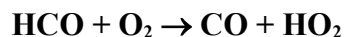


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet R_Oxygen_10

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: 16th November 2006.



$$\Delta H^\circ = -139.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(5.6 \pm 0.9) \times 10^{-12}$	300	Shibuya et al., 1977	FP-AS (a)
$(4.0 \pm 0.8) \times 10^{-12}$	300	Clark et al., 1978	PLP-AS
$(3.8 \pm 1.0) \times 10^{-12}$	300	Nadtochenko et al., 1979	FP-AS
$5.5 \times 10^{-11} T^{-(0.4 \pm 0.3)}$	298-503	Veyret and Lesclaux, 1981	FP-AS (b)
$(5.6 \pm 0.6) \times 10^{-12}$	298		
$(4.65 \pm 0.6) \times 10^{-12}$	295	Langford and Moore, 1984	PLP-AS (c)
$(4.2 \pm 0.7) \times 10^{-12}$	300	Gill et al., 1981	FP-AS
$(5.1 \pm 1.0) \times 10^{-12}$	296	Temps and Wagner, 1984	DF-LMR
$1.3 \times 10^{-11} \exp[-(204 \pm 180)/T]$	295-713	Timonen et al., 1988	PLP-MS (d)
6.2×10^{-12}	295		
$3.2 \times 10^{-12} \exp(87/T)$	200-398	Stief et al., 1990	DF-MS (e)
4.3×10^{-12}	298		
4.3×10^{-12}	298	Dóbe et al., 1995	DF-LMR (f)
$(2.2) \times 10^{-12} \exp[(170 \pm 22)/T]$	200-298	Nesbitt et al., 1999	DF-MS (g)
$(4.0 \pm 0.6) \times 10^{-12}$	298		
$(5.9 \pm 0.5) \times 10^{-12}$	295	Ninomiya et al., 2000	PLP-AS (h)
$(5.0 \pm 0.7) \times 10^{-12}$	294±2	Hanoune et al., 2001	PLP-AS (i)
$(5.6 \pm 0.3) \times 10^{-12}$	296	DeSain et al., 2001	PLP-LIF (j)
$(5.9 \pm 0.1) \times 10^{-12}$	295	Colberg and Friedrichs, 2006	PLP-AS (k)
<i>Relative Rate Coefficients</i>			
$(5.7 \pm 1.2) \times 10^{-12}$	297	Washida et al., 1974	RR (l)
$(6.3 \pm 1.5) \times 10^{-12}$	295	Ninomiya et al., 2000	RR (m)

Comments

- Flash photolysis of $\text{CH}_3\text{CHO}-\text{O}_2$ mixtures; HCO monitored by time-resolved absorption at 613.8 nm. There was no pressure effect on k for pressures of up to 690 mbar (520 Torr) of He.
- Flash photolysis of HCHO and CH_3CHO ; HCO was monitored by laser absorption at 614.5 nm at total pressures of 17 mbar to 660 mbar (13 Torr to 500 Torr).
- Pulsed laser photolysis of HCHO or $(\text{CHO})_2$ with monitoring of HCO by absorption at total pressures of up to 1330 mbar (1000 Torr).
- Pulsed laser photolysis of CH_3CHO ; HCO was monitored by photoionization MS at pressures of 0.69 mbar to 1.22 mbar (0.52 Torr to 0.92 Torr).

- (e) Discharge-flow system. HCO radicals were generated from Cl + HCHO and monitored by photoionization MS.
- (f) HCO radicals were generated by the reaction of F atoms with HCHO. The total pressure was 1.7 mbar of He. The yield of HO₂ radicals was measured relative to the formation yield of HO₂ radicals from the reaction of F atoms with H₂O₂, and determined to be 1.00 ± 0.05.
- (g) Same experimental technique as in comment (e). The rate constant measured at 398 K seems to indicate a small positive temperature dependence for T > 300 K in qualitative agreement with Timonen *et al.*, 1988.
- (h) Pulsed laser photolysis of CH₃CHO at 266 nm; HCO was monitored by cavity ring-down spectroscopy at 613.5 nm at total pressures of 5.32-13.3 mbar (4-10 Torr) of N₂.
- (i) Pulsed laser photolysis of a mixture of H₂CO and Cl₂ at 355 nm with monitoring of the R5 or R6 transition in CO by tunable diode laser absorption in the range 6.65-63.84 mbar (6-48 Torr). Only data with [O₂] > 5 × 10¹⁵ molecule cm⁻³ have been used in the analysis.
- (j) Pulsed 193 nm laser photolysis of CCl₄ or CCl₃F in the presence of CH₂O or direct photolysis of CH₂O or CH₃CHO at 284 and 305 nm, respectively, coupled to cw LIF of HCO at 258 nm in the range 10.5-40 mbar He. No kinetic isotope effect for DCO + O₂ has been observed ($k_H/k_D = 1.00 \pm 0.07$) in contrast to theoretical predictions by Hsu *et al.*, (1996). Small positive temperature dependence of *k* in the range 296 – 673 K.
- (k) 193 nm photolysis of glyoxal ((CHO)₂) in 50-200 mbar Ar in a slow flow reactor coupled to FM absorption spectroscopy of HCO at 614.752 nm. The rate constant was obtained from observed differences between HCO concentration-time profiles measured with and without added O₂ (245-3985 ppm) using numerical modelling. Secondary reactions of photolytically generated H atoms were taken into account. A small positive temperature dependence observed in the range 739–1108 K.
- (l) Discharge flow system with HCO being monitored by photoionization MS. *k* measured relative to $k(\text{O} + \text{HCO} \rightarrow \text{products}) = 2.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (measured in the same apparatus) by observing the effect of O₂ on [HCO] in a flowing mixture of O₂-C₂H₄; $k/k(\text{O} + \text{HCO}) = (2.74 \pm 0.21) \times 10^{-2}$.
- (m) Based on the ratio of the rate constants $k(\text{HCO} + \text{O}_2)/k(\text{HCO} + \text{Cl}_2) = 0.85 \pm 0.02$ measured in a smog chamber coupled to FTIR detection. The absolute value of *k* (HCO + Cl₂) used to put the relative rate on an absolute basis was $(7.4 \pm 1.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

$k = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K with a small negative temperature dependence in the range 200 to 300 K.

Reliability

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

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is the average of the room-temperature rate coefficients of Shibuya *et al.* (1977), Veyret and Lesclaux (1981), Langford and Moore (1984), Temps and Wagner (1984), Timonen *et al.* (1988), Stief *et al.* (1990), Dobé *et al.* (1995), Nesbitt *et al.* (1999), Ninomiya *et al.* (2000), Hanoune *et al.* (2001), DeSain *et al.* (2001) and Colberg and Friedrichs (2006). The earlier studies performed in static reactors (Clark *et al.* (1978), Nadochenko *et al.* (1979), Gill *et al.* (1981)) were not taken into account. Taken together, the temperature-dependent studies of Veyret and Lesclaux (1981), Timonen *et al.* (1988), Stief *et al.* (1990), and Nesbitt *et al.* (1999) show that the rate coefficient of this reaction has a small negative temperature dependence over the range 200 to 298 K on the order of -1.4 kJ/Mol or less. In the range 300 to 650 K the activation energy seems to be close to zero and increases up to 13 kJ/Mol in the range 650 to 1100 K (Colberg and Friedrichs,

2006) within the error limits of the measurements. High level ab initio calculations predict barriers of 12.5 and 9.5 kJ/mol for the direct abstraction channel vs. formation of the addition complex HCO-O₂, respectively (Martinez-Avila et al. (2003)). The transition state for the four-center elimination separating the addition complex and the HO₂ + CO products lies below the entrance channel.

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