

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.46 NO<sub>x</sub>16

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This data sheet last evaluated: November 2017; last change in preferred values: June 2012.



$$\Delta H^\circ = -100.5 \text{ kJ}\cdot\text{mol}^{-1}$$

## Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.09 \pm 0.52) \times 10^{-31} [\text{N}_2]$	300	Howard, 1977	DF-LMR (a)
$(2.5 \pm 0.5) \times 10^{-31} [\text{N}_2]$	283	Cox and Patrick, 1979	(b)
$(2.3 \pm 0.6) \times 10^{-31} (T/300)^{-4.6} [\text{N}_2]$	229-362	Sander and Peterson, 1984	(c)
$1.5 \times 10^{-31} [\text{N}_2]$	298	Kurylo and Ouellette, 1986	(d)
$1.8 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2]$	228-358	Kurylo and Ouellette, 1987	(d)
$2.1 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2]$	220-298	Christensen et al., 2004	PLP-IR/UVA (e)

## Comments

- Discharge flow system study with laser magnetic resonance detection of HO<sub>2</sub>. The pressure range was 0.5-3 Torr. The linear plot of  $k_0$  as a function of [M] with a non-zero intercept was interpreted as contribution from the reaction HO<sub>2</sub> + NO<sub>2</sub> → HONO + O<sub>2</sub>. As this reaction channel is not present (see comments on preferred values), the nonzero intercept has to be attributed to a falloff effects.
- Molecular modulation UV spectrometry. HO<sub>2</sub> radicals were generated by Cl<sub>2</sub> photolysis in the presence of H<sub>2</sub> and O<sub>2</sub>. O<sub>2</sub>-N<sub>2</sub> mixtures used in the pressure range 40-600 Torr.
- Flash photolysis-UV absorption study in the pressure range 50-700 Torr. A strong enhancement of reaction in the presence of water vapor was observed, suggested to be due to formation of HO<sub>2</sub>-H<sub>2</sub>O complexes.
- Flash photolysis of Cl<sub>2</sub>-CH<sub>3</sub>OH-NO<sub>2</sub> mixtures in the presence of O<sub>2</sub> or N<sub>2</sub>, with HO<sub>2</sub> detection at 225 nm. The falloff curve measured over the pressure range 25-600 Torr. The rate coefficient was evaluated using  $F_c = 0.6$  and  $k_\infty = 4.7 \times 10^{-12} (T/300)^{-1.4 \pm 1.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- Photolysis of F<sub>2</sub> (or Cl<sub>2</sub>)-CH<sub>3</sub>OH-NO<sub>2</sub> mixtures in N<sub>2</sub> with UV- or near IR-detection of HO<sub>2</sub> at bath gas pressures in the range 45-200 Torr. Evaluation using  $F_c = 0.6$  and  $k_\infty = 2.4 \times 10^{-12} (T/300)^{-1.9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . A strong enhancement of the reaction by CH<sub>3</sub>OH was noted and accounted for.

## Preferred Values

$k_0 = 1.4 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 220-360 K.

### Comments on Preferred Values

The studies of Howard (1977), Cox and Patrick (1979), Sander and Peterson (1984), Kurylo and Ouellette (1986, 1987) and Christensen et al. (2004) are in rough agreement. However, the effects of added H<sub>2</sub>O or CH<sub>3</sub>OH have to be accounted for. Therefore, the preferred values are based on the study of Christensen et al. (2004) which did this correction most systematically. The rate coefficient  $k_0$  by Christensen et al. (2004) was evaluated with the value for  $k_\infty$  given below and  $F_c = 0.6$ . Modification of  $F_c$  leads to minor changes in  $k_0$  and  $k_\infty$ , however, without changing the agreement between the experimental data and their representation by the falloff expression. By analogy to the reaction  $\text{HO} + \text{NO}_2 + \text{N}_2 \rightarrow \text{HONO}_2 + \text{N}_2$ , for which  $F_c$  was calculated by detailed theory (Troe, 2001) and analysis of experiments (Troe, 2012), instead of  $F_c = 0.6$  we employ  $F_c = 0.4$  independent of the temperature. This then increases  $k_\infty$  over the values from Kurylo and Ouellette (1987) and Christensen et al. (2004) to a temperature independent value of  $k_\infty = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . At the same time it decreases  $k_0$  to the given preferred values. Unsuccessful search for HONO as a reaction product by Graham et al. (1978) indicates that the reaction  $\text{HO}_2 + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2$  (at a pressure of 120 Torr) does not occur. Measurements by Bacak et al. (2011) extend down to 200 K. Rate constants from McKee et al. (2016) over the range 50 – 400 Torr at 298 K were about 20 % larger than the values from Christensen et al. (2004) which are preferred here.

### High-pressure rate coefficients Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$>1.7 \times 10^{-12}$	283	Graham, Winer and Pitts, 1977	(a)
$>(1.5 \pm 0.5) \times 10^{-12}$	283	Cox and Patrick, 1979	(b)
$(4.2 \pm 1.0) \times 10^{-12} (T/300)^{0.2}$	229-362	Sander and Peterson, 1984	(c)
$5.5 \times 10^{-12}$	298	Kurylo and Ouellette, 1986	(d)
$4.7 \times 10^{-12} (T/300)^{-1.4}$	228-358	Kurylo and Ouellette, 1987	(d)
$2.4(\pm 0.1) \times 10^{-12} (T/300)^{-1.9}$	220-298	Christensen et al., 2004	(e)

### Comments

- From thermal decomposition of HO<sub>2</sub>NO<sub>2</sub> in a static reactor with FTIR spectroscopic analysis of HO<sub>2</sub>NO<sub>2</sub>. Measurements at 1 bar of N<sub>2</sub> converted to recombination rate coefficients with the equilibrium constants given in Graham et al. (1978).
- See comment (b) for  $k_0$ . Determination of  $k_\infty$  by extrapolation of a curved Lindemann-Hinshelwood plot gave an internally consistent falloff plot. The measured value was  $k = 9.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 600 Torr of a 1:1 mixture of N<sub>2</sub> and O<sub>2</sub>.
- See comment (c) for  $k_0$ .
- See comment (d) for  $k_0$ .
- See comment (e) for  $k_0$ .

## Preferred Values

$k_{\infty} = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , independent of temperature over the range 220-360 K.

### Comments on Preferred Values

The preferred values are based on the measurements from Christensen et al. (2004). Different from the representation of the falloff curves by these authors using  $F_c = 0.6$ , we use  $F_c = 0.4$  (see comments on preferred values of  $k_0$ ). The higher rate constants suggested by Sander and Peterson (1984) and Kurylo and Ouellette (1986, 1987) according to Christensen et al. (2004) are caused by enhancement of the rate by the added hydrogen sources such as H<sub>2</sub>O and CH<sub>3</sub>OH. These values, therefore, are discarded in the present evaluation. Experiments by Bacak et al. (2011) in the falloff range agreed with the results from Christensen et al. (2004) at 298 K, however led to about 70 % smaller values of  $k$  over the range 300 – 600 Torr at 223 K.

## Preferred Values

Parameter	Value	T/K
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.4 \times 10^{-31} [\text{N}_2]$	298
$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.4 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2]$	200-400
$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$4 \times 10^{-12}$	298
$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$4 \times 10^{-12}$	200-400
$k(1 \text{ bar N}_2)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.5 \times 10^{-13}$	298
$F_c$	0.4	200-400
<i>Reliability</i>		
$\Delta \log k_0$	$\pm 0.1$	298
$\Delta n_0$	$\pm 0.1$	200-400
$\Delta \log k_{\infty}$	$\pm 0.1$	298
$\Delta n_{\infty}$	$\pm 0.1$	200-400

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of  $k$ :

$$= ((1.4e-31*(T/300)^{-3.1}*M*(4.0e-12))/((1.4e-31*(T/300)^{-3.1}*M+(4.0e-12))*10^{(\log10(0.4)/(1+(\log10((1.4e-31*(T/300)^{-3.1}*M/(4.0e-12))/(0.75-1.27*\log10(0.4))))^2}))$$

The molecular density,  $M = 7.243 \times 10^{21} \text{ P}(\text{bar})/\text{T}(\text{K})$

## References

- Bacak, A., Cooke, M. C., Bardwell, M. W., McGillen, M. R., Archibald, A. T., Huey, L. G., Tanner, D., Utembe, S. R., Jenkin, M. E., Derwent, R. G., Shallcross, D. E., and Percival, C. J.: *Atm. Environ.* 45, 6414, 2011.
- Christensen, L. E., Okumura, M., Sander, S. P., Friedl, R. R., Miller, C. E., and Sloan, J. J.: *J. Phys. Chem. A* 108, 80, 2004.
- Cox, R. A. and Patrick, K.: *Int. J. Chem. Kinet.* 11, 635, 1979.
- Dransfield, T. J., Donahue, N. M., and Anderson, J. G.: *J. Phys. Chem. A* 105, 1507, 2001.
- Graham, R. A., Winer, A. M., and Pitts, J. N.: *J. Chem. Phys.* 68, 4505, 1978.
- Howard, C. J.: *J. Chem. Phys.* 67, 5258, 1977.
- Kurylo, M. J. and Ouellette, P. A.: *J. Phys. Chem.* 90, 441, 1986.
- Kurylo, M. J. and Ouellette, P. A.: *J. Phys. Chem.* 91, 3365, 1987.
- McKee, K., Blitz, M. A., and Pilling, M. J.: *J. Phys. Chem. A* 120, 1408, 2016.

Sander, S. P. and Peterson, M. E.: J. Phys. Chem. 88, 1566, 1984.  
Sander, S. P. and Peterson, M. E.: J. Phys. Chem. 91, 3365, 1987.  
Troe, J.: Int. J. Chem. Kinet. 33, 878, 2001.