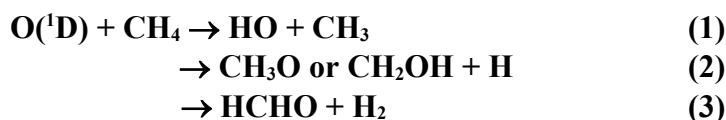


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC2

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 updated: 23rd August 2002.



$$\Delta H^\circ(1) = -180.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -128.9 \text{ kJ}\cdot\text{mol}^{-1} \text{ or } -163.9 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -472.7 \text{ kJ}\cdot\text{mol}^{-1}$$

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
Absolute Rate Coefficients			
$(1.3 \pm 0.2) \times 10^{-10}$	298	Davidson <i>et al.</i> , 1976 ¹	PLP (a)
$(1.4 \pm 0.4) \times 10^{-10}$	200-350	Davidson <i>et al.</i> , 1977 ²	PLP (a)
$(1.57 \pm 0.13) \times 10^{-10}$	295	Amimoto <i>et al.</i> , 1979 ³	PLP-RA (b)
Branching Ratios			
$k_1/k = 0.9$	295	Lin and DeMore, 1973 ⁴	P-GC (c)
$k_3/k = 0.09$	295		
$k_1/k = (0.90 \pm 0.02)$	298	Jayanty, Simonaitis and Heicklen, 1976 ⁵	P-GC (d)
$k_3/k = (0.11 \pm 0.02)$			
$k_1/k = 0.8$	293	Addison, Donovan and Garraway, 1979 ⁶	FP-AS (e)
$k_3/k_2 < 0.25$	-	Casavecchia <i>et al.</i> , 1980 ⁷	(f)
$k_1/k = (0.75 \pm 0.08)$	-	Sataypal <i>et al.</i> , 1989 ⁸	PLP-LIF (g)
$k_2/k = (0.25 \pm 0.08)$	-		
$k_2/k = (0.15 \pm 0.03)$	-	Matsumi <i>et al.</i> , 1993 ⁹	PLP-LIF
$k_1/k = 0.90(+0.1,-0.2)$	298	Hack and Thiesemann, 1995 ¹⁰	PLP-LIF
$k_2/k = 0.30 \pm 0.11$	298	Brownsword <i>et al.</i> , 1998 ¹¹	PLP-LIF
$k_1/k = 0.71 \pm 0.05$	298	Ausfelder, Hippler, and Striebel, 2000 ¹²	PLP-LIF

Comments

- Pulsed laser photolysis of O₃ at 266 nm. O(¹D) atoms were monitored by time-resolved emission from the transition O(¹D) → O(³P) at 630 nm.
- Pulsed laser photolysis at 248 nm of O₃-CH₄-He mixtures with time-resolved measurement of O(³P) atoms by resonance absorption.
- Photolysis of N₂O-CH₄ mixtures at 184.9 nm with end-product analysis by GC.
- Photolysis of N₂O-CH₄-O₂ mixtures at 216 nm with measurement of H₂ by GC.
- Flash photolysis of O₃ at 200 nm to 300 nm with [OH] monitored by AS at 308.15 nm.

- (f) Molecular beam study with MS detection of CH₃O or CH₂OH. Experimental temperature not stated.
- (g) Pulsed laser photolysis of O₃ at 248.4 nm with LIF determination of [H]. Experimental temperature not stated.

Preferred Values ($k = k_1 + k_2 + k_3$)

$k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200 K to 350 K.

$k_1/k = 0.70$ at 298 K.

$k_2/k = 0.23$ at 298 K.

$k_3/k = 0.05$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta k_1/k = \pm 0.15$ at 298 K.

$\Delta k_2/k = \pm 0.07$ at 298 K.

$\Delta k_3/k = \pm 0.05$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred value of k at 298 K is the mean of the results of Davidson *et al.*² and Amimoto *et al.*,³ and the temperature dependence is that from Davidson *et al.*²

The preferred branching ratios are based on the critical review by Lee and co-workers¹³ of the results of the Hack and Thiesemann,¹⁰ of Brownsword *et al.*,¹¹ of Satayapal *et al.*,⁸ and of their own crossed-beam experiments.^{7,13,14} Reaction channel (2) has been shown by Lee and co-workers^{13,14,15} to produce mainly CH₂OH + H, and the production of CH₃O + H is at most a minor channel. In addition, the experiments of Wine and Ravishankara,¹⁶ Matsumi *et al.*⁹ and Takahashi *et al.*¹⁷ have shown that the yield of O(³P) atoms is small or zero. The 248 nm pulsed laser photolysis study¹⁸ of O₃-CH₄ mixtures with low-pressure FTIR emission spectroscopy to monitor the HO* product, has provided evidence that the partitioning of energy in the vibrationally excited HO radical (up to $n = 4$, the maximum allowable based on the energetics of the reaction) is non-statistical.

A discussion of kinetic isotope effects in this reaction can be found in the publication of Saueressig *et al.*¹⁹ and references cited therein.

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