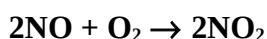


**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.53 NO<sub>x</sub>23**

Datasheets 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 datasheet is: IUPAC Subcommittee for Gas Kinetic Data Evaluation, <http://iupac.pole-ether.fr/>.

This datasheet last evaluated: 20<sup>th</sup> May 2014; last change in preferred values: 20<sup>th</sup> May 2014.



$$\Delta H^\circ = -114.1 \text{ kJ mol}^{-1}$$

**Rate coefficient data**

$k / \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.65 \times 10^{-38}$	298	Smith, 1943	(a)
$1.93 \times 10^{-38}$	298	Johnston and Slentz, 1951	(b)
$2.92 \times 10^{-40} (T/298)^{2.13} \exp(1521/T)$	377-779	Ashmore et al., 1962	(c)
$4.81 \times 10^{-38}$	298		
$4.33 \times 10^{-38}$	296	Glasson and Tuesday, 1963	(d)
$8.52 \times 10^{-39}$	478	Morecroft and Thomas, 1967	(e)
$5.51 \times 10^{-38}$	293	Greig and Hall, 1966	(f)
$1.06 \times 10^{-38} \exp(481/T)$	293-372	Greig and Hall, 1967	(f)
$5.33 \times 10^{-38}$	298		
$2.09 \times 10^{-38} \exp(186/T)$	277-329	Hisatsune and Zafonte, 1969	(g)
$3.67 \times 10^{-38}$	298		
$3.83 \times 10^{-38}$	298	Mahenc et al., 1971	(h)
$3.15 \times 10^{-39} \exp(744.5/T)$	273.5-333		
$(3.90 \pm 0.20) \times 10^{-38}$	298	Stedman and Niki, 1973	(i)
$5.33 \times 10^{-39} \exp(602/T)$	298-348	England and Corcoran, 1975	(j)
$(4.02 \pm 0.08) \times 10^{-38}$	298		
$3.58 \times 10^{-39} \exp(512/T)$	270-600	Olbrechts, 1985	(k)
$2.0 \times 10^{-38}$	298		

**Comments**

- (a) Static 3 l Pyrex vessel with NO<sub>2</sub> monitored in absorption in the range 460 to 600 nm. Used 2.0 (1.5) to 66.7 mbar (Torr) NO and 2.0 (1.5) to 33.3 (25) mbar (Torr) O<sub>2</sub>. No correction for NO<sub>2</sub> dimerization despite the fact that high NO partial pressures resulted in a rate constant a factor of two lower compared to low NO partial pressures.
- (b) Static reaction vessel at partial pressures of NO ranging from 10.7 (8) to 453 (340) mbar (Torr). O<sub>2</sub> partial pressure ranged from a tenfold excess to equimolar to 10% relative to NO partial pressure.
- (c) Static quartz vessel equipped with pressure gauge and photometric NO<sub>2</sub> detection. Partial pressures of NO and O<sub>2</sub> were in the range 2.7(2) to 267 (200) and 33.3 (25) to 533 (400) mbar (Torr), respectively, with variable amounts of N<sub>2</sub> added.

- (d) Static reaction vessel consisting of a 3 m base IR multipath cell of 120 m total pathlength used to monitor NO<sub>2</sub> at 6.15 μm. NO partial pressures ranged from 2-50 ppm and O<sub>2</sub> from 2 to 20% (v/v). Added olefins, NO<sub>2</sub> and NO<sub>2</sub> photolysis did not affect value of rate constant.
- (e) Static quartz reactor equipped with pressure gauge and photometric NO<sub>2</sub> detection in the temperature range 478 – 593 K. Partial pressures of NO and O<sub>2</sub> were 26.7-33.3 (20-25) and 13.3-36.4 mbar (10-27.3) (Torr), respectively. Addition of 374.6 (281) mbar (Torr) of N<sub>2</sub> did not affect the rate constant.
- (f) Static system equipped with 0.3 m base long-path IR absorption cell with 7.5 m effective pathlength.
- (g) Static system of 100 ml Pyrex absorption cell equipped with rapid scanning IR absorption spectrometer. The maximum partial pressures of NO and O<sub>2</sub> were 320 (240) and 640 (480) mbar (Torr). The concentrations were varied by two orders of magnitude and the maximum partial pressure of NO<sub>2</sub> did not exceed 18.7 (14) mbar (Torr). Corrections for NO<sub>2</sub> dimerization have been performed.
- (h) Oxidation reaction performed in a Pyrex ac-discharge vessel. Starting with typically 30 mbar of pure NO the 9000 V/400 Hz discharge converts part of the NO exclusively according to the reaction  $2\text{NO} \rightarrow \text{O}_2 + \text{N}_2$  into the reactive gas mixture. The oxidation reaction starts after turning off the ac discharge and the kinetics is followed by measuring the change in total pressure. The gas composition is monitored using off-line residual gas mass spectrometry. The measured termolecular rate constant is independent of the presence of buffer gas, initial concentrations of reactants and of the reaction product NO<sub>2</sub> or N<sub>2</sub>O<sub>4</sub>.
- (i) Static system operated as photochemical smog chamber. Use of 5-1000 ppm mixing ratios of NO in air using NO/O<sub>3</sub> chemiluminescence detectors to monitor NO, NO<sub>2</sub>, and O<sub>3</sub>. Despite the multicomponent gas mixture the title reaction was studied directly without interference from other reactions. However, there were indications of photocatalysis of the title reaction at low NO concentrations (< 1 ppm NO) that was attributed to impurities in NO.
- (j) Static system at atmospheric pressure. Dry system of 50 to 150 ppm NO, 3.33% (v/v) O<sub>2</sub>, wet system contained 100 to 150 ppm O<sub>2</sub>, 3.33% O<sub>2</sub> and 0.30 to 1.21% H<sub>2</sub>O vapour. NO<sub>2</sub> was analyzed using GC. The formation of HONO and HNO<sub>3</sub> in the wet system was accounted for as were wall reactions that lowered the observed NO<sub>2</sub> concentrations. The title reaction was not influenced by the presence of H<sub>2</sub>O vapour although it had to be studied above 35°C in order to minimize wall reactions. HONO vapour was not directly monitored, but its formation was accounted for by the deviation of NO<sub>2</sub> concentration from third order behaviour of the title reaction under conditions where formation of HNO<sub>3</sub> was unimportant.
- (k) Static 165 ml or 1 L glass or fused quartz reactor. Total pressure variation was measured using a differential micromanometer, and [NO<sub>2</sub>] measured in absorption at 435.8 nm. Owing to large NO<sub>2</sub> product pressure an allowance was made for the equilibrium  $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  in the NO<sub>2</sub> detection for T ≤ 370 K. Partial pressures of NO and O<sub>2</sub> ranged from 1 (1.3) to 35 (26) mbar (Torr). Non-Arrhenius behaviour was observed with *k* first decreasing with increasing temperature, reaching a minimum value at 600 K, and then increasing with increasing temperature up to the upper limit of measurement at 768 K.

### Preferred Values

$k = 3.95 \times 10^{-38} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  at 298 K.

$k = 4.25 \times 10^{-39} \exp(663.5/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  over the temperature range 273.5-333 K.

$\log k / \text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} = 44700(1/T)^2 - 10.2/T - 37.875$  over the temperature range 273.5 - 780 K (parabolic fit).

### Reliability

$\Delta \log k = 0.2$  at 298 K.

$\Delta(E/R) = \pm 50$  K.

### Comments on Preferred Values

The preferred rate constant at 298 K is an arithmetic mean of values obtained by Glasson and Tuesday (1963), Hisatsune and Zafonte (1969), Mahenc et al. (1971), Stedman and Niki (1973) and England and Corcoran (1975). Figure 1 presents an Arrhenius plot of all evaluated rate constants displayed in the Table. The rate constant has been checked by numerous authors in the past and has been found to be independent of buffer gas pressure, the presence of H<sub>2</sub>O vapour and added NO<sub>2</sub> as well as the sequence in which the gases were mixed in the reaction vessel. The rate law  $r = k[\text{NO}]^2[\text{O}_2]$  is valid over the full temperature range. We have excluded from our evaluation a number of studies that disagreed on the rate law of NO oxidation, i.e. quadratic in NO and linear in O<sub>2</sub> concentration, or were reporting a dependence of the rate law on the nature of the buffer gas.

We are weighting the work of England and Corcoran (1975) more heavily than any other for the following reasons: (i) it is part of only three studies in addition to that of Greig and Hall (1966, 1967) that compare the dry system with one that has a significant and controlled partial pressure of H<sub>2</sub>O vapour. One of the main conclusions of this work as well as that of Greig and Hall (1966, 1967) is that H<sub>2</sub>O vapour does not affect the value of  $k$ ; (ii) it uses low partial pressures in the ppm range for NO and therefore avoids the problem of correction for NO<sub>2</sub> dimerization; (iii) it quantitatively takes into account competing reactions such as  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO}$  and  $3\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HNO}_3 + \text{NO}$  thought to affect the kinetics, especially in the presence of H<sub>2</sub>O vapour. England and Corcoran (1975) measured the deviation of the reaction rate from expected third order behaviour at later reaction times albeit at low extent of reaction whereby they minimized the incidence of HNO<sub>3</sub> formation; (iv) it is the only work that systematically investigated the influence of wall reactions on the kinetics as a function of temperature. Owing to the limited temperature range (50 K) covered by England and Corcoran (1975) one may take the three-parameter (parabolic) expression given above for purposes of extrapolation of  $k$  to higher temperatures up to approximately 780 K. The Arrhenius plot over the temperature range 273.5 to 333 K is linear as displayed in Figure 1, but when taken over the full temperature range (273.5 – 780 K) it is non-linear as displayed in Figure 2 and has therefore been treated as a three-parameter fit. Beware of the fact that the absolute values of  $k$  resulting from the work of Olbregts are a factor of two lower than the recommended value, however, the complex temperature dependence including the turn-over from a negative to a positive value in the neighbourhood of 600 K is very similar to the recommended data sets given in Figure 2.

Olbregts (1985) observed marked non-Arrhenius behaviour over the entire temperature range studied (226-758 K) and expressed  $k$  by a modified Arrhenius expression and also as the sum of two Arrhenius expressions, one with a negative and one with positive value of  $E_a$ . However, from 250 K to about 600 K the total rate coefficient of Olbregts (1985) follows the recommended temperature dependence given above.

The reaction generally is interpreted in terms of a multi-step mechanism involving NO<sub>3</sub> (peroxynitrite radical ON-O-O<sup>•</sup>) or the NO dimer, (NO)<sub>2</sub>, both mechanisms being kinetically equivalent from an experimental point of view. The slight negative (observed) activation energy of -5.5 kJ mol<sup>-1</sup> is close to the measured stability of the NO dimer (-4.5 kJ mol<sup>-1</sup>) measured by Forte and van den Bergh (1978). Gadzhiev et al. (2009) have used *ab initio* methods to compute a potential energy diagram on the singlet as well as the triplet surface for NO oxidation and come to the conclusion that the intermediate peroxide ONOONO is formed without the incidence of a barrier. A complex sequence of isomerization steps and multiple reaction paths lead from the above peroxide to 2NO<sub>2</sub>.

Most investigations of the last 100 years, starting with Bodenstein and Meinecke (1909) agreed on the termolecular nature of the oxidation of NO by O<sub>2</sub>. The same goes for the evidence of a small, but significant negative activation energy at low temperature. A list of earlier works may be found in Mahenc et al. (1971) and Olbregts (1985).

The role of H<sub>2</sub>O vapour in the measurement of k has systematically only been addressed in the work of England and Corcoran (1975) although many workers have qualitatively noticed the connection between water vapour and wall effects. The latter usually leads to a decrease of the NO<sub>2</sub> product through wall-catalyzed reactions to ultimately lead to (wall-adsorbed) HNO<sub>3</sub>. In newer work (Olbregts, 1985) the dimerization of NO<sub>2</sub> is quantitatively taken into account and is shown to have a significant effect in high pressure studies where the partial pressure of NO<sub>2</sub> exceeds 1 mbar or so. However, the wall-catalyzed reaction  $3\text{NO} \rightarrow \text{N}_2\text{O} + \text{NO}_2$ , investigated by Smith (1988) and Chughtai (1990) for static (pure) and reasonably dry NO samples at several mbar (Torr) partial pressure has not been taken into account by monitoring for instance N<sub>2</sub>O. This reaction is not expected to contribute to NO loss at concentrations typically used in photochemical smog chambers (tens of ppb to ppm's). In addition to the title reaction, England and Corcoran (1975) are the only workers who took into account the effect of H<sub>2</sub>O vapour and heterogeneous reactions including  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HONO}$  and  $3\text{NO} \rightarrow \text{N}_2\text{O} + \text{NO}_2$ . The published heterogeneous interaction of NO on pure Pyrex/quartz vessel walls with or without adsorbed H<sub>2</sub>O (Smith, 1988; Chughtai 1990) is most probably not the reason for kinetic complications in reactions of NO in view of both the low NO solubility in H<sub>2</sub>O as well as the low propensity for surface adsorption of NO. The reason for the factor of two disagreement between the present recommended values and the results of Olbregts (1985) is not known with certainty.

## References

- Ashmore, P.G., Burnett, M.G. and Tyler, B.J.: *Trans. Faraday Soc.* 58, 685, 1962.  
Bodenstein, M. and Meinecke, J.L.G.: *Z. Angew. Chem.* 22, 1153, 1909.  
Chughtai, A.R., Welch, W.F., Akhter, M.S. and Smith, D.M.: *Appl. Spectrosc.* 44, 294, 1990.  
England, C. and Corcoran, W.H.: *Ind. Eng. Chem. Fundam.* 14, 55, 1975.  
Forte, E. and van den Bergh, H.: *Chem. Phys.* 30, 325 (1978).  
Gadhziev, O.B., Ignatov, S.K., Razuvaev, A.G. and Masunov, A.E.: *J. Phys. Chem. A* 113, 9092, 2009.  
Glasson, W.A. and Tuesday, C.S.: *J. Amer. Chem. Soc.* 85, 2901, 1963.  
Greig, J.D. and Hall, P.G.: *Trans. Faraday Soc.* 63, 655, 1967.  
Greig, J.D. and Hall, P.G.: *Trans. Faraday Soc.* 62, 652, 1966.  
Hisatsune, I.C. and Zafonte, L.: *J. Phys. Chem.* 73, 2980, 1969.  
Johnston, H.S. and Slentz, L.W.: *J. Amer. Chem. Soc.* 73, 2948 1951.  
Mahenc, J., Clot, G. and Bes, R.: *Bull. Soc. Chim. de France* 5, 1578, 1971.  
Morecroft, M.J. and Thomas, J.H.: *J. Phys. Chem.* 71, 1543, 1967.  
Olbregts, J.: *Int. J. Chem. Kinet.* 17, 835, 1985.  
Smith, D.M., Welch, W.F., Graham, S.M., Chughtai, A.R., Wicke, B.G. and Grady, K.A.: *Appl. Spectrosc.* 42, 674, 1988.  
Smith, J.H.: *J. Amer. Chem. Soc.* 65, 74, 1943.  
Stedman, D. H. and Niki, H.: *J. Phys. Chem.* 77, 2604, 1973.

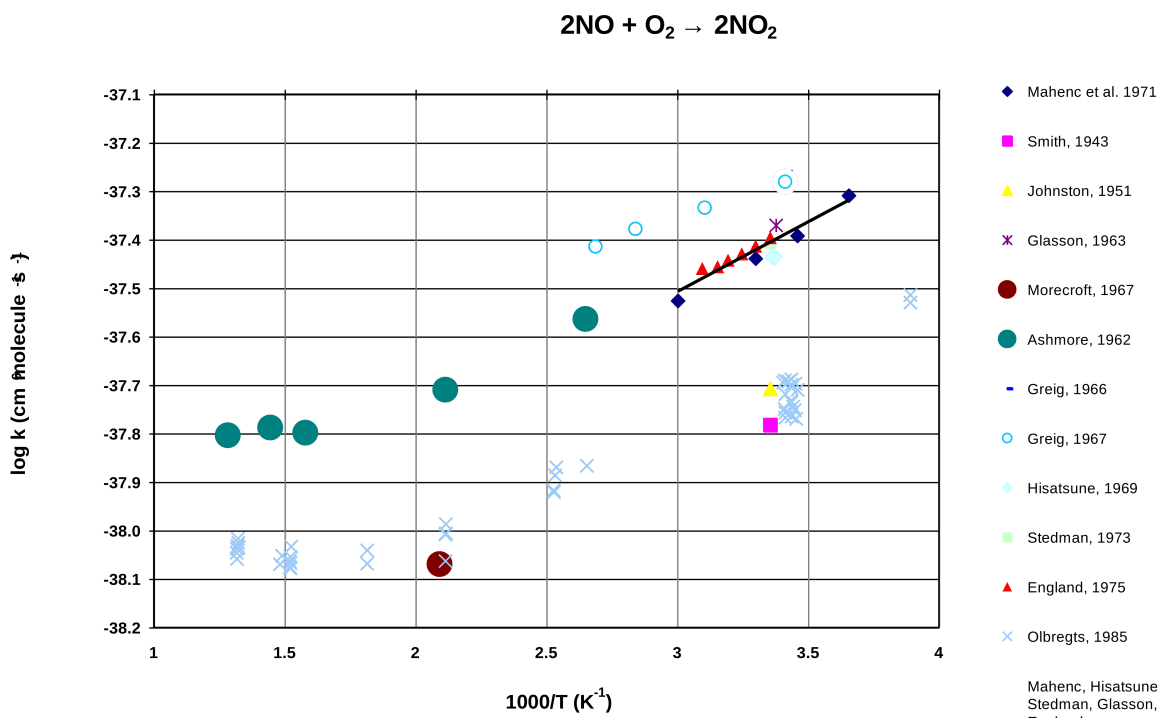


Figure 1: Evaluated rate constants  $k$ . (The data point of Stedman and Niki (1969) lies below the point at 298 K of England and Corcoran (1975). The straight line corresponds to the expression  $k = 4.25 \times 10^{-39} \exp(663.5/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  over the temperature range 273.5-333 K and encompasses the data of Glasson and Tuesday (1963), Hisatsune and Zafonte (1969), Mahenc et al. (1971), Stedman and Niki (1973) and England and Corcoran (1975)).

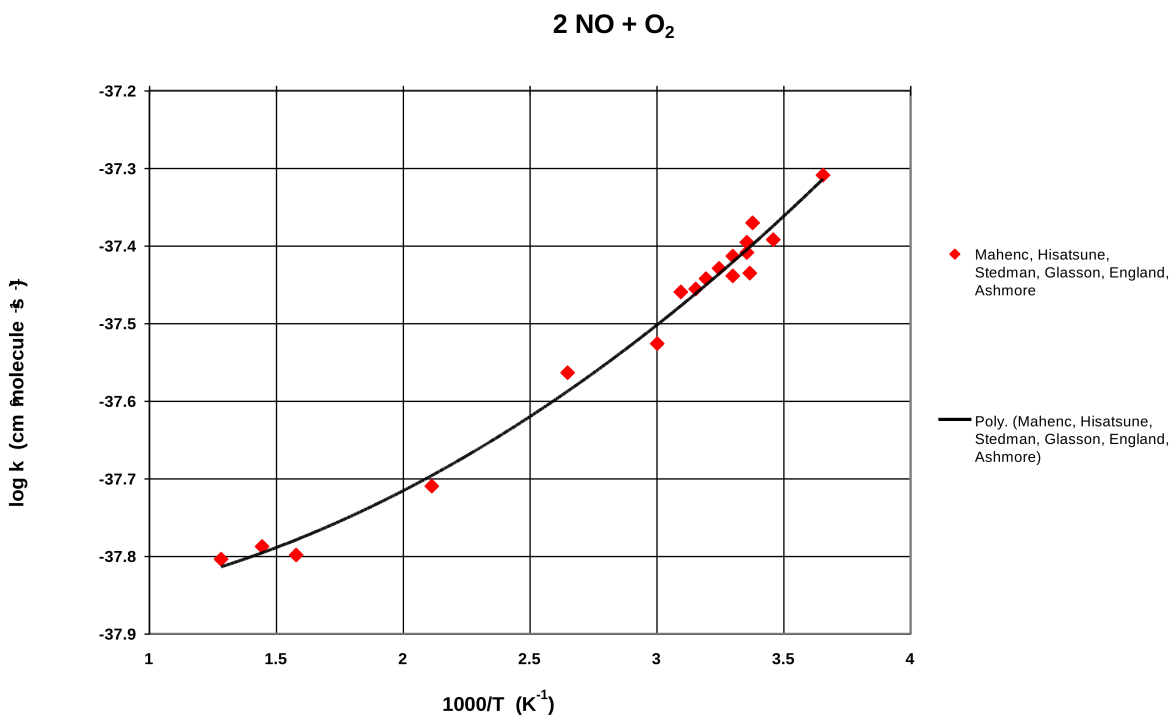


Figure 2: Three-parameter representation of rate constants  $k$  in the range 273.5 – 779 K.