IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A5.116

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$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M \quad (1)$$
$$CH_3O + NO_2 \rightarrow HCHO + HONO \quad (2)$$

$\Delta H°(1) = -171.5$ kJ·mol^{-1}
$\Delta H°(2) = -238.5$ 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			
$2.6 \times 10^{-29} (T/300)^{-4.5}$ [He]	220-473	McCaulley et al., 1985	DF-LIF (a)
$(5.2 \pm 1.9) \times 10^{-29}$ [He]	298	Frost and Smith, 1990	PLP-LIF (b)
$(9.0 \pm 1.9) \times 10^{-29}$ [Ar]	298		
$(11 \pm 3) \times 10^{-29}$ [CF_4]	298		
$(4.9 \pm 1.2) \times 10^{-29}$ [Ar]	390		
$(5.3 \pm 0.2) \times 10^{-29}$ [He]	298	Biggs et al., 1993	DF-LIF (c)
$(5.3 \pm 0.3) \times 10^{-29} (T/297)^{-4.4}$ [Ar]	233-356	Wollenhaupt and Crowley, 2000	PLP-LIF (d)
$(3.93 \pm 0.05) \times 10^{-29} (T/300)^{-1.74}$ [He]	250-390	Martinez et al., 2000	PLP-LIF (e)

Comments

(a) CH_3O radicals were produced by IR laser dissociation of $C_6F_5OCH_3$ to yield CH_3, followed by $CH_3 + NO_2 \rightarrow CH_3O + NO$. Pressure range 0.8 mbar to 5 mbar. Direct measurements of the branching ratio k_1/k_2 were not possible. A separation was performed by assuming that reaction (1) was in the low pressure limit. A value of $k_2 = 9.6 \times 10^{-12} \exp(-1150/T)$ cm^3 molecule^{-1} s^{-1} (with relatively large error limits) was estimated.

(b) Pulsed laser photolysis of CH_3ONO-NO mixtures at 266 nm. Rate coefficients were measured over the pressure ranges 40 mbar to 130 mbar of He, 8 mbar to 130 mbar of Ar, and 40 mbar to 100 mbar of CF_4. Falloff curves were fitted to the experimental data using the F_c values of 0.41, 0.44, and 0.48 for He, Ar, and CF_4, respectively. The recombination reaction (1) appears to dominate over reaction (2).

(c) Pressures of He varied from 1.3 mbar to 13 mbar. Extrapolations were performed using $F_c = 0.6$, an RRKM analysis was also done. A value $k_{01} = 5.9 \times 10^{-29}$ [He] cm^3 molecule^{-1} s^{-1} was obtained.

(d) Pulsed laser photolysis of CH_3ONO. Rate coefficients were measured over the range 13-263 mbar of Ar. Falloff curves represented with temperature-independent $F_c = 0.6$, alternatively temperature-dependent F_c between 0.66 at 223 K and 0.55 at 356 K was used. $k_2/k_1 \approx 13$ mbar and 356 K, whereas $k_2/k_1 < 0.01$ followed for 13 mbar and 233 K.

(e) Measurements over the pressure range 66-789 mbar. Falloff extrapolation with $F_c = 0.6$.

Preferred Values

k_{01} = 8.1 x 10^{-29} (T/300)$^{-4.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200 to 400 K.
k_2 = 9.6 x 10^{-12} exp (-1150/T) cm^3 molecule^{-1} s^{-1}.

Reliability

$\Delta \log k_{01} = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.
$\Delta \log k_2 = \pm 0.5$.

Comments on Preferred Values

The agreement between the studies of Frost and Smith (1990), Biggs et al., (1993), Wollenhaupt and Crowley (2000) and Martinez et al (2000) appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_{01} for M = Ar and N_2. Falloff curves are constructed with F_c = 0.44 at 300 K such as chosen by Frost and Smith, (1990). The preferred value is average of the results from Frost and Smith (1990) and Wollenhaupt and Crowley (2000), the latter after reevaluation with F_c = 0.44. Reaction (2) appears to play only a minor role at pressures above 10 mbar. The value of k_2 remains relatively uncertain.

High-pressure rate coefficients
Rate coefficient data

$k_{\infty 1}$/cm^3 molecule^{-1} s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
(2.0 ± 0.4) x 10^{-11}	295	Frost and Smith, 1990	LP-LIF (a)
(1.86 ± 0.05) x 10^{-11} (T/297)$^{-1.87}$	233-356	Wollenhaupt and Crowley, 2000	PLP-LIF (b)
(2.40 ± 0.02) x 10^{-11} (T/300)$^{-0.88}$	250-390	Martínez et al., 2000	PLP-LIF (c)
(1.3 ± 0.1) x 10^{-11}	300	Kukui et al., 2000	PLP-LIF (d)
Relative Rate Coefficients			
1.5 x 10^{-11}	298	Wiebe et al., 1973	(e)
(1.0 ± 0.5) x 10^{-11}	392-420	Batt and Rattray, 1979	(f)
(1.4 ± 0.1) x 10^{-11}	298	Biggs et al., 1993	DF-LIF (g)
Branching Ratios			
k_1/k = 0.92 ± 0.08	298	Wiebe et al.,1973	(e)
k_2/k_1 = ≤0.05	384-424	Batt and Rattray, 1979	(f)

Comments

(a) See comment (b) for k_0.
(b) See comment (d) for k_0.
(c) See comment (e) for k_0.
(d) Photolysis of CH_3SSCH_3/NO_2 mixtures with LIF detection of CH_3O. Measurements over the range 16-805 mbar of He. The given value is for about 750 mbar. No falloff extrapolation.
(e) Steady-state photolysis of CH_3ONO in the presence of $NO-O_2$ and $NO-NO_2-N_2$ mixtures at 10 mbar to 500 mbar. Relative rate coefficients were derived from $\Phi(CH_3ONO_2)$, with $k(CH_3O + NO)/k$ = 1.3 at 298 K. This rate coefficient ratio is placed on an absolute basis by use of a rate

coefficient of $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200 K to 400 K.

(f) Static reaction vessel, CH_3O formed from pyrolysis of CH_3OOCH_3 in the presence of NO-NO_2-CF_4 at a total pressure of 675 mbar. Relative rate coefficients were determined from end-product analysis of CH_3ONO and CH_3ONO_2 (GC). $k(CH_3O + NO \rightleftharpoons CH_3ONO)/k = 2.03 \pm 0.47$ was obtained over the range 392 K to 420 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(CH_3O + NO \rightarrow CH_3ONO) = 2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the range 200 K to 400 K. k_1/k_2 was determined from pyrolysis of CH_3OOCH_3 in presence of NO_2 and N_2 and shown to be pressure dependent.

(g) See comment (c) for k_0. An RRKM extrapolation leads to the value $k_\infty = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

(h) See comment (b) for k_∞.

Preferred Values

$k_1 = 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.

$k_{\infty 1} = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200 K to 400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred $k_{\infty 1}$ value is based on the data reported by Frost and Smith (1990), Wollenhaupt and Crowley (2000), Martinet et al. (2000) and Kukui et al (2000).

Falloff curves are constructed with $F_c = 0.44$ (Frost and Smith, 1990). Reaction (2) appears to be only of minor importance. Differences in the apparent temperature dependences of $k_{\infty 1}$ in part are due to different F_c-values used in the falloff extrapolations.

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:

=((8.1e-29*(*T*/300)^-4.5)*M*(2.1e-11))/((8.1e-29*(*T*/300)^-4.5)*M+(2.1e-11))*10^(log10(0.44)/(1+(log10((8.1e-29*(*T*/300)^-4.5)*M/(2.1e-11))/(0.75-1.27*log10(0.44)))^2))

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

References

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