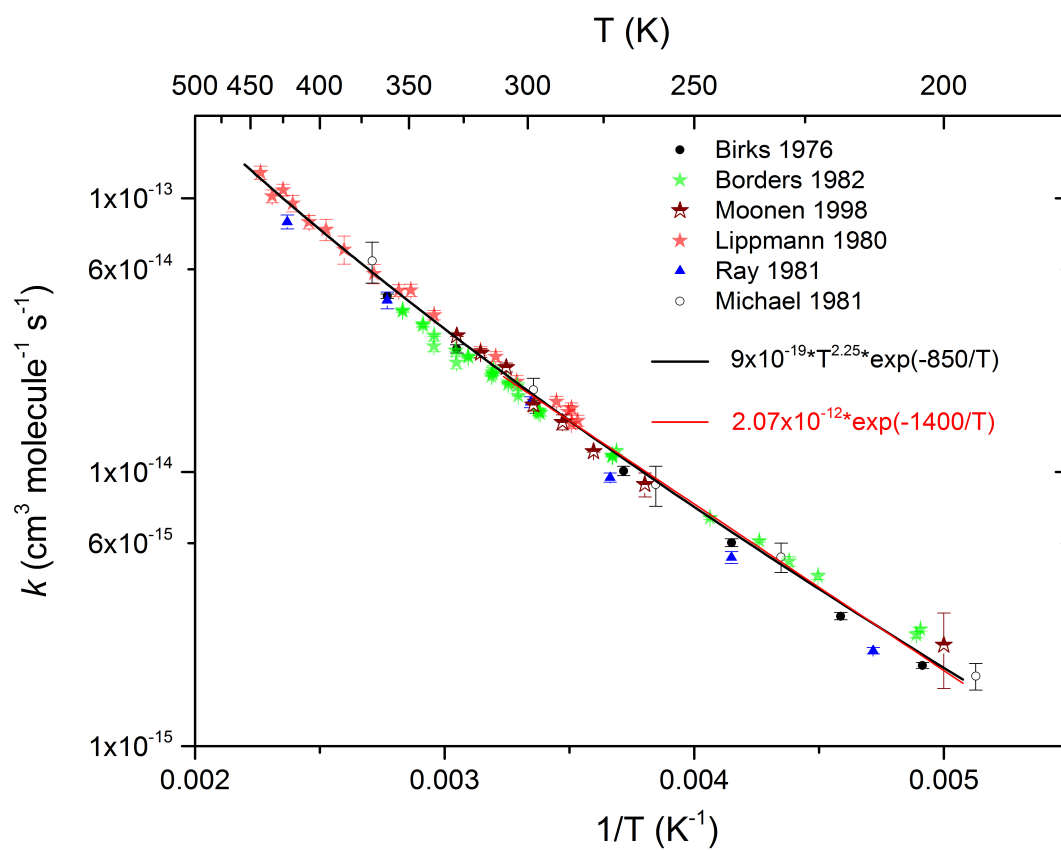
### Comments on Preferred Values

The temperature dependent data of Birks et al. (1976), Lippmann et al. (1980), Ray and Watson (1981), Michael et al. (1981), Borders and Birks (1982), and Moonen et al. (1998) are described by the expression  $k(T) = 9.0 \times 10^{-19} T^{2.25} \exp(-850/T)$  which adequately reproduces all datasets and captures the slight curvature in the temperature dependence in  $k$  over the range 195 to 450 K, which was also observed by Clyne et al. (1964), Clough and Thrush (1967). The preferred Arrhenius expression for 195 to 310 K is based on the same datasets and agrees with the fuller parameterisation to within 4 % at all temperatures in this range. Earlier room temperature results of Stedman and Niki (1973) and Bemand et al. (1974) are in good agreement with the preferred value at 298 K.

Clyne et al. (1964), Birks et al. (1976), Schurath et al. (1981), and Michael et al. (1981) have reported individual Arrhenius expressions for each of two primary channels, one to produce  $\text{NO}_2$  in its electronic ground state and the other leading to electronically excited  $\text{NO}_2$ .

### References

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Temperature dependent measurements of  $k(\text{NO} + \text{O}_3)$ .