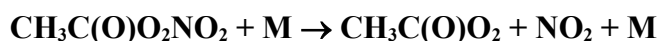


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.133

Datasheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Subcommittee for Gas Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).

This datasheet last evaluated: Feb 2014. Last change in preferred values: Feb 2014.



$$\Delta H^\circ = 119 \text{ kJ}\cdot\text{mol}^{-1}$$

### Low-pressure rate coefficients Rate coefficient data

$k_0 / \text{s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.9 \pm 0.3) \times 10^{-3} \exp(-12100/T) [\text{N}_2]$	300-330	Bridier et al., 1991	FTIR (a)
$1.1 \times 10^{-20} [\text{N}_2]$	298*		

### Comments

- (a) Rate of the thermal decomposition of  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  (PAN) measured by FTIR absorption spectroscopy in the presence of an excess of NO to scavenge  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  radicals. Pressure range 10 mbar to 790 mbar of  $\text{N}_2$ . Falloff curves were analyzed with  $F_c = 0.30$ .

### Preferred Values

Parameter	Value	T/K
$k_0 / \text{s}^{-1}$	$1.10 \times 10^{-5} \exp(-10100/T) [\text{N}_2]$	300-330
<i>Reliability</i>		
$\Delta \log k_0$	$\pm 0.3$	298
$\Delta(E/R)$	$\pm 1000$	300-330

### Comments on Preferred Values

The preferred values for low and high-pressure rate coefficients were obtained by fitting the rate coefficients reported by Bridier et al (1991), Tuazon et al. (1991), Roberts and Bertman (1992), and Sehested (1998) to fall-off expressions with  $F_c$  set at 0.3 (as modelled by Bridier et al., 1991).

### High-pressure rate coefficients Rate coefficient data

$k_{\infty}/s^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.3 \pm 0.2) \times 10^{-4}$	297	Niki et al., 1985	FTIR (a)
$2.2 \times 10^{-4}$	298	Senum, Fajer, and Gaffney, 1986	FTIR (b)
$2.52 \times 10^{16} \exp(-13573/T)$	283-313	Tuazon, Carter, and Atkinson, 1991	FTIR (c)
$4.2 \times 10^{-4}$	298		
$(4.0 \pm 0.8) \times 10^{16} \exp(-13600/T)$	300-330	Bridier et al., 1991	(d)
$6.1 \times 10^{-4}$	298*		
$2.5 \times 10^{17} \exp[-(14340 \pm 250)/T]$	302-323	Roberts and Bertman, 1992	GC (e)
$3.2 \times 10^{-4}$	298*		
$3.1 \times 10^{-4}$	298	Roumelis and Glavas, 1992	GC (f)
$1.6 \times 10^{16} \exp[-(13539 \pm 1060)/T]$	288-298	Grosjean et al., 1994	GC (g)
$3.0 \times 10^{-4}$	298		
$0.371 \pm 0.058$ (700 Torr)	296.4	Sehested et al., 1998	FTIR (h)
$9.78 \pm 0.09 \times 10^{-4}$ (1 bar)	289	Kabir et. al., 2014	FTIR (i)
$4.4 \pm 0.13 \times 10^{-4}$ (1 bar)	298		
21.4	308		

### Comments

- (a) Decay of  $\text{CH}_3\text{CO}_3^{15}\text{NO}_2$  in the presence of  $^{14}\text{NO}_2$  at a total pressure of 900 mbar of  $\text{N}_2$ .
- (b) Decay of  $\text{CH}_3\text{CO}_3\text{NO}_2$  in the presence of  $\text{NO}$  at a total pressure of 16 mbar.
- (c) Thermal decomposition of PAN in an environmental chamber in the presence of 970 mbar of synthetic air or  $\text{N}_2$ .
- (d) See comment (a) for  $k_0$ .
- (e) Thermal decomposition of PAN at 1 bar total pressure. PAN concentrations were measured by GC with electron capture detection.
- (f) Thermal decomposition of PAN in  $\text{N}_2$  as well as in the presence of  $\text{O}_2$ ,  $\text{NO}_2$  and  $\text{NO}$  at 1 bar total pressure. The products methyl nitrate and  $\text{NO}_2$  in PAN- $\text{N}_2$  mixtures were measured by GC. In the presence of large amounts of  $\text{O}_2$ , no methyl nitrate was formed at 333 K, indicating that the decomposition of PAN to methyl nitrate and  $\text{CO}_2$  does not occur.
- (g) Thermal decomposition of PAN in 1 bar of air. PAN was measured by GC with electron capture detection.
- (h) Exponential loss of PAN in presence of  $\text{NO}$  followed by FTIR. Experiments were carried out at 30, 100 or 700 Torr  $\text{N}_2$ . And between 293 and 308.3 Torr. No parameterisation was given.
- (i) Loss of PAN in 200 L quartz reactor in presence of  $\text{NO}$  was monitored by FTIR. Corrections for wall loss of PAN and recombination of  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  with  $\text{NO}_2$  made.

### Preferred Values

Parameter	Value	T/K
$k_{\infty} / s^{-1}$	$1.9 \times 10^{17} \exp(-14100/T)$	280-330
$k / s^{-1}$ (1 bar)	$4.30 \times 10^{-4}$	298
<i>Reliability</i>		
$\Delta \log k_{\infty}$	$\pm 0.3$	298
$\Delta(E/R)$	$\pm 200$	300-330

### Comments on Preferred Values

The values reported by Bridier et al. (1991), Tuazon et al. (1991), Roberts and Bertman (1992), and Sehested et al (1998) are in good agreement and form the basis of the preferred values. The data of the recent study of Kabir et al (2014) at 1 bar are entirely consistent with this. The direct PAN decompositions to methyl nitrate and CO<sub>2</sub> (Roumelis et al 1992; Orlando et al., 1992) or to CH<sub>3</sub>CO<sub>2</sub> and NO<sub>3</sub> (Orlando et al., 1992) are very slow compared to the decomposition to CH<sub>3</sub>CO<sub>3</sub> + NO<sub>2</sub>.

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*:

$$=((1.10e-5*\exp(-10100/T))*M*(1.9e17*\exp(-14100/T)))/((1.10e-5*\exp(-10100/T))*M+(1.9e17*\exp(-14100/T)))*10^{(\log10(0.3)/(1+(\log10((1.10e-5*\exp(-10100/T))*M/(1.9e17*\exp(-14100/T)))/(0.75-1.27*\log10(0.3))))^2)}$$

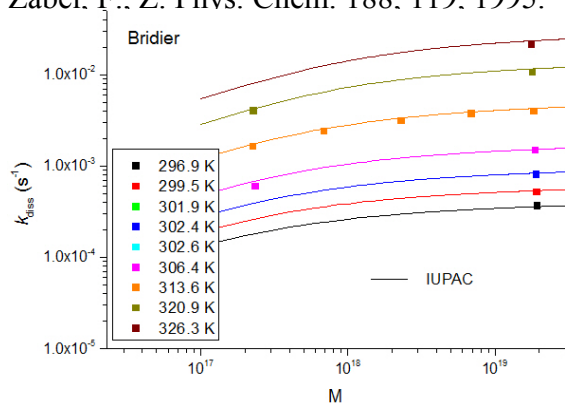
The molecular density,  $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

Combining the rate coefficient for dissociation of CH<sub>3</sub>C(O)O<sub>2</sub>NO<sub>2</sub> (*k*<sub>diss</sub>) with the parameterised rate constant (*k*<sub>ass</sub>) for association (datasheet II.A6.132) enables a temperature dependent equilibrium constant to be derived:  $K_{\text{eq}} = 2.5 \times 10^{-29} \exp(14350/T)$ .

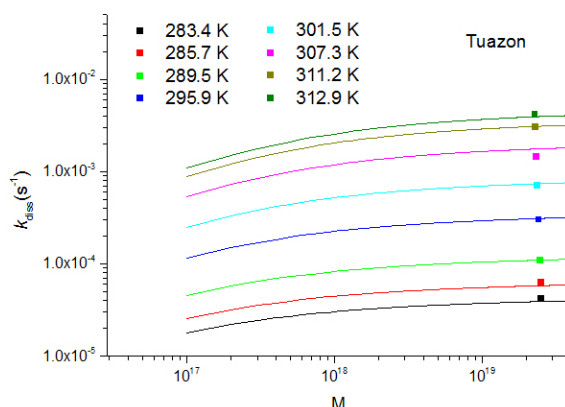
This can be compared to a value derived from a 3<sup>rd</sup>-law analysis: Following Bridier et al. (1991) and using only the experimental data at room-temperature, which is expected to be most reliable, we derive  $k_{\text{diss}}(298\text{K}, 1\text{bar}) = 4.17 \times 10^{-4} \text{ s}^{-1}$ . Combining this with  $k_{\text{ass}}(298\text{K}, 1\text{bar}) = 9.43 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (datasheet II.A6.132) we derive an experimental equilibrium coefficient at this temperature of  $K_{\text{eq}}(298 \text{ K}) = 2.26 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1}$ . Taking the value of  $\Delta S = -174 \text{ J K}^{-1} \text{ mol}^{-1}$  (from Bridier et al., 1991) we derive  $\Delta H = -118.8 \text{ kJ mol}^{-1}$  at 298 K or  $K_{\text{eq}} = 3.3 \times 10^{-29} \exp(14290/T)$ , which is very similar to the value derived from analysis of association and dissociation rate constants.

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IUPAC parameterisation and data of Bridier et al (1991)



IUPAC parameterisation and data of Tuazon et al (1991)