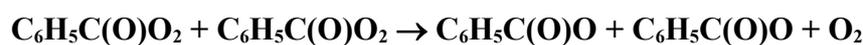


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AROM_RAD12

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. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>. This data sheet last evaluated: June 2011; last change in preferred values: June 2011.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.35 \pm 0.30) \times 10^{-11}$	298	Caralp et al., 1999	FP-UVA (a,b)
$3.1 \times 10^{-13} \exp[(1110 \pm 160)/T]$	298-460		
$(1.5 \pm 0.6) \times 10^{-11}$	293	Roth et al., 2010	PLP-UVA (a,c)

Comments

- (a) k is defined by $-d[\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2]/dt = 2k [\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2]^2$.
- (b) $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$ generated from the flash photolysis of Cl_2 -benzaldehyde- O_2 - N_2 mixtures at 1013 mbar (760 Torr). Absorption spectrum characterised over the wavelength range 245-300 nm, with $\sigma_{250\text{nm}} = (1.95 \pm 0.10) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. k was determined from simulation of the transient decay traces recorded in the range 245-260 nm, using a detailed chemical mechanism which included a description of secondary removal of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$ via reactions with $\text{C}_6\text{H}_5\text{O}_2$ and $\text{C}_6\text{H}_5\text{O}$, and the changes in the concentrations of absorbing reagents and products. Spectrum of reagent benzaldehyde characterised as part of the study, with $\sigma_{250\text{nm}} = 2.75 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.
- (c) $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$ generated from the pulsed laser photolysis of Cl_2 -benzaldehyde- O_2 - N_2 mixtures at 107-160 mbar (80-120 Torr). Absorption spectrum characterised over the wavelength range 220-280 nm, with $\sigma_{250\text{nm}} = (1.30 \pm 0.22) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. k was determined from simulation of the transient decay traces recorded at 250-255 nm, using a detailed chemical mechanism which included a description of secondary removal of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$ via reaction with $\text{C}_6\text{H}_5\text{O}_2$ and $\text{C}_6\text{H}_5\text{O}$, and the changes in the concentrations of absorbing reagents and products. Spectrum of reagent benzaldehyde taken from El Dib et al. (2006), with $\sigma_{250\text{nm}} = (1.3 \pm 0.3) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.4×10^{-11}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.4 \times 10^{-13} \exp(1110/T)$	293 - 460
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298
$\Delta E/R$	$\pm 500 \text{ K}$	

Comments on Preferred Values

The two studies report room temperature values of k that are in good agreement, despite some notable differences in UV absorption cross-sections for $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$ and reagent benzaldehyde used in the analyses. The more recent study of Roth et al. (2010) made use of benzaldehyde cross-sections reported by El Dib et al. (2006), which agree well with those reported by Thiault et al. (2004). The benzaldehyde cross-sections determined by Caralp et al. (1999) appear to be too large by a factor of 2 – 3 at the wavelengths used in the kinetics determination, and this may be a contributory factor in explaining the ~50 % higher cross-sections determined for $\text{C}_6\text{H}_5\text{C}(\text{O})\text{O}_2$; although these systematic errors largely appear to cancel out in the determination of the room temperature value of k .

Despite these apparent inconsistencies, the temperature dependence of the preferred value of k is based on that reported by Caralp et al. (1999), but with the pre-exponential factor adjusted slightly to give the value of k reported by Roth et al. (2010) at 293 K. It is noted that the preferred value of k at 298 K is comparable to those recommended for the structurally-similar radicals, $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2$. Additional studies (or re-interpretation of the data of Caralp et al. (1999) using updated cross-sections) would be valuable in confirming, and reducing the uncertainty in, E/R . Further studies of the oxidation of benzaldehyde in the absence of NO_x , and of the relevant reactions of $\text{C}_6\text{H}_5\text{O}_2$ and $\text{C}_6\text{H}_5\text{O}$ (see Caralp et al., 1999; Roth et al., 2010), would also help to confirm the details of the secondary chemistry in the system, and reduce the uncertainty in k .

References

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