IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A5.110 RO_11

This datasheet last evaluated: June 2009. Last change in preferred values: March 2005.

$$CH_3O + NO + M \rightarrow CH_3ONO + M \quad (1)$$

$$CH_3O + NO \rightarrow HCHO + HNO \quad (2)$$

$\Delta H°(1) = -172.7$ kJ·mol^{-1}
$\Delta H°(2) = -103.1$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_{01}/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.35 x 10^{-29} (T/298)$^{-3.8}$ [Ar]	296-573	Frost and Smith, 1990	PLF-LIF (a)
1.8 x 10^{-29} (T/300)$^{-3.2}$ [Ar]	220-473	McCaulley et al., 1990	DF-LIF (b)
(4.8 ± 0.4) x 10^{-12} (k_2)	298	Daële et al., 1995	DF-LIF (c)
2.65 x 10^{-29} (T/298)$^{-2.8}$ [He,Ar]	248-473	Caralp et al., 1998	DF/PLP-LIF (d)
1.25 x 10^{-11} exp(-1015/T) + 1.92 x 10^{-12} (T/298)$^{-2.56}$ (k_2)			

Comments

(a) Rate coefficients measured up to 165 mbar of Ar or CF_4 diluent. Evaluation of the chemical activation system $CH_3O + NO \rightarrow CH_3ONO^*$, $CH_3ONO^* + M \rightarrow CH_3ONO + M$, and $CH_3ONO^* \rightarrow HCHO + HNO$ carried out using an extended Lindemann-Hinshelwood mechanism. At low pressures the disproportionation reaction $CH_3O + NO \rightarrow HCHO + HNO$ dominates ($k_2 = 5.0 \times 10^{-12} (T/298)^{-0.6}$ cm^3 molecule^{-1} s^{-1}). Assuming that reactions (1) and (2) involve the same intermediate complex, k_2 is expected to decrease with increasing pressure.

(b) Measurements over the pressure range 1-6.6 mbar in He or Ar. The disproportionation reaction $CH_3O + NO \rightarrow HCHO + HNO$ was measured by molecular beam MS ($k_2 = 1.3 \times 10^{-12} \exp(250/T)$ cm^3 molecule^{-1} s^{-1}).

(c) Analysis by LIF and mass spectrometry. Experiments at 298 K and 1.3 mbar of He.

(d) Two sets of experiments, using DF over the range 0.6-7 mbar and 248-473 K, or PLP over the range 39-658 mbar and 284-364 K. Results with the bath gases He (mostly used) and Ar (some experiments) essentially agreed. Extensive RRKM modelling allowed to separate k_1 and k_2. Falloff curves for k_1 evaluated with $F_c = \exp(-T/900)$. The overall rate constant is assumed to be of the form $k = k_1([M]) + k_2$.

Preferred Values

$k_{01} = 2.6 \times 10^{-29} (T/300)^{-2.8}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K.
$k_2 = 2.3 \times 10^{-12} (T/300)^{-0.7}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_{01} = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.5$.

$\Delta \log k_2 = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred values are based on the extensive work by Caralp et al. (1998) which includes and supersedes the earlier results from Frost and Smith (1990), McCaulley et al., 1990, Daële et al., 1995 as well as by Ohmori et al. (1993) in the middle of the falloff curve. The results are represented in the form of $k = k_1([M]) + k_2$, where $k_1(M)$ is based on k_{01} such as preferred here, $k_{\infty 1}$ such as given below and $F_c = \exp(-T/900)$ for M = He, Ar and N_2. It remains to be investigated whether k_2 decreases with increasing pressure (common intermediate of reactions (1) and (2)) or is pressure independent (direct reaction (2)).

High-pressure rate coefficients
Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
2.1×10^{-11}	440-473	Batt, Milne and McCulloch, 1977	(a)
$(2.08 \pm 0.12) \times 10^{-11}$	298	Sanders et al., 1980	(b)
1.4×10^{-11}	298	Zellner, 1987	PLP-AS (c)
$3.6 \times 10^{-11} (T/298)^{-0.6}$	296-573	Frost and Smith, 1990	PLF-LIF (d)
$(2.45 \pm 0.31) \times 10^{-11}$	300	Dóbé et al. 1994	DF-LIF (e)
$3.26 \times 10^{-11} (T/298)^{-0.6}$	248-473	Caralp et al., 1998	PLP-LIF (f)

Comments

(a) Thermal decomposition of methyl nitrite in the presence of NO and $(CH_3)_3CH$. Combination of these data with the equilibrium constant gives the value indicated. For the second channel, $k(CH_3O + NO \rightarrow CH_2O + HNO)/k_\infty(CH_3O + NO \rightarrow CH_3ONO) = 0.17$ was estimated.

(b) Photolysis of methyl nitrite at 266 nm with CH_3O detection by LIF at He pressure of 13-66 mbar. HNO as a reaction product was also detected by LIF; however, no absolute estimate of its yield could be made.

(c) Falloff curve was measured over the range 5-500 mbar. Extrapolations carried out using $F_c = 0.6$.

(d) See comment (a) for k_0.

(e) CH_3O radicals and HCHO from reaction (2) detected by LIF. The branching ratio for HCHO formation varied between 0.84 and 0.26 over the pressure range 1-11 mbar.

(f) See comment (d) for k_0.

Preferred Values

$k_{\infty 1} = 3.3 \times 10^{-11} (T/300)^{-0.6}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.5$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The recommended value is from the most extensive study by Caralp et al. (1998) which supersedes and includes earlier work. The results are in accord with an RRKM modelling of the chemical activation system. Batt (1987) cites a rate coefficient ratio of k_2/k <0.05 from a study at 433-473 K, consistent with our preferred values.

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:

=((2.6e-29*(*T*/300)^-2.8)*M*(3.3e-11*(*T*/300)^-0.6))/((2.6e-29*(*T*/300)^-2.8)*M+(3.3e-11*(*T*/300)^-0.6))*10^(log10((exp(-*T*/900)))/(1+(log10((2.6e-29*(*T*/300)^-2.8)*M/(3.3e-11*(*T*/300)^-0.6))/(0.75-1.27*log10((exp(-*T*/900)))))^2))

The molecular density, M = 7.243×10^{21}P(bar)/T(K)

References

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