IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO22

$$CH_2CHO + O_2 \rightarrow CH_2CO + HO_2 \quad (1)$$
$$\rightarrow (CHO)_2 + HO \quad (2)$$
$$\rightarrow HCHO + CO + HO \quad (3)$$
$$CH_2CHO + O_2 (+M) \rightarrow CH_2O_2CHO(+M) \quad (4)$$
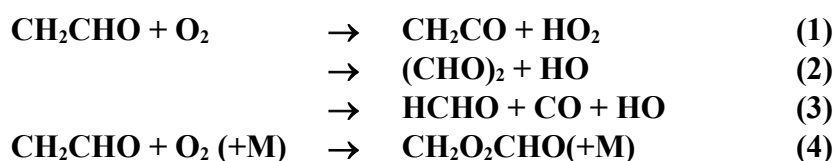
$\Delta H°_{298}(1) = -50.1 \text{ kJ mol}^{-1}$

$\Delta H°_{298}(2) = -189.2 \text{ kJ mol}^{-1}$

$\Delta H°_{298}(3) = -196.4 \text{ kJ mol}^{-1}$

$\Delta H°_{298}(4) = -101 \text{ kJ mol}^{-1}$

Rate Coefficient Data ($k = k_1 + k_2 + k_3 + k_4$)

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Absolute Rate Coefficient			
2.46×10^{-13} (133 mbar N$_2$)	295	Gutman and Nelson, 1983	PLP-LIF(a)
2.50×10^{-13} (120 mbar SF$_6$)	292		
1.65×10^{-13} (133 mbar N$_2$)	476		
2.21×10^{-13} (120 mbar SF$_6$)	473		
$k = 2.7 \times 10^{-14} \exp(668/T)$ (133 mbar He)	300 – 500	Lorenz *et al*, 1984	PLP-LIF (b)
$k_0 = (2 \pm 2) \times 10^{-30}[M]$			
$k_\infty = (2.6 \pm 0.5) \times 10^{-13}$			
$k_0 = (1.6 \pm 0.3) \times 10^{-30}[M]$		Zhu and Johnson, 1995	PLP-CRDS (c)
$k_\infty = (1.9 \pm 0.2) \times 10^{-13}$			
$F_c = 0.50 \pm 0.06$			
$k(0) = 5.14 \times 10^{-14} \exp(210/T)$	298-660	Delbos *et al*, 2006	PLP-LIF (d)
$k_{(\infty)} = 1.7 \times 10^{-12} \exp(-520/T)$			
Branching Ratio Measurements			
$(k2 + k3)/k = 0.2$ (25 mbar He)	298	Lorenz *et al*, 1984	PLP-LIF(b)
$k2/k = 0.15 \pm 0.05$ (>200 mbar N$_2$)	298	Zhu and Johnson, 1995	PLP-CRDS (e)
$k2/k = 0.10$ (~20 mbar N$_2$)	298		

Comments

(a) CH$_2$CHO radicals were produced by the laser-flash photolysis of methyl vinyl ether at 193 nm and measured by LIF at 337 nm. Reaction shows a weak pressure dependence between 2-133

mbar, for both SF_6 and N_2 over T range ~292-475 K. Data cited for highest pressures of SF_6 and N_2 used. HO observed by LIF as product but appearance was significantly delayed compared to vinoxy loss rate.

(b) Same experimental method as in (a). Reaction pressure dependent between 13-372 mbar (M = He). Falloff analysis using $F_c = 0.6$. Yield of HO product = 20% as determined by LIF.

(c) CH_2CHO radical decay monitored by its absorption at 347.6 nm . The overall bimolecular rate constants were measured over the major portion of the transition region from the low-pressure to the high-pressure limits (3.2 mbar < p < 532 mbar) and were well fit by the Troe fall-off expression with $k_0 = (1.6 \pm 0.3) \times 10^{-30}$ cm^6molecule^{-2}-s^{-1}, $k_\infty = (1.9 \pm 0.2) \times 10^{-13}$ cm^3molecule^{-1}s^{-1}, and $F_c = 0.50 \pm 0.06$.

(d) Two quasi-static reactors and a discharge flow-reactor used to cover temperatures ranging from 298 to 660 K and pressures between 1 mbar and 46 bar with helium as the bath gas. CH_2CHO radicals were produced by the laser-flash photolysis of ethyl vinyl ether at 193 nm and by the reaction F + CH_3CHO, respectively. CH_2CHO LIF excited at 337 or 347.4 nm. The reaction shown to proceed via reversible complex formation with subsequent isomerization and fast decomposition: $CH_2CHO + O_2 \Leftrightarrow O_2CH_2CHO \rightarrow HO_2CH_2CO \rightarrow$ products (k_d). The rate coefficients for the first and second steps were determined (k_4, k_{-4}, k_d) and analyzed by a master equation with specific rate coefficients from the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Molecular and transition-state parameters were obtained from quantum chemical calculations. A third-law analysis allowed evaluation of the thermodynamic parameters for adduct formation. From the fall-off analysis, the temperature dependencies for the cited overall low- and high-pressure limiting bimolecular rate coefficients were obtained. These two expressions, together with the following expressions: $k_{4(0)} = 1.0 \times 10^{-32}$ exp(-923/T) cm^6molecule^{-2}-s^{-1}, to account for adduct formation at low pressure, and F_c = exp(-T/730 K) + exp(3000K/T) were applied to give an analytical representation for the pressure and temperature dependence of k, i.e. $k(T,[M]) = k_{4(0)}[M]\{(1+y)/(1+x)\}F(x)+k_{(0)}\{1-(xF(x))/(1+x)\}$, with $x = k_{4(0)}$ $[M]/ (k_{(\infty)} - k_{(0)})$, $y = k_{(0)}/ (k_{(\infty)} - k_{(0)})$ and log$[F(x)] = (\log F_c)/[1 + \log^2 x]$

(e) Glyoxal was identified as a product of the reaction; however, its rate of appearance ($\tau \sim$ 900 ms) was not comparable to the rate of disappearance of the vinoxy radical (τ < 90 ms). Varying the third body carrier gas from N_2 to SF_6 or CF_4 had no obvious effect on the glyoxal appearance rates. The disparity between the rate of disappearance of the reactant and the rate of appearance of glyoxal is attributed to the formation of a long-lived O_2CH_2CHO adduct which decomposes to glyoxal + HO. Yield decreased with pressure below ~ 200 mbar. HCHO was also observed as a product but not quantified.

Preferred Values

$k = k_{4(0)}[M]\{(1+y)/(1+x)\}F(x)+k_{(0)}\{1-(xF(x))/(1+x)\}$ cm^3 molecule^{-1} s^{-1} over the range 290-900 K

with $x = k_{4(0)}[M]/ (k_{(\infty)} - k_{(0)})$, $y = k_{(0)}/ (k_{(\infty)} - k_{(0)})$, and log$[F(x)] = (\log F_c)/[1 + \log^2 x]$

$k_{(0)} = 5.14 \times 10^{-14}$ exp(210/T) cm^3 molecule^{-1} s^{-1}
$k_{(\infty)} = 1.7 \times 10^{-12}$ exp(-520/T) cm^3 molecule^{-1} s^{-1}
$k_{4(0)} = 1.0 \times 10^{-32}$ exp(-923/T) cm^6molecule^{-2} s^{-1}

F_c F_c = exp(-T/730 K) + exp(3000K/T)

Reliability

Δlog k = $\pm$ 0.2 over the range 300-500 K.

Comments on Preferred Values

There is reasonable agreement between the results of all studies of this reaction, although the rate coefficients measured by CRDS are lower by ~30% at high pressure and >50% in the low pressure regime. The reaction shows a complex pressure and temperature dependence, with a high pressure limit above ~ 400 mbar, and a poorly defined low pressure region, which contains a bimolecular component. The temperature dependence is complex because of fall-off effects. The experiments of Delbos *et al* (2005) covering a wide pressure range, reveal a weak positive T-dependence at the high pressure limit and a weak negative T-dependence at low pressure, consistent with earlier studies. Delbos *et al* (2005) gave a parameter set which gives an adequate representation of k(P,T) over the temperature and pressure range studied and we suggest these for calculation of the preferred value for *k*.

Products which have been identified are HO, glyoxal and formaldehyde. Both HO and $(CHO)_2$ are formed as secondary products, resulting from isomerisation/decomposition of the initially formed adduct. There is only very limited information on the branching ratios at 298 K. The yield of $(CHO)_2$ increases with pressure to a maximum of ~15% above ~200 mbar. The yield of HO at lower pressure (27 mbar) is ~20%, and a preliminary report (Oguchi et al, 2004) suggests a decreased yield at 270 mbar of 10%. Since the yield of OH must be at least that of glyoxal there is clearly an inconsistency here and we cannot recommend a branching ratio at this time.

References

Delbos, E., Fittschen, C., Hippler, H., Krasteva, N., Olzmann, M., Viskolcz, B., J. Phys.Chem., A 110, 3238, 2006.
Gutman, D., and Nelson, H.H., J. Phys. Chem. 87, 3902, 1983.
Lorenz,K. Rhasa, D, Zellner, R. and Fritz, B., Ber. Bunsenges.Phys.Chem., 87, 3902, 1985.
Oguchi, T, Sato, Y., Matsui, H., 18th Symposium on Gas Kinetics, Bristol, UK, 2004. Poster B13.
Zhu, Lei, and Johnston, G., J. Phys.Chem., 99, 15114, 1995.