IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx11

This data sheet last evaluated: 28th July 2007; no revision of preferred values.

$$HO + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2 \qquad (1)$$
$$\rightarrow H_2O_2 + NO_3 \qquad (2)$$
$$\rightarrow HO_2 + HNO_3 \qquad (3)$$
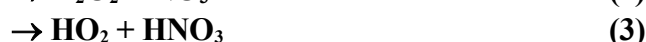
$\Delta H°(1) = -193$ kJ mol^{-1}

$\Delta H°(2) = -47$ kJ mol^{-1}

$\Delta H°(3) = -105$ kJ mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(4.0 ± 1.6) x 10^{-12}	246-324	Trevor et al., 1982	PLP-RF (a)
5.9 x 10^{-13} exp$[(650 \pm 30)/T]$	241-336	Smith et al., 1984	FP-RF (b)
(5.2 ± 1.1) x 10^{-12}	295		
8.8 x 10^{-19} T^2 exp$[(1130 \pm 20)/T]$	218-335	Jiménez et al., 2004	PLP-LIF (c)
(3.4 ± 1.0) x 10^{-12}	298		
Relative Rate Coefficients			
(4.8 ± 1.3) x 10^{-12}	268-295	Barnes et al., 1986	RR (d)
Branching Ratios			
$k_3/k <0.1$	298	Jiménez et al., 2004	PLP-LIF (c,e)
$k_2/k <0.05$	298	Jiménez et al., 2004	PLP-CRDS (f)

Comments

(a) The rate coefficient was independent of total pressure over the range 4-20 mbar He.

(b) The total pressure was 1.01 bar (760 Torr) of He.

(c) The concentration of HO_2NO_2 was measured by UV absorption using a diode array spectrometer and by FTIR, and the concentrations of the potential impurities H_2O_2, HNO_3 and NO_2 were monitored by MS and/or FTIR, MS and FTIR, and UV absorption, respectively. The rate coefficient was determined to be independent of pressure over the range 10-100 Torr (13-133 mbar) of He diluent. Over the temperature range 218-298 K the rate coefficients were well fitted by the Arrhenius expression $k = 3.18$ x 10^{-13} exp$[(690 \pm 40)/T]$ cm^3 molecule^{-1} s^{-1}.

(d) Carried out in a 420 L vessel, using in situ FTIR to monitor the concentration of HO_2NO_2. The concentrations of the reference hydrocarbons (C_3H_6 and n-C_4H_{10}) were monitored by GC. The effect of pressure was studied over the range 1.3-400 mbar (1-300 Torr) of He or N_2. The measured rate coefficient ratios have been placed on an absolute basis using the rate coefficient of $k(HO + n$-$C_4H_{10})$ $= 1.81$ x 10^{-17} T^2 exp$(114/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2007) and the fall-off expression for $k(HO + C_3H_6)$ recommended by Atkinson (1997). The rate coefficients were observed to be pressure and temperature independent over the ranges studied. In particular, the rate coefficient, measured relative to that for HO + n-butane (which is pressure-independent), showed no effect of total pressure of He

diluent over the range 6.7-400 mbar at 278 K. Results from this study supersede earlier results obtained using similar but less sensitive techniques (Barnes et al., 1981).

(e) Using the same apparatus as used for the kinetic measurements, the branching ratio for the formation of HO_2 was determined by converting HO_2 to HO radicals and measuring the HO radical concentrations by LIF. Computer calculations were used to assess the effects of the branching ratio for HO_2 production on the HO radical time-concentration profiles.

(f) NO_3 radical concentrations during the $HO + HO_2NO_2$ reaction were measured by cavity ring-down spectroscopy. From the CRDS signals with and without PLP (to initiate the reaction), computer modeling provided the upper limit to the branching ratio cited in the table.

Preferred Values

$k = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 3.2 \times 10^{-13}$ exp(690/T) cm^3 molecule^{-1} s^{-1} over the temperature range 210-300 K.
$k_1/k = 1.0$ at 298 K.

Reliability
Δlog $k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.
$\Delta(k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The measured rate coefficients at room temperature range from 3.4×10^{-12} cm^3 molecule^{-1} s^{-1} to 5.2×10^{-12} cm^3 molecule^{-1} s^{-1} (Trevor et al., 1982; Smith et al., 1984; Barnes et al., 1986; Jiménez et al., 2004), and the reported temperature dependency varies from being essentially temperature independent (Trevor et al., 1982; Barnes et al., 1986) to having (E/R) ~ -670 K over the temperature range 218-300 K (Smith et al., 1984; Jiménez et al., 2004). The preferred values are based on the recent and extensive absolute rate study of Jiménez et al. (2004) in which the concentrations of HO_2NO_2 and of potential impurities (H_2O_2, HNO_3 and NO_2) were monitored in the slow flow system prior to and/or after the reaction cell. The preferred Arrhenius expression $k = A$ exp(-B/T) is that derived by Jiménez et al. (2004) from a least-squares analysis of their data at temperatures ≤298 K. The preferred Arrhenius expression should not be used outside of the restricted temperature range of 210-300 K; at temperatures outside of this range the expression $k = 8.8 \times 10^{-19}$ T^2 exp(1130/T) cm^3 molecule^{-1} s^{-1} (Jiménez et al., 2004) should be used. The rate coefficient has been shown to be independent of pressure over the ranges 6.7-400 mbar (5-300 Torr) of He diluent at 278 K (Barnes et al., 1986) and 13-133 mbar of He diluent at 298 K (Jiménez et al., 2004).

The upper limits to the branching ratios k_2/k and k_3/k determined by Jiménez et al. (2004) at 298 K imply that the reaction proceeds entirely by channel (1). A TST calculation by Lamb et al. (1984) suggests that the pressure dependence of this rate coefficient will be much less than that for the corresponding reaction of HO radicals with HNO_3.

References

Atkinson, R.: J. Phys. Chem. Ref. Data 26, 215, 1997.
Barnes, I., Bastian, V., Becker, K. H., Fink, E. H. and Zabel, F.: Chem. Phys. Lett. 123, 28, 1986.
Barnes, I., Bastian, V., Becker, K. H., Fink, E. H. and Zabel, R.: Chem. Phys. Lett. 83, 459, 1981.
IUPAC,: http://iupac.pole-ether.fr, 2007.
Jiménez, E., Gierczak, T., Stark, H., Burkholder, J. B. and Ravishankara, A. R.: J. Phys. Chem. A 108, 1139, 2004.
Lamb, J. J., Mozurkewich, M. and Benson, S. W.: J. Phys. Chem. 88, 6441, 1984.

Smith, C. A., Molina, L. T., Lamb, J. J. and Molina, M. J.: Int. J. Chem. Kinet. 16, 41, 1984.
Trevor, P. L., Black, G. and Barker, J. R.: J. Phys. Chem. 86, 1661, 1982.

○ Trevor et al. (1982)
■ Smith et al. (1984)
▲ Barnes et al. (1986)
▼ Jimenez et al. (2004)
—— Recommendation
- - - 3-Parameter fit (Jimenez et al., 2004)