IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.129 ROO_10

This datasheet last evaluated June 2009. Last change in preferred values: June 2003.

$$CH_3O_2NO_2 + M \rightarrow CH_3O_2 + NO_2 + M$$

$\Delta H° = 92.7$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/ s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
9.0 x 10^{-5} exp(-9694/T) [N_2]	248-273	Zabel *et al.*, 1989[1]	(a)
6.7 x 10^{-19} [N_2]	298*		

Comments

(a) Rate of decomposition of $CH_3O_2NO_2$ followed by FTIR spectroscopy after generation in a reaction chamber, with subsequent addition of NO to scavenge CH_3O_2 radicals. Falloff curves were fitted with $F_c = 0.4$.

Preferred Values

$k_0 = 6.8 \times 10^{-19}$ [N_2] s^{-1} at 298 K.
$k_0 = 9 \times 10^{-5}$ exp(-9690/T) [N_2] s^{-1} over the temperature range 250 K to 300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values correspond to the data and analysis from ref. 1. A theoretical analysis of these data and those of the reverse reaction from refs. 2 and 3 in ref. 4 gave an internally consistent picture (with $\Delta H° = 88.5$ kJ·mol^{-1}). Slightly lower limiting rate coefficients were obtained in ref. 5 where a value of $F_c = 0.6$ was used. Direct measurements of the equilibrium constant $K_c = k/k_1 = 2.73 \times 10^{-28}$ exp(10910/T) cm^3 molecule^{-1} from ref. 6 lead to $\Delta H = 92.7$ kJ mol^{-1} and provide an indication for the internal consistency of the rate data.

High-pressure rate coefficients
Rate coefficient data

k_∞/s^{-1}	Temp./K	**Reference**	Technique/ Comments
Absolute Rate Coefficients			
2.1 x 10^{16} exp(-10920/*T*)	256-268	Bahta, Simonaitis, and Heicklen, 1982[5]	(a)
2.6	298*		
1.1 x 10^{16} exp(-10560/*T*)	248-273	Zabel *et al.*, 1989[1]	(b)
4.5	298*		

Comments

(a) $CH_3O_2NO_2$ generated by photolysis of Cl_2 in the presence of NO_2, CH_4 and O_2. Kinetics were monitored in the presence of NO by UV absorption at 250 nm. At 460 mbar, k = 6 x 10^{15} exp(-10620/*T*) s^{-1}. The given value of k_∞ is derived with F_c = 0.6. The data depend to some extent on the rate coefficient for the reaction $CH_3O_2 + NO \rightarrow CH_3O + NO_2$.

(b) See comment (a) for k_0.

Preferred Values

k = 1.5 s^{-1} at 298 K and 1 bar of air.
k_∞ = 4.5 s^{-1} at 298 K.
k_∞ = 1.1 x 10^{16} exp(-10560/*T*) s^{-1} over the temperature range 250 K to 300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

See comments on preferred values of k_0.

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:

=((9e-5*exp(-9690/*T*))*M*(1.1e16*exp(-10560/*T*)))/((9e-5*exp(-9690/*T*))*M+(1.1e16*exp(-10560/*T*)))*10^(log10(0.36)/(1+(log10((9e-5*exp(-9690/*T*))*M/(1.1e16*exp(-10560/*T*)))/(0.75-1.27*log10(0.36)))^2))

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

References

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