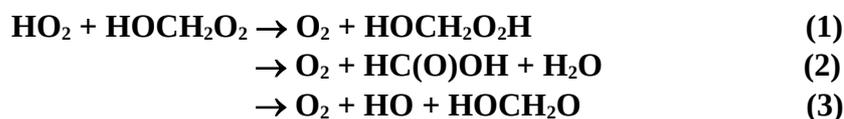


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC52

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: January 2009; last change in preferred values: August 2008



$$\Delta H^\circ(2) = -473.1 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$5.6 \times 10^{-15} \exp[(2300 \pm 1100)/T]$	275-333	Veyret et al., 1989	FP-AS (a)
$(1.2 \pm 0.4) \times 10^{-11}$	295		
$(1.2 \pm 0.3) \times 10^{-11}$	298	Burrows et al., 1989	MM-IR (b)
<i>Branching Ratios</i>			
$k_2/k = 0.40 \pm 0.15$	298	Burrows et al., 1989	MM-IR (c)
$k_2/k = 0.30 \pm 0.06$	296	Jenkin et al., 2007	UVP-FTIR (d)
$k_3/k = 0.20 \pm 0.05$			

Comments

- Flash photolysis of Cl₂ in the presence of HCHO or CH₃OH and O₂ at total pressures of 110 mbar to 230 mbar (85 Torr to 170 Torr), with time-resolved absorption spectroscopy detection of HO₂ and HOCH₂O₂ radicals. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of nine elementary reactions.
- MM study of Cl₂-HCHO-O₂ mixtures at total pressures of 930 mbar (700 Torr), with diode laser IR spectroscopy detection of HO₂ and HOCH₂O₂ radicals. The rate coefficient k was obtained from a computer simulation of [HO₂] absorption profiles based on a mechanism of eight elementary reactions.
- Same experimental system as for comment (b). The branching ratio was determined from a simulation of the quantum yields of HC(O)OH formation.
- UV irradiation of Cl₂-CH₃OH-air and Cl₂-HCHO-air mixtures in a smog chamber fitted with an FTIR detection system, at a total pressure of 930 mbar. Channel (3) was investigated through addition 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 and k_3/k derived from simulation of HC(O)OH and phenol formation, using a detailed chemical mechanism in which the balance of the reaction was assigned to channel (1).

Preferred Values

Parameter	Value	T/K
k	$1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	298

k	$5.6 \times 10^{-15} \exp(2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	275-335
k_1/k	0.5	298
k_2/k	0.3	298
k_3/k	0.2	298
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta E/R$	$\pm 1500 \text{ K}$	
$\Delta(k_1/k)$	± 0.25	298
$\Delta(k_2/k)$	± 0.15	298
$\Delta(k_3/k)$	± 0.1	298

Comments on Preferred Values

The two studies of the rate coefficient at 298 K are in good agreement, and the temperature dependence expression of Veyret et al. (1989) provides the basis for the preferred values of k . The results demonstrate that this reaction is fast compared with the HO₂ radical reactions with CH₃O₂ and C₂H₅O₂. The preferred branching ratios k_2/k and k_3/k at 298 K are based on the recent study of Jenkin et al. (2007), in which evidence for the minor contribution from the radical-forming channel (3) was reported. Because HOCH₂O formed from this channel subsequently generates HC(O)OH (HOCH₂O + O₂ → HC(O)OH + HO₂), the combined preferred branching ratio $(k_2+k_3)/k$ is fully compatible with the earlier results of Burrows et al. (1989) in which HC(O)OH formation was attributed to channel (2) alone. The balance of the reaction is assigned to channel (1), the formation of HOCH₂OOH via this channel being consistent with its detection in product studies of HCHO oxidation (Fu et al., 1979; Niki et al., 1980).

The existence of the radical-forming channel (3) provides the possibility of a systematic underestimation of k in the kinetics studies, through the likely regeneration of the reagent radicals from subsequent reactions of HO and HOCH₂O. However, the magnitude of this effect is likely to be small compared with the assigned uncertainties in the preferred values. Confirmatory studies of the kinetics and branching ratios as a function of temperature are required, and independent confirmation of channel (3) by direct observation of HO formation would be valuable.

References

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