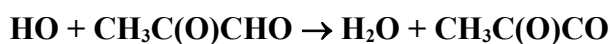


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC18

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated 29th May 2008 (with revision of preferred values).



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(7.1 \pm 1.6) \times 10^{-12}$	297	Kleindienst et al., 1982	FP-RF
$8.4 \times 10^{-13} \exp[(830 \pm 300)/T]$	260-333	Tyndall et al., 1995	DF-LIF (a)
$(1.32 \pm 0.30) \times 10^{-11}$	298		
$1.83 \times 10^{-12} \exp[(560 \pm 70)/T]$	223-500	Baeza-Romero et al., 2007	PLP-LIF (b)
$(1.28 \pm 0.27) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(1.60 \pm 0.12) \times 10^{-11}$	298 ± 2	Plum et al., 1983	RR (c)

Comments

- (a) Mixtures of methylglyoxal in He diluent were stored in glass bulbs and the CH₃C(O)CHO concentrations in these mixtures were measured by UV-visible spectroscopy. Experiments were carried out at total pressures of 2.0-3.0 Torr (2.7-4.0 mbar). Rate coefficients were obtained from experiments carried out in the absence of O₂. When O₂ was added, essentially complete regeneration of HO radicals was observed.
- (b) Mixtures of methylglyoxal in He diluent were stored in glass bulbs and the CH₃C(O)CHO concentrations in these mixtures were measured by IR spectroscopy. HO radicals were generated by the 248 nm laser photolysis of *t*-butyl hydroperoxide, and corrections were made for photolytic loss of CH₃C(O)CHO. The total pressure was varied over the range 5-300 Torr (6.7-400 mbar). Rate coefficients were determined from experiments carried out in the presence of $\sim 1 \times 10^{14}$ molecule cm⁻³ of O₂, leading to HO radical generation from the reaction of CH₃CO radicals with O₂. Non-exponential HO radical decays were observed under these conditions, and the rate coefficients for the reaction of HO radicals with methylglyoxal were extracted from fits to the assumed mechanism. These rate coefficients were independent of pressure. Rate coefficients for the reaction DO + CH₃C(O)CHO were also measured over the temperature range 233-500 K, resulting in $k = 9.4 \times 10^{-13} \exp[(780 \pm 70)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (c) HO radicals were generated by the photolysis of CH₃ONO in air at atmospheric pressure. The concentrations of CH₃C(O)CHO and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CHO})/k(\text{HO} + \text{cyclohexane}) = 2.29 \pm 0.16$ is placed on an absolute basis by use of a rate coefficient $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

$k = 1.9 \times 10^{-12} \exp(575/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-410 K.

$k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta \log (E/R) = \pm 300$ K

Comments on Preferred Values

The room temperature rate coefficients from the relative rate study of Plum et al. (1983) and the absolute rate studies of Tyndall et al. (1995) and Baeza-Romero et al. (2007) are in good agreement. The absolute studies of Tyndall et al. (1995) and Baeza-Romero et al. (2007) both obtain significant negative temperature dependencies and are in reasonable agreement concerning its magnitude. The absolute rate coefficient measured by Kleindienst et al. (1982) may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal samples used, and is hence not used in the evaluation. The preferred values are based on an unweighted least-squares analysis of the rate coefficients of Plum et al. (1983) and Tyndall et al. (1995) and the 223-409 K rate coefficients of Baeza-Romero et al. (2007). Note that in both of the Tyndall et al. (1995) and Baeza-Romero et al. (2007) studies, the uncertainties associated with the reported rate coefficients are quite high in a number of cases, and this is reflected in the uncertainties associated with the 298 K preferred value. The reaction proceeds via H-atom abstraction to form $\text{H}_2\text{O} + \text{CH}_3\text{C}(\text{O})\text{CO}$. Green et al. (1990) have shown that the dominant fate of the $\text{CH}_3\text{C}(\text{O})\text{CO}$ radical under atmospheric conditions is decomposition to form $\text{CH}_3\text{CO} + \text{CO}$.

References

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- Recommendation
- Kleindienst et al. (1982)
- ▲ Plum et al. (1983)
- ▼ Tyndall et al. (1995)
- Baeza-Romero et al. (2007)

