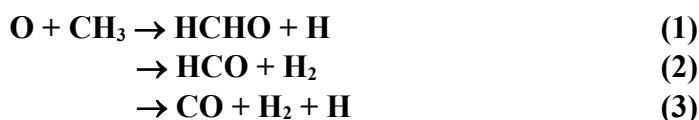


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC1

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

This datasheet updated: 14th March 2005.



$$\Delta H^\circ(1) = -286.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -352.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -288.1 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
$(1.2 \pm 0.17) \times 10^{-10}$	1700-2300	Bhaskaran, Franck and Just, 1979	SH-RA (a)
$(1.14 \pm 0.29) \times 10^{-10}$	295	Plumb and Ryan, 1982	DF-MS (b)
$(1.4 \pm 0.3) \times 10^{-10}$	294-900	Slagle, Sarzynski and Gutman, 1987	F-MS (c)
$k_1 = (1.1 \pm 0.4) \times 10^{-10}$	298	Zellner et al., 1988	LP-LIF (d)
$(1.3 \pm 0.2) \times 10^{-10}$	300	Oser et al., 1991	DF-MS (e)
$(9.4 \pm 3.0) \times 10^{-11}$	~298	Seakins and Leone, 1992	PLP-FTIR (f)
$(1.4 \pm 0.3) \times 10^{-10}$	1609-2002	Lim and Michael, 1993	SH-RA (g)
$(1.7 \pm 0.3) \times 10^{-10}$	299	Fockenberg et al., 1999	PLP-MS (h)
<i>Branching Ratios</i>			
$k_1/k > 0.85$	300	Niki, Daby and Weinstock, 1968	DF-MS (i)
$k_2/k \leq 0.2$	300	Hoyermann and Sievert, 1979	F-MS (j)
$k_1/k = 0.84 \pm 0.15$	299	Fockenberg et al., 1999	PLP-MS (h)
$k_3/k = 0.17 \pm 0.11$	299		
$k_3/k = 0.18 \pm 0.04$	296	Preses, Fockenberg and Flynn, 2000	PLP-IRA (k)

Comments

- Decomposition of C₂H₆-O₂ mixtures in a shock tube. k was derived from computer simulation of [O] and [H] profiles determined by RA.
- Discharge flow system with MS detection of O and CH₃, k was determined from the decay of [CH₃] with [O] \gg [CH₃].
- Flow system with generation of CH₃ radicals and O(³P) atoms from simultaneous *in situ* photolysis of CH₃COCH₃ and SO₂, and determination of [CH₃] and [O] by photoionization MS. Experiments were performed under conditions such that [O]/[CH₃] > 20 , and rate coefficients were determined from the decay of CH₃ radicals. The rate coefficient k was found to be independent of pressure over the range 1.3 mbar to 15 mbar (1 Torr to 11 Torr), and its value was confirmed by measurement of the rate of formation of HCHO. HCO and CH₂ were not detected as products but the analytical system could not detect CO or H₂.

- (d) Laser photolysis at 193 nm of flowing mixtures of N₂-N₂O-(CH₃)₂N₂. *k* was determined from the rate of formation of HCHO (using LIF) with [O] > [CH₃]. Mass balance estimates indicated that channel (1) predominates.
- (e) Discharge flow system with generation of CH₃ from F + CH₄ in He-O₂ mixtures at pressures of 0.25 mbar to 1.0 mbar (0.17 Torr to 0.78 Torr). *k* was determined from the decay of [CH₃] by MS with [O]/[CH₃] > 10.
- (f) Obtained from the rate of formation of HCHO product by monitoring the C-H stretch emission by FTIR spectroscopy.
- (g) Shock heating of CH₃Cl in Ar coupled with laser photolysis of SO₂. *k* was determined from computer simulation of [O] profiles measured by RA.
- (h) Pulsed laser photolysis at 193 nm of mixtures of CH₃COCH₃, CH₃Br, and SO₂ at P = 1.3 mbar. Product analysis by time-of-flight mass spectrometry.
- (i) DF-MS study of O + C₂H₄ reaction in which CH₃ is a product. HCHO assumed to arise from channel (1).
- (j) Discharge flow system with CH₃ being generated from F + CH₄ and O from a microwave discharge. Electron impact MS analysis of HCO and HCHO. No evidence found for channel (2).
- (k) Pulsed laser photolysis at 193 nm of mixtures of CH₃COCH₃, SO₂, and Ar at P = 6.6 mbar. Product analysis by tunable infrared diode laser absorption

Preferred Values

$k = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290-900 K.

$k_1/k = 0.83$ at 298 K.

$k_3/k = 0.17$ at 298 K.

Reliability

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

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

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

$\Delta(k_3/k) = \pm 0.11$ at 298 K.

Comments on Preferred Values

The recommended value of *k* is the mean of the results of Plumb and Ryan (1982), Slagle et al. (1987), Zellner et al. (1988), Oser et al. (1991), Seakins and Leone (1992), and Fockenberg et al. (1999) which are in good agreement. The data of Bhaskaran et al. (1980) and Lim and Michael (1993) indicate that the rate coefficient is independent of temperature up to at least 2300 K.

The preferred branching ratios are based on the studies of Fockenberg et al. (1999) and Preses et al. (2000). The values of the branching ratio *k*₃/*k* reported in these studies, using completely different detection methods, are in excellent agreement. These results are consistent with earlier results reported in Seakins and Leone (1992), Niki et al. (1968), and Hoyermann and Sievert (1979). Seakins and Leone (1992) found CO to be a primary product, and they also estimated the overall branching ratio for CO formation to be 0.40 ± 0.10 . Fockenberg et al. (1999) and Preses et al. (2000) suggest that the overall branching ratio for CO formation estimated in Seakins and Leone (1992) includes CO formed in an oxidation chain beginning with HCHO.

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