IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx10

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

$$HO + HONO_2 \rightarrow H_2O + NO_3 \qquad\qquad (1)$$
$$\rightarrow [H_2NO_4] \rightarrow H_2O + NO_3 \qquad\qquad (2)$$

ΔH° = -70.2 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			
$(8.9 \pm 1.3) \times 10^{-14}$	272-464	Margitan et al., 1975	DF-RF (a)
$(8 \pm 2) \times 10^{-14}$	240-298	Smith and Zellner, 1975	FP-RA (b)
$1.52 \times 10^{-14} \exp[(649 \pm 69)/T]$	224-366	Wine et al., 1981	FP-RF
$(1.25 \pm 0.28) \times 10^{-13}$	298		
$(1.25 \pm 0.13) \times 10^{-13}$	298	Ravishankara et al., 1982	PLP-RA (c)
$5.7 \times 10^{-15} \exp[(896 \pm 145)/T]$	228-298	Margitan and Watson, 1982	FP-RF (d)
$(1.19 \pm 0.12) \times 10^{-13}$	298		
$1.05 \times 10^{-14} \exp[(759 \pm 100)/T]$	225-296	Kurylo et al., 1982	FP-RF (e)
$(1.38 \pm 0.20) \times 10^{-13}$	296		
$7.3 \times 10^{-15} \exp[(867 \pm 85)/T]$	251-403	Jourdain et al., 1982	DF-EPR (f)
$(1.25 \pm 0.07) \times 10^{-13}$	296		
$1.52 \times 10^{-14} \exp[(644 \pm 79)/T]$	218-363	Marinelli and Johnston, 1982	FP-RF (g)
$(1.31 \pm 0.24) \times 10^{-13}$	298		
$8.3 \times 10^{-15} \exp[(850 \pm 40)/T]$	240-370	Smith et al., 1984	FP-RF (h)
$(1.36 \pm 0.04) \times 10^{-13}$	295		
$5.43 \times 10^{-15} \exp(843/T)$	253-295	Devolder et al., 1984	DF-RF (i)
$(9.3 \pm 1.0) \times 10^{-14}$	295		
$2.0 \times 10^{-14} \exp[(430 \pm 60)/T]$	237-330	Connell and Howard, 1985	DF-LMR
$(8.4 \pm 0.18) \times 10^{-14}$	301		
$(1.26 \pm 0.11) \times 10^{-13}$	297	Jolly et al., 1985	PLP-RA (j)
$(1.28 \pm 0.10) \times 10^{-13}$	297	Stachnik et al., 1986	PLP-RA (k)
See comment	200-373	Brown et al., 1999	PLP-LIF (l)

Comments

(a) The value given is the mean of the rate coefficients measured at 295, 420 and 464 K. A slightly higher value obtained at 272 K was considered to be less reliable.

(b) The measured rate coefficient was observed to increase with increasing temperature above 298 K, to 1.0×10^{-13} cm^3 molecule^{-1} s^{-1} at 406 K.

(c) The value of k tabulated is at 67 mbar (50 Torr) Ar; k was also measured at 80 mbar (60 Torr) SF$_6$ and at 251 K. The reaction stoichiometry was measured by monitoring NO$_3$ radical production using optical absorption at 662 nm and using the initial [HO] value. The figures given for the stoichiometry have since been revised as a result of a remeasurement of the absorption coefficient of

NO$_3$ (Yokelson et al., 1994). The new values are 0.85 at 298 K and 0.88 at 251 K for [NO$_3$]$_{produced}$/[HO]$_{consumed}$.

(d) k was found to depend on both temperature and pressure. k was reported to increase by 10% over the pressure range 27-133 mbar (20-100 Torr) He at 298 K and by 40% over the same pressure range at 238 K. The Arrhenius expression tabulated is a least-squares fit to the data at 53 mbar (40 Torr) He over the temperature range 228-298 K. Significant non-Arrhenius behavior was observed above 298 K at each value of the total pressure. k was also determined at 27 mbar (20 Torr) He and 133 mbar (100 Torr) He. For the linear portion of the Arrhenius plots (at or below 298 K) the following values of E/R are derived: -735 K (27 mbar He) and -1000 K (133 mbar He). The authors made linear extrapolations to zero pressure and reported an E/R value of -700 K for data at or below 298 K.

(e) k was studied over the temperature range 225-443 K and over the pressure range 40-67 mbar (30-50 Torr) of Ar and SF$_6$. The rate coefficient k exhibited significant non-Arrhenius behavior above 296 K, with no dependence on total pressure.

(f) Pressure ~1.3 mbar (1 Torr). The rate coefficient k was reported to exhibit linear Arrhenius behavior over the entire temperature range, but a greater temperature dependence (E/R = -1119 K) is derived using only data at or below 298 K. The NO$_3$ radicals produced were measured by adding excess NO and monitoring its removal by EPR. The stoichiometry so obtained was [NO$_3$]$_{produced}$/[HO]$_{consumed}$ = 1.03 ± 0.05.

(g) Pressure of 13-67 mbar (10-50 Torr) Ar. k was reported to exhibit linear Arrhenius behavior over the entire temperature range, but a greater temperature dependence (E/R = -697 K) is derived using only data at and below 298 K.

(h) The pressure was varied from 0.067-1.01 bar (50-760 Torr) He, with no observed effect on the value of k. Linear Arrhenius behavior was observed.

(i) The rate coefficient was measured up to 373 K. The rate coefficient was observed to level off above room temperature. The Arrhenius expression tabulated applies to results below room temperature.

(j) The value given is for pressures of 13-21 mbar (1-16 Torr) HNO$_3$. Experiments were also carried out in the presence of 0.667 bar (500 Torr) N$_2$ and 0.800 bar (600 Torr) SF$_6$. After corrections for the contribution of the reaction HO + NO$_2$ + M were made, no significant effect of total pressure on k was observed.

(k) Measurements were made at 248 and 297 K and at total pressures of 0.013, 0.080 and 0.973 bar (10, 60 and 730 Torr) of He, N$_2$ and SF$_6$ (the value cited being at 0.013 bar N$_2$). NO$_2$ impurity levels were determined to be less than 0.1%. The data were fitted to the fall-off function given by Lamb et al. (1984). The extrapolated zero-pressure rate constant corresponds to E/R = -710 K.

(l) Rate coefficients were measured as a function of pressure (27-677 mbar) for the diluent gases N$_2$, O$_2$, He and SF$_6$ over the temperature range 200-373 K. The measured rate coefficients increased with increasing pressure, with the pressure dependence being more marked at lower temperatures (and not being evident at temperatures ≥325 K), and a distinct dependence on the identity of the diluent gas was observed at temperatures ≤250 K. At temperatures ≤350 K, the measured rate coefficient at a given total pressure (of a specific diluent gas) increased with decreasing temperature, with the (negative) temperature dependence increasing with increasing total pressure. The data obtained, together with those of Margitan and Watson (1982), Devolder et al. (1984) and Stachnik et al. (1986), for the diluent gases He, N$_2$ and SF$_6$ were fit to the expression proposed by Lamb et al. (1984) (see Comments on Preferred Values).

Preferred Values

k = 1.5 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

See Comments on Preferred Values for the expression to be used under other conditions of temperature and pressure.

Reliability

Δlog k = $\pm$ 0.1 at 298 K.

Similar error limits apply to values of k at other temperatures and pressures over the range 200-350 K.

Comments on Preferred Values

The rate coefficient data have been carefully assessed by the NASA Panel (2000), and their recommendations and analysis are adopted in this evaluation. Based in large part on the recent extensive study of Brown et al. (1999) on the HO + HNO_3 reaction, there is now general agreement on the following major features of the data for k at temperatures $\leq$350 K: (a) a negative temperature dependence (which appears to level off near 500 K); (b) a small but measurable pressure dependence at room temperature which increases at low temperatures

Lamb et al. (1984) have proposed a mechanism involving formation of a bound, relatively long-lived, intermediate complex (channel 2) as well as the direct reaction (channel 1). This mechanism gives a rate coefficient which combines a low pressure limiting rate constant, k_1, and a Lindemann-Hinshelwood expression for the pressure dependence. This mechanism has been used by Brown et al. (1999) and by the NASA Panel (2000) to fit the data of Brown et al. (1999), Margitan and Watson (1982), Devolder et al. (1984) and Stachnik et al. (1986), their expression (Brown et al., 1999; NASA, 2000) is adopted here. The overall rate constant can be expressed as:

$$k = k_1(T) + k_2(M,T)$$

where, $k_2(M,T) = k_3[M]/(1 + k_3[M]/k_4)$.

The expressions for the elementary rate constants are (Brown et al., 1999; NASA, 2000):

k_1 = 2.4 x 10^{-14} exp(460/T) cm^3 molecule^{-1} s^{-1}
k_3 = 6.5 x 10^{-34} exp(1335/T) cm^6 molecule^{-2} s^{-1}
k_4 = 2.7 x 10^{-17} exp(2199/T) cm^3 molecule^{-1} s^{-1}

The expressions are valid over the temperature range 200-350 K for air diluent.

This expression has been used to calculate the preferred value at 298 K and a pressure of 1 bar of air. There is no evidence for products other than NO_3 and H_2O. Studies of the reaction stoichiometry have given values of 0.85 (Ravishankara et al., 1982; Yokelson et al., 1994) and 1.03 (Jourdain et al., 1982). Rate coefficients for the reaction DO + DNO_3 as a function of temperatrure and pressure have been reported by Bossard et al. (1987), Singleton et al. (1991) and Brown et al. (2001), and Brown et al. (2001) have also investigated the kinetics of the reactions DO + HNO_3, HO + DNO_3 and $H^{18}O$ + $HN^{16}O_3$.

Brown et al. (2001) measured the NO_3 radical formation yield from the HO + HNO_3 reaction over the temperature and pressure ranges 240-330 K and 31-1027 mbar N_2, respectively, and from the DO + DNO_3 reaction at 296 K and 99-480 mbar N_2. The NO_3 radical formation yield from both reactions was determined to be unity, within the experimental uncertainties (Brown et al., 2001).

Carl et al. (2001) have shown, by monitoring the NO_3 radical formation rate, that the rate coefficient at 295 $\pm$ 3 K and 267 mbar N_2 is independent of water vapor (0-13.3 mbar). These data (Carl et al., 2001) show that there will be no effect of water vapor on the rate coefficient k under atmospheric conditions.

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