

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_26

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$$\Delta H^\circ(1) = 23.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -345.8 \text{ kJ}\cdot\text{mol}^{-1}$$

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>			
$k_{\text{obs}} = (1.31 \pm 0.12) \times 10^{-13}$	298	Adachi et al., 1979	FP-UVA (a,b)
$k_{\text{obs}} = 2.46 \times 10^{-13} \exp[-387/T]$	303-457	Anastasi et al., 1983	MM-UVA (a,c)
$k_{\text{obs}} = (6.92 \pm 0.95) \times 10^{-14}$	303		
$k_{\text{obs}} = (1.31 \pm 0.16) \times 10^{-13}$	266-348	Cattell et al., 1986	MM-UVA (a,d)
$k_{\text{obs}} = (4.55 \pm 0.22) \times 10^{-14}$	298	Munk et al., 1986	
$k_{\text{obs}} = 1.49 \times 10^{-13} \exp[-(110 \pm 40)/T]$	228-380	Wallington et al., 1988	FP-UVA (a,e)
$k_{\text{obs}} = (1.05 \pm 0.79) \times 10^{-13}$	298		
$k_{\text{obs}} = [5.14 \times 10^{-13} \exp(-518/T) + 9.67 \times 10^{-16} \exp(960/T)]$	220-330	Bauer et al., 1992	MM-UVA (a,f)
$k_{\text{obs}} = 1.91 \times 10^{-13} \exp[-(147 \pm 30)/T]$	250-330		
$k_{\text{obs}} = (1.17 \pm 0.10) \times 10^{-13}$	298		
$k_{\text{obs}} = 1.29 \times 10^{-13} \exp[(-20 \pm 40)/T]$	248-460	Fenter et al., 1993	FP-UVA (a,g)
$k_{\text{obs}} = (1.19 \pm 0.07) \times 10^{-13}$	298		
$k_{\text{obs}} = (1.26 \pm 0.41) \times 10^{-13}$	295	Atkinson and Hudgens, 1997	PLP-UVA (a,h)
$k_{\text{obs}} = 1.18 \times 10^{-13} \exp[(58 \pm 45)/T]$	221-295	Noell et al., 2010	PLP-UVA (a,i)
$k_{\text{obs}} = (1.42 \pm 0.07) \times 10^{-13}$ (67 mbar)	295		
$k_{\text{obs}} = (1.20 \pm 0.09) \times 10^{-13}$ (267 mbar)	295		
<i>Branching Ratios</i>			
$k_1/k_2 = 1.3$	298	Niki et al., 1982	UVP-FTIR (j)
$k_3/k_2 < 0.22$	298		
$k_1/k_2 = (1.75 \pm 0.05)$	302	Anastasi et al., 1983	MM-GC (c)
$k_1/k_2 = (2.12 \pm 0.10)$	333		
$k_1/k_2 = (2.45 \pm 0.15)$	373		
$k_1/k_2 = 2.1$	295	Wallington et al., 1989	UVP-FTIR (k)
$k_3/k_2 < 0.26$	295		
$k_1/k_2 = (0.28 \pm 06)$	221-295	Noell et al., 2010	PLP-IR-UVA (a,i)

Comments

- (a) k is defined by $-d[C_2H_5O_2]/dt = 2k[C_2H_5O_2]^2$. k_{obs} denotes an upper limit rate coefficient derived from an experimentally observed decay without correction for secondary removal of $C_2H_5O_2$. All studies to date have used UV absorption spectroscopy to monitor $C_2H_5O_2$, such that the primary observable is k_{obs}/σ . The values of k_{obs} presented above have been normalised using the $C_2H_5O_2$ cross sections recommended by Tyndall et al. (2001).
- (b) Flash photolysis of $(C_2H_5)_2N_2$ in the presence of about 350 mbar O_2 at a total pressure of about 400 mbar (balance Ar). $C_2H_5O_2$ absorption spectrum characterised over the range 215 nm to 280 nm, maximising at 235 nm. Above value of k_{obs} derived from 16 observations of the decay kinetics at wavelengths in the range 230 nm to 250 nm. The system was also simulated using a complex mechanism to extract a value of k , which was reported as $(1.1 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (c) Modulated photolysis of $(C_2H_5)_2N_2$ in the presence of O_2 at pressures of 7 mbar to 200 mbar (5 Torr to 152 Torr) and N_2 at pressures of 550 mbar to 730 mbar (418 Torr to 555 Torr). $k_{obs}/\sigma(240 \text{ nm})$ and $\sigma(240 \text{ nm})$ were found to be temperature dependent. Branching ratios were determined from analysis of products, C_2H_5OH and CH_3CHO , by GC. k_1/k_2 determined from the relative yields of C_2H_5OH and CH_3CHO , with the assumption that C_2H_5O formed in channel (1) reacts exclusively with O_2 to form CH_3CHO and HO_2 . Kinetics and branching ratio information combined to report values of $k_1 = 3.22 \times 10^{-13} \exp[(-683 \pm 24)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_2 = 5.80 \times 10^{-14} \exp[(-316 \pm 164)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Modulated photolysis of $Cl_2-C_2H_6-O_2-N_2$ mixtures at pressures of 3.2 mbar to 1013 mbar (2.4 Torr to 760 Torr). $C_2H_5O_2$ absorption spectrum characterised over the range 220 nm to 270 nm, maximising at 236 nm. $k_{obs}/\sigma(260 \text{ nm}) = (4.07 \pm 0.04) \times 10^4 \text{ cm s}^{-1}$ and $\sigma(260 \text{ nm}) = (3.20 \pm 0.38) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ were obtained, leading to a reported value of $k_{obs} = (1.30 \pm 0.16) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of pressure and temperature.
- (e) Flash photolysis of $Cl_2-C_2H_6-O_2-N_2$ mixtures at pressures of 33 mbar to 533 mbar (25 Torr to 400 Torr) total pressure. $C_2H_5O_2$ absorption spectrum characterised over the range 215 nm to 300 nm, maximising at 240 nm. $k_{obs} = (1.41 \pm 0.19) \times 10^{-13} \exp[-(110 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was reported, independent of pressure, based on a value of $\sigma(250 \text{ nm}) = (3.89 \pm 0.54) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (f) Modulated photolysis of $Cl_2-C_2H_6-O_2-N_2$ mixtures at a total pressure of 133 mbar (100 Torr). $C_2H_5O_2$ absorption spectrum characterised over the range 215 nm to 295 nm, maximising at 240 nm. Values of k_{obs}/σ were mainly determined at 250 nm, $\sigma(250 \text{ nm}) = (4.0 \pm 0.2) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. Temperature dependence in k_{obs} over the range 220-330 K was interpreted in terms of the expression: $k_{obs} = A_1 \exp(B_1/T) + A_2 \exp(B_2/T) = 2k_1 + k_2$. Expressions for k_1 and k_2 were obtained by constraining k_1/k_2 to a value of 0.65 at 298 K (based on reported product studies), leading to $k_1/k_2 = 3.8 \times 10^{-3} \exp(1478/T)$.
- (g) Flash photolysis-UV absorption study of $Cl_2-C_2H_6-O_2-N_2$ mixtures at 1013 mbar (760 Torr) total pressure. $C_2H_5O_2$ absorption spectrum characterised over the range 210 nm to 290 nm, maximising at 240 nm; $\sigma(240 \text{ nm}) = (4.89 \pm 0.60) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. $k_{obs} = (1.40 \pm 0.11) \times 10^{-13} \exp[(-20 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was reported, along with $k = (6.7 \pm 0.6) \times 10^{-14} \exp[(60 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained from $k = k_{obs}/(1+(k_1/k_2))$, where $k_1/k_2 = \beta/(1 + \beta)$ and $\beta = 10.2 \exp(-533/T)$, based on the temperature-dependent branching ratios of Anastasi et al. (1983), as recommended by Lightfoot et al. (1992).
- (h) Pulsed laser photolysis of $Cl_2-C_2H_6-O_2-Ar$ mixtures at (7.3 ± 1.0) mbar (5.5 Torr) total pressure with $C_2H_5O_2$ radicals being monitored by UV CRDS at 265 nm and 270 nm, using $\sigma(265 \text{ nm}) = 2.65 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ and $\sigma(270 \text{ nm}) = 2.14 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The

reported value of k , $(7.26 \pm 2.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was obtained using $k = k_{\text{obs}}/(1 + (k_1/k))$, with $k_1/k = 0.65$.

- (i) Pulsed laser photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures, mainly at 67 mbar (50 Torr) total pressure. Absorption due to $\text{C}_2\text{H}_5\text{O}_2$ monitored in UV at 250 nm, with HO_2 production monitored in the near IR using a TDL source tuned for HO_2 at the ${}^9\text{Q}_2$ band head (6638.2 cm^{-1}) of the first overtone of the HO stretch. A limited series of experiments also performed at 267 mbar (200 Torr) total pressure, with only $\text{C}_2\text{H}_5\text{O}_2$ monitored. k_{obs} determined from decay in absorption at 250 nm. Values of k and k_1/k derived from simulation of the system using a detailed mechanism, with HO_2 production (following reaction of $\text{C}_2\text{H}_5\text{O}$ with O_2) providing a direct characterisation of the flux through channel (1). Additional experiments, in which $[\text{O}_2]$ was varied, provided evidence for a competing reaction of $\text{C}_2\text{H}_5\text{O}$ with $\text{C}_2\text{H}_5\text{O}_2$, with a rate coefficient of $(1.5 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (j) Photolysis of $(\text{C}_2\text{H}_5)_2\text{N}_2\text{-O}_2$ mixtures and of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at a total pressure of 930 mbar (700 Torr). Products CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OOH}$ monitored by FTIR. k_1/k_2 determined from the relative yields of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO , with the assumption that $\text{C}_2\text{H}_5\text{O}$ formed in channel (1) reacts exclusively with O_2 to form CH_3CHO and HO_2 . No evidence for formation of $\text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$ observed, leading to upper limit for k_3/k_2 .
- (k) Photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6$ mixtures in 930 mbar (700 Torr) air. Products CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OOH}$ monitored by FTIR. k_1/k_2 determined from the relative yields of $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO , with the assumption that $\text{C}_2\text{H}_5\text{O}$ formed in channel (1) reacts exclusively with O_2 to form CH_3CHO and HO_2 . No evidence for formation of $\text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$ observed, leading to upper limit for k_3/k_2 .

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	7.6×10^{-14}	250 - 450
k_1/k	0.63	298
k_2/k	0.37	298
k_3/k	0	298
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	+ 200 K, - 100 K	
$\Delta k_1/k$	+ 0.1, - 0.4	298
$\Delta k_2/k$	+ 0.4, - 0.1	298
$\Delta k_3/k$	+ 0.1, - 0.0	298

Comments on Preferred Values

The end product studies of Niki et al. (1982), Anastasi et al. (1983) and Wallington et al. (1989) provide evidence for the significant participation of channels (1) and (2). The lack of evidence for $\text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$ formation in the studies of Niki et al. (1982) and Wallington et al. (1989) suggests that channel (3) is at most very minor ($k_3/k < 0.06$), and a value of $k_3/k = 0$ is therefore recommended at 298 K. Niki et al. (1982), Anastasi et al. (1983) and Wallington et al. (1989) report product ratios for CH_3CHO and $\text{C}_2\text{H}_5\text{OH}$ that are in fair agreement, with an average value of k_1/k_2 of 1.7 at temperatures close to 298 K, leading to the recommended

values of $k_1/k = 0.63$ and $k_2/k = 0.37$. It is noted that the three studies also report yields of C_2H_5OOH which are consistent with significant secondary HO_2 generation via channel (1), leading to lower but less well-determined values of k_1/k . The data of Wallington et al. (1989), which were reported to be free from heterogeneous C_2H_5OOH losses, allow a value of $k_1/k = (0.50 \pm 0.15)$ to be derived, with the (reasonable) assumption that HO_2 reacts exclusively with $C_2H_5O_2$ in the system. In addition, Hasson et al. (2004) have also reported yields of CH_3CHO and C_2H_5OOH which are compatible with a value of $k_1/k \approx 0.6$. However, the recent kinetics study of Noell et al. (2010), in which HO_2 formation was monitored directly in the near infrared, reports a much lower yield of HO_2 and a value of $k_1/k = (0.28 \pm 0.06)$, independent of temperature over the range 221 K to 295 K. The inconsistency of these data and the earlier end product studies therefore suggest the presence of systematic errors or complications in one or more of the studies and/or an incomplete understanding of the secondary chemistry in the system. As indicated above, the preferred branching ratios currently remain based on the end product data, because these allow a reliable description of the chemical development of the system within prevailing understanding of the broader chemical mechanism. However, further confirmatory studies are clearly required, and the reliability limits of k_1/k and k_2/k have been increased to encompass the results of Noell et al. (2010). The Anastasi et al. (1983) data suggest that k_1/k and k_2/k depend weakly on temperature (k_1/k increasing with temperature), which is also supported by the interpretation of the non-linear Arrhenius behaviour reported in the kinetic study of Bauer et al. (1992) (see comment (f)). At present, and in view of the temperature independence of k_1/k reported by Noell et al. (2010), no recommendation is made for the temperature dependence of the branching ratios, and further studies are clearly required.

The rate coefficients for this reaction have all been determined using UV absorption to monitor $C_2H_5O_2$. The measured quantity in all the studies is k_{obs}/σ , where σ is the absorption cross-section at the monitoring wavelength and k_{obs} is the observed second order rate coefficient, uncorrected for secondary removal of $C_2H_5O_2$. Because the studies report or apply various values for σ , and derive k using varying values of k_1/k (see comments (b)-(i)), the above table lists values of k_{obs} (rather than k) which have been normalised here using the cross-sections recommended in the review of Tyndall et al. (2001). The (normalised) values of k_{obs} at or near 298 K from majority of the studies are in good agreement, lying in the approximate range 1.1×10^{-13} to 1.4×10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$; the exceptions being the studies of Anastasi et al. (1983) and Munk et al. (1986), for which the values are somewhat lower than the consensus at 298 K. The room temperature data of Adachi et al. (1979), Cattell et al. (1986), Wallington et al. (1988), Bauer et al. (1992), Fenter et al. (1993), Atkinson and Hudgens (1997) and Noell et al. (2010) (their preferred 67 mbar data) thus provide a mean value of k_{obs} of 1.24×10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$, which is corrected using the preferred value of k_1/k , to yield the recommended value of k given above, where $k = k_{obs}/(1+(k_1/k))$. Because of the uncertainties in k_1/k commented on above, the reliability limits on k have been increased. Where the temperature dependence in k_{obs} has been investigated, within this subset of studies, it has been found to be either insignificant (Cattell et al., 1986; Fenter et al, 1993), weakly positive (Wallington et al., 1988; Bauer et al. 1992 – data above 250 K) or very weakly negative (Noell et al., 2010); with Bauer et al. (1992) also reporting a switch in the temperature dependence below 250 K (see comment (f)). On the basis of these studies, a temperature independent value of k is recommended over the range 250 K to 450 K, which also intrinsically assumes that k_1/k is insensitive to temperature. The uncertainties assigned to E/R encompass the reported range.

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