IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC53

$HO_2 + C_2H_5O_2 \rightarrow O_2 + C_2H_5OOH$
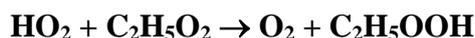
$\Delta H° = -159 \text{ kJ·mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comment
Absolute Rate Coefficients			
$(6.3 \pm 0.9) \times 10^{-12}$	295	Cattell et al., 1986	MM-IR-UVA (a)
$5.6 \times 10^{-13} \exp[(650 \pm 125)/T]$	248-380	Dagaut et al., 1988	FP-UVA (b)
$(5.3 \pm 1.0) \times 10^{-12}$	298		FP-UVA (c)
$1.6 \times 10^{-13} \exp[(1260 \pm 130)/T]$	248-480	Fenter et al., 1993	
$(1.10 \pm 0.21) \times 10^{-11}$	298		
$6.9 \times 10^{-13} \exp[(702 \pm 69)/T]$	210-363	Maricq and Szente, 1994	FP-UVA (d)
$(8.3 \pm 1.5) \times 10^{-12}$	295		
$(8.14 \pm 0.38) \times 10^{-12}$	298	Boyd et al., 2003	PLP-UVA (e)
$2.08 \times 10^{-13} \exp[(864 \pm 79)/T]$	195-298	Raventos-Duran et al., 2007	DF-CIMS (f)
$(4.0 \pm 0.5) \times 10^{-12}$	298		
$6.01 \times 10^{-13} \exp[(638 \pm 73)/T]$	221-295	Noell et al., 2010	PLP-IR-UVA (g)
$(5.57 \pm 0.36) \times 10^{-12}$	295		

Comments

(a) MM spectrometry with HO_2 and $C_2H_5O_2$ radicals generated simultaneously by photolysis of Cl_2 in the presence of C_2H_6-CH_3OH-O_2-N_2 mixtures at a pressure of 3.2 mbar (2.4 Torr). HO_2 radicals were monitored by IR absorption with a TDL and $C_2H_5O_2$ radicals were monitored by UV absorption at 260 nm. The rate coefficient, k, was determined from the observed perturbation of the second-order kinetics of the HO_2 self-reaction when $C_2H_5O_2$ was present in large excess. Additional experiments at 1013 mbar (760 Torr), with only UV monitoring (at 210 nm and 260 nm), allowed a consistent, but less well-determined value of k $\approx$ 9.3 x 10^{-12} cm^3 molecule^{-1} s^{-1} to be reported.

(b) Flash photolysis of Cl_2 in the presence of C_2H_6-CH_3OH-O_2-N_2 mixtures at total pressures of 33 mbar to 533 mbar (25 Torr to 400 Torr). Composite transient absorption decay curves for HO_2 and $C_2H_5O_2$ radicals were measured at 230 nm, 250 nm and 280 nm. Kinetic analysis derived from computer modelling of experimental data.

(c) FP-UV absorption study of Cl_2-C_2H_6-O_2-N_2 mixtures at 1013 mbar (760 Torr) total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths.

(d) FP-UV absorption study of F_2-H_2-C_2H_6-O_2-N_2 mixtures at a total pressure of ca. 270 mbar (ca. 200 Torr). Rate coefficients were derived from computer simulation of time-resolved decay curves.

(e) PLP-UV absorption study of H_2O_2-C_2H_6-O_2-N_2 mixtures at 1013 mbar (760 Torr) and 298 K.

Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[HO_2]/[C_2H_5O_2]$ in the range 4 - 10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by $C_2H_5O_2$ absorption, with its decay being almost entirely due to the reaction with HO_2. The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

(f) Turbulent fast-flow system operating at total pressures over the range 100 to 267 mbar. $C_2H_5O_2$ was produced by reaction of C_2H_6 with F atoms and subsequent addition of O_2. The $C_2H_5O_2$ was mixed with excess HO_2 produced by the $H+O_2+M$ reaction. Concentrations of $C_2H_5O_2$ and HO_2 were monitored following chemical ionization using SF_6^- as the reagent ion. k obtained from simulation of the system. Upper limit branching ratios reported for channels forming $C_2H_5OH + O_3$ and $C_2H_5O + HO + O_2$, based on failure to detect O_3 and HO as products.

(g) Pulsed laser photolysis of Cl_2-C_2H_6-CH_3OH-O_2-N_2 mixtures at 67 mbar (50 Torr) total pressure. Initial concentration ratios, $[HO_2]/[C_2H_5O_2]$, were varied in the range 0.1 - 3. HO_2 monitored in the near IR using a TDL source tuned for HO_2 at the $^qQ_2$ band head (6638.2 cm^{-1}) of the first overtone of the HO stretch. UV monitoring at 250 nm, such that signals dominated by $C_2H_5O_2$ at low $[HO_2]/[C_2H_5O_2]$, but with a contribution from HO_2 at high $[HO_2]/[C_2H_5O_2]$. k was determined from simulation of transient decay traces, using a detailed chemical mechanism. Interpretation of data at low $[HO_2]/[C_2H_5O_2]$ required reduction of HO_2 formation from $C_2H_5O_2$ self reaction to allow consistent values of k across the range of conditions.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	6.9×10^{-12}	298
k/cm^3 molecule^{-1} s^{-1}	6.4×10^{-13} exp(710/T)	200-400
Reliability		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	± 200 K	

Comments on Preferred Values

The reported values of k at 298 K show some level of disagreement, covering almost a range of a factor of three. There are potential complications in several of the determinations, which include uncertainties associated with errors in the UV absorption cross sections used for HO_2 and $C_2H_5O_2$ in the analyses, consideration of only small reagent depletions and the extraction of rate coefficients from the simulation of complex systems. The more recent purely UV absorption studies of Maricq and Szente (1994) and Boyd et al. (2003), which are in good agreement, have used cross-sections for $C_2H_5O_2$ and HO_2 which are either close to, or taken from, the recommendation of Tyndall et al. (2001), and can be considered as the most well-defined of the UV absorption studies. In particular, Boyd et al. (2003) determined k under essentially pseudo-first order conditions (HO_2 in excess), with almost complete separation of the absorptions due to HO_2 and $C_2H_5O_2$ at the chosen monitoring wavelengths (see comment (e)). The most recent study of Noell et al. (2010) also monitored the reagents essentially independently, with HO_2 measurement in the near IR, and the UV measurements generally dominated by $C_2H_5O_2$ (see comment (g)). Despite this, these studies report room temperature values of k that differ by a factor of about 1.5. The DF-CIMS study of Raventos-Duran et al. (2007) also supports a lower value of k, although it is noted that it is the only study where the reported value of k at 298 K is lower than that reported for the $CH_3O_2 + HO_2$ reaction using the same apparatus (see evaluation of $CH_3O_2 + HO_2$ reaction). The preferred value of k at 298 K is based on the mean of the values reported by Boyd et al. (2003) and Noell et al. (2010), but with reliability limits which reflect the level of disagreement between

these studies.

The temperature dependence studies of Dagaut et al. (1988), Maricq and Szente (1994), Raventos-Duran et al. (2007) and Noell et al. (2010) report values of E/R which are in reasonable agreement; with that of Fenter et al. (1993) apparently being systematically high. The recommendation is based on the mean of the E/R values reported in the former studies, with the pre-exponential factor adjusted to return the preferred value of k at 298 K.

The FTIR spectroscopic product study of Wallington and Japar (1990) has shown that this reaction is dominated by a single channel at 298 K, to yield $C_2H_5OOH + O_2$. The results of Spittler et al. (2000) and Hasson et al. (2004) have confirmed this, with the former study demonstrating that this continues to be the case over the temperature range 284 K to 312 K. Raventos-Duran et al. (2007) have confirmed that channels forming $C_2H_5OH + O_3$ and $C_2H_5O + HO + O_2$ are not significant, assigning respective upper limit ratios of about 0.02 and 0.1 at 298 K, decreasing to about 0.01 and 0.02 at 195 K.

References

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Figure (top): $HO_2 + C_2H_5O_2$

Plot of $\log_{10}(k/cm^3\ molecule^{-1}\ s^{-1})$ versus $T^{-1}\ (K^{-1})$

- ● (green) Cattell et al., 1986
- ▲ Dagaut et al., 1988
- ● Fenter et al., 1993
- ○ Maricq and Szente, 1994
- ◆ (red) Boyd et al., 2003
- □ Raventos-Duran et al., 2007
- △ Noell et al., 2010
- — Recommendation

Figure (bottom): Plot of k versus Pressure (Torr)

- ● (green) Cattell et al., 1986
- ▲ Dagaut et al., 1988
- ● Fenter et al., 1993
- ○ Maricq and Szente, 1994
- ◆ (red) Boyd et al., 2003
- □ Raventos-Duran et al., 2007
- △ Noell et al., 2010