

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A6.132 ROO_14

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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

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$5.1 \times 10^{-29} [\text{N}_2]$	298	Basco and Parmar, 1987	FP-AS (a)
$(2.7 \pm 1.5) \times 10^{-28} (T/298)^{-7.1} [\text{air}]$	248-393	Bridier et al., 1991	FP-AS (b)

Comments

- (a) Photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2\text{-N}_2$ and NO_2 at total pressures of 100 mbar to 800 mbar. Extrapolation of falloff curve with theoretically modelled value of $F_c = 0.19$.
- (b) $\text{CH}_3\text{C(O)O}_2$ formed by flash photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2$ with detection of $\text{CH}_3\text{C(O)O}_2$. Pressure varied between 15 and 760 Torr. The falloff curves were fitted using $F_c = 0.30$.

Preferred Values

Parameter	Value	T/K
$k_0 / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.28 \times 10^{-28} (T/300)^{-6.87} [\text{N}_2]$	250-300
<i>Reliability</i>		
$\Delta \log k_0$	± 0.4	298
Δn	± 2	

Comments on Preferred Values

The data from Basco and Parmar (1987) and Addison et al (1980) are a factor of 2-3 lower than those from Bridier et al (1991) or Sehested et al (1998) and are considered less reliable owing to use of to an oversimplified kinetic scheme.

The preferred values for low and high-pressure rate coefficients were obtained by simultaneously fitting the rate coefficients reported by Bridier et al (1991) and Sehested (1998) at all temperatures and pressures to a fall-off expression with F_c set at 0.3 (as modelled by Bridier et al., 1991). In 1991, the reaction between $\text{CH}_3\text{C(O)}$ and O_2 was believed to make only the $\text{CH}_3\text{C(O)O}_2$ peroxy radical. Recent

work (Carr et al., 2011, Groß et al., 2014) has shown that a significant yield (several tens of percent) of OH radicals is formed at 15 Torr N₂, the lowest pressure used by Bridier et al. It is not clear how the presence of an unexpected OH source would have influenced the kinetic analysis of Bridier et al. 1991 and therefore only data obtained at pressures above 50 Torr has been used to derive the preferred value.

High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
6.1×10^{-12}	298	Basco and Parmar, 1987	FP-AS (a)
$(1.21 \pm 0.05) \times 10^{-11} (T/298)^{-0.9}$	248-393	Bridier et al., 1991	FP-AS (b)
$(1.0 \pm 0.2) \times 10^{-11} (0.93 \text{ bar SF}_6)$	295	Sehested et al., 1998	PR-A (c)
<i>Relative Rate Coefficients</i>			
$1.03 \times 10^{-11} (700 \text{ Torr})$	243	Sehested et al., 1998	RR (d)
$9.5 \times 10^{-12} (700 \text{ Torr})$	283		
$9.7 \times 10^{-12} (700 \text{ Torr})$	295		

Comments

- (a) See comment (a) for k_0 .
 (b) See comment (b) for k_0 .
 (c) CH₃C(O)O₂ radicals were generated from the pulsed radiolysis of CH₃CHO-O₂-CO₂-NO₂ and CH₃CHO-SF₆-O₂-NO₂ mixtures and the disappearance rate of NO₂ monitored by absorption at 400.5 and 452 nm.
 (d) Photolysis of Cl₂-CH₃CHO-O₂-N₂ and NO₂. Analysis of CO₂ / PAN ratio with FTIR to determine the rate coefficient relative to CH₃C(O)O₂ + NO. Reported rate constant ratios were put on absolute basis using $k(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}) = 2.00, 2.09 \text{ and } 2.47 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295, 283 and 243 K, respectively (IUPAC, 2014).

Preferred Values

Parameter	Value	T/K
$k_{\infty} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.125 \times 10^{-11} (T/300)^{-1.105}$	250-300
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (1 \text{ bar})$	8.9×10^{-12}	298
<i>Reliability</i>		
$\Delta \log k_{\infty}$	± 0.2	298
Δn	± 1	

Comments on Preferred Values

See comments on k_0 . The measurement of Sehested et al. (1998) is in very good agreement with the results from Bridier et al. (1991) which together form the basis of the preferred value.

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 :

$$=((3.28e-28*(T/300)^{-6.87}*M*(1.125e-11*(T/300)^{-1.105}))/((3.28e-28*(T/300)^{-6.87}*M+(1.125e-11*(T/300)^{-1.105})*10^{(\log_{10}(0.3)/(1+(\log_{10}((3.28e-28*(T/300)^{-6.87}*M/(1.125e-11*(T/300)^{-1.105}))/0.75-1.27*\log_{10}(0.3)))^2))$$

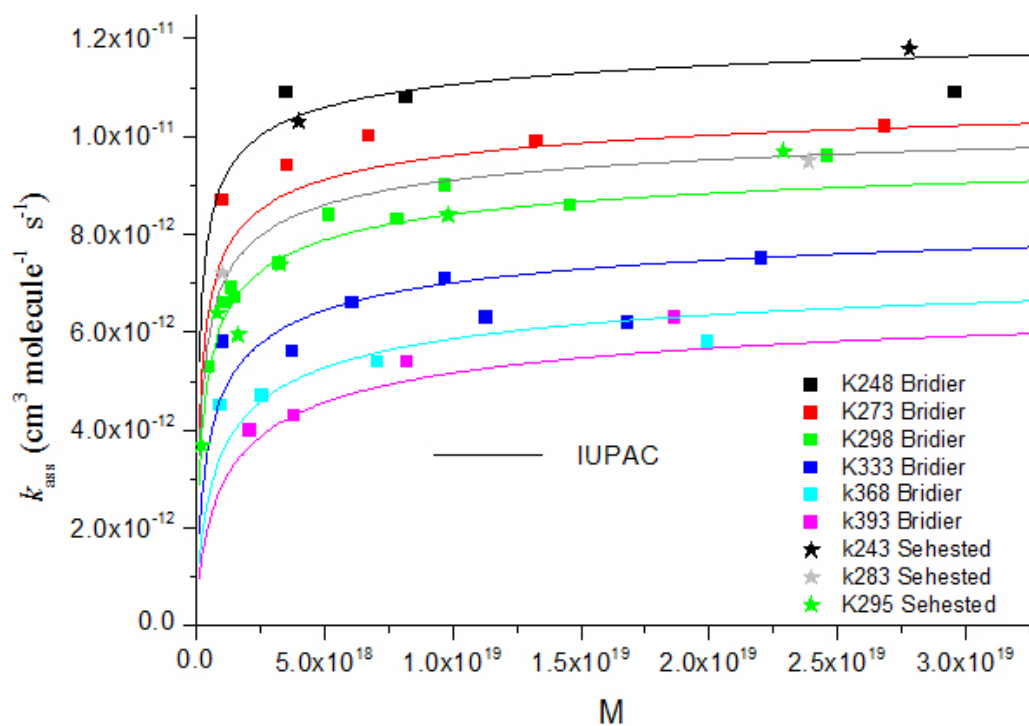
The molecular density, $M = 7.243 \times 10^{21} P(\text{bar})/T(\text{K})$

Combining the association rate coefficient (k_{ass}) with the parameterised rate constant for dissociation (k_{diss}) of $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ (datasheet II.A6.133) a temperature dependent equilibrium constant can be derived: $K_{\text{eq}} = 2.5 \times 10^{-29} \exp(14350/T)$.

This value for the equilibrium constant can be compared to one derived from a 3rd-law analysis: Following Bridier et al. (1991) and using only the experimental data at room-temperature, which is suggested to be most reliable, we derive $k_{\text{ass}}(298\text{K}, 1\text{bar}) = 9.43 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Combining this with $k_{\text{diss}}(298\text{K}, 1\text{bar}) = 4.17 \times 10^{-4} \text{ s}^{-1}$ (datasheet II.A6.133) 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.

References

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Pressure and temperature dependent rate coefficients from Bridier et al. 1991 and Sehested et al., 1998. The solid lines are the IUPAC preferred values calculated using the expression given.