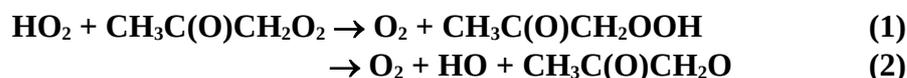


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC57

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: February 2009; last change in preferred values: August 2008.



$$\Delta H^\circ(1) = -161 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.0 \pm 1.0) \times 10^{-12}$	298	Bridier et al., 1993	FP-AS (a)
<i>Branching Ratios</i>			
$k_1/k = 0.33 \pm 0.10$	298	Hasson et al., 2004	UVP-FTIR/HPLC (b)
$k_2/k = 0.67 \pm 0.20$	298		
$k_2/k = 0.15 \pm 0.08$	296	Jenkin et al., 2008	UVP-FTIR (c)
$k_2/k = 0.15 \pm 0.10$	298	Dillon and Crowley, 2008	PLP-LIF (d)

Comments

- Flash photolysis of Cl₂ in the presence of CH₃C(O)CH₃-CH₃OH-O₂-N₂ mixtures at a total pressure of 1013 mbar (760 Torr). The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 nm and 230 nm.
- Continuous photolysis of Cl₂ in the presence of CH₃C(O)CH₃-CH₃OH-O₂-N₂ mixtures at a total pressure of 1066 mbar (800 Torr). Yields of CH₃OOH, CH₃C(O)OOH and CH₃C(O)CH₂OOH (by HPLC) and CH₃C(O)OOH, HCHO, CO and CO₂ (by FTIR) were measured as a function of the initial concentration ratio [CH₃OH]₀/[CH₃C(O)CH₃]₀ over the range 0 to 0.5, corresponding to conditions over which dominant removal of CH₃C(O)CH₂O₂ changes from its self reaction to the reaction with HO₂. The results were analysed by simulation using a detailed chemical mechanism taking account of the sequential formation of CH₃C(O)O₂ and CH₃O₂ in the system.
- UV irradiation of Cl₂-CH₃C(O)CH₃-CH₃OH-air mixtures in a smog chamber fitted with an FTIR detection system, at a total pressure of 930 mbar. Channel (2) was investigated through addition of variable quantities of benzene to scavenge HO, using the formation of phenol as the diagnostic, based on a phenol yield of 0.531 ± 0.066 (Volkamer et al., 2002). k_2/k derived from simulation of phenol formation, for a range of conditions, using a detailed chemical mechanism.
- Pulsed laser photolysis of Cl₂-CH₃C(O)CH₃-CH₃OH-O₂-N₂ mixtures to generate the reagent radicals with HO₂ in large excess, at a total pressure of 230 mbar. The production and removal of HO radicals, formed in channel (2), was followed using direct detection by LIF. k_2/k was determined from simulation of the time dependence of the HO radical concentration, using a detailed chemical mechanism.

Preferred Values

Parameter	Value	T/K
k	$9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	298
k_1/k	0.85	298
k_2/k	0.15	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta k_1/k$	± 0.1	298
$\Delta k_2/k$	± 0.1	298

Comments on Preferred Values

The preferred value of k is provisionally based on the sole determination, reported by Bridier et al. (1993). Although this value seems reasonable in comparison with other $\text{RO}_2 + \text{HO}_2$ reactions, it has been obtained from the kinetic analysis of a complex chemical system, with only product channel (1) represented in the mechanism.

The preferred value of k_2/k is based on the studies of Jenkin et al. (2008) and Dillon and Crowley (2008), which provide more direct determinations than the earlier product study of Hasson et al. (2004). The balance of the reaction is provisionally assigned to channel (1), $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OOH}$ being positively identified as a product by Hasson et al. (2004). The participation of the radical-forming channel (2) provides the possibility of a systematic underestimation of k in the kinetics study of Bridier et al. (1993), through the likely regeneration of the reagent radicals from subsequent reactions of HO and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$. However, given the low value of k_2/k , the magnitude of this effect is likely to be small compared with the assigned uncertainties in the preferred value of k . Further kinetics studies are required to reduce the uncertainty in this preferred value.

References

- Bridier, I., Veyret, B., Lesclaux, R. and Jenkin, M. E.: J. Chem. Soc. Faraday Trans., 89, 2993, 1993.
Dillon, T. J. and Crowley, J. N.: Atmos. Chem. Phys., 8, 4877, 2008.
Hasson, A. S., Tyndall, G. S. and Orlando, J. J.: J. Phys. Chem. A, 108, 5979, 2004.
Jenkin, M. E., Hurley, M. D. and Wallington, T. J.: Phys. Chem. Chem. Phys., 10, 4274, 2008.
Volkamer, R., Klotz, B., Barnes, I., Imamura, T., Wirtz, K., Washida, N., Becker, K. H. and Platt, U.: Phys. Chem. Chem. Phys., 4, 1598, 2002.