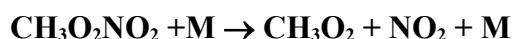


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.129 ROO\_10

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



$$\Delta H^\circ = 92.7 \text{ kJ}\cdot\text{mol}^{-1}$$

### Low-pressure rate coefficients Rate coefficient data

$k_0/\text{s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$9.0 \times 10^{-5} \exp(-9694/T) [\text{N}_2]$	248-273	Zabel <i>et al.</i> , 1989 <sup>1</sup>	(a)
$6.7 \times 10^{-19} [\text{N}_2]$	298*		

### Comments

- (a) Rate of decomposition of  $\text{CH}_3\text{O}_2\text{NO}_2$  followed by FTIR spectroscopy after generation in a reaction chamber, with subsequent addition of NO to scavenge  $\text{CH}_3\text{O}_2$  radicals. Falloff curves were fitted with  $F_c = 0.4$ .

### Preferred Values

$$k_0 = 6.8 \times 10^{-19} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 9 \times 10^{-5} \exp(-9690/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 250 \text{ K to } 300 \text{ K.}$$

### Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 500 \text{ K.}$$

### 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  $\Delta H^\circ = 88.5 \text{ kJ}\cdot\text{mol}^{-1}$ ). 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  $K_c = k/k_1 = 2.73 \times 10^{-28} \exp(10910/T) \text{ cm}^3 \text{ molecule}^{-1}$  from ref. 6 lead to  $\Delta H = 92.7 \text{ kJ mol}^{-1}$  and provide an indication for the internal consistency of the rate data.

## High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{16} \exp(-10920/T)$	256-268	Bahta, Simonaitis, and Heicklen, 1982 <sup>5</sup>	(a)
2.6	298*		
$1.1 \times 10^{16} \exp(-10560/T)$	248-273	Zabel <i>et al.</i> , 1989 <sup>1</sup>	(b)
4.5	298*		

### Comments

- (a)  $\text{CH}_3\text{O}_2\text{NO}_2$  generated by photolysis of  $\text{Cl}_2$  in the presence of  $\text{NO}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$ . Kinetics were monitored in the presence of  $\text{NO}$  by UV absorption at 250 nm. At 460 mbar,  $k = 6 \times 10^{15} \exp(-10620/T) \text{ s}^{-1}$ . The given value of  $k_{\infty}$  is derived with  $F_c = 0.6$ . The data depend to some extent on the rate coefficient for the reaction  $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$ .
- (b) See comment (a) for  $k_0$ .

### Preferred Values

$k = 1.5 \text{ s}^{-1}$  at 298 K and 1 bar of air.

$k_{\infty} = 4.5 \text{ s}^{-1}$  at 298 K.

$k_{\infty} = 1.1 \times 10^{16} \exp(-10560/T) \text{ s}^{-1}$  over the temperature range 250 K to 300 K.

#### Reliability

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

$\Delta(E/R) = \pm 500 \text{ K}$ .

#### 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,  $M = 7.243 \times 10^{21} \text{ P(bar)}/\text{T(K)}$

### References

- <sup>1</sup> F. Zabel, A. Reimer, K. H. Becker, and E. H. Fink, *J. Phys. Chem.* **93**, 5500 (1989).
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- <sup>3</sup> A. R. Ravishankara, F. L. Eisele, and P. H. Wine, *J. Chem. Phys.* **73**, 3743 (1980).
- <sup>4</sup> M. Destriau and J. Troe, *Int. J. Chem. Kinet.* **22**, 915 (1990).
- <sup>5</sup> A. Bahta, R. Simonaitis, and J. Heicklen, *J. Phys. Chem.* **86**, 1849 (1982).

<sup>6</sup> I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).