IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_AROM25

This data sheet last evaluated: June 2009.

HO + C_6H_5CHO (benzaldehyde) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Cofficients			
$(1.26 \pm 0.08) \times 10^{-11}$	298 ± 2	Niki et al., 1978	RR (a, f)
$(1.1 \pm 0.2) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (b, f)
5.7×10^{-12} exp [(225±57)/T)]	294-343	Semadeni et al., 1995	RR (c, g)
$(1.22 \pm 0.07) \times 10^{-11}$	299		
$(1.20 \pm 0.14) \times 10^{-11}$	298 ± 2	Thiault et al., 2002	RR (d, g)
$(1.12 \pm 0.16) \times 10^{-11}$	298 ± 2	Thiault et al., 2002	RR (d, h)
$(1.15 \pm 0.13) \times 10^{-11}$	298 ± 2	Thiault et al., 2002	RR (d, i)
$(1.30 \pm 0.07) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, g)
$(1.31 \pm 0.12) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, j)
$(1.36 \pm 0.04) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, k)
$(1.46 \pm 0.20) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, l)
$(1.44 \pm 0.07) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, m)

Comments

(a) HO radicals were generated by the photolysis of HONO in air at atmospheric pressure in a 70 L Pyrex chamber. The concentrations of benzaldehyde and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + benzaldehyde)/k(HO + ethene) = 1.6 ± 0.1 is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 7.9 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson et al., 2006).

(b) HO radicals were generated by the photolysis of HONO at λ = 300-450 nm in air at atmospheric pressure in a 220 L Tedlar chamber. The concentrations of benzaldehyde and ethene (the reference compound) were measured by GC-FID. The measured rate coefficient ratio of k(HO + benzaldehyde)/k(HO + ethene) = 1.39 ± 0.27 is placed on an absolute basis using k(HO + ethene) = 7.9 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Atkinson et al., 2006).

(c) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Tedlar chamber. Benzaldehyde and diethyl ether (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + benzaldehyde)/k(HO + diethyl ether) = 0.721 exp[(89.5 ± 84.7)/T] over the temperature range 294-343 K is placed on an absolute basis using a rate coefficient of k(HO + diethyl ether) = 1.15 × 10^{-17} T^2 exp(743/T) cm^3 molecule^{-1} s^{-1} (Calvert et al., 2009).

(d) HO radicals were generated by the photolysis of HONO at λ = 300-460 nm in air at atmospheric pressure in a 200 L Teflon chamber. The concentrations of benzaldehyde, di-isopropyl ether, diethyl

ether and 1,3-dioxolane (the reference compounds) were measured by GC-FID. The measured rate coefficient ratios of k(HO + benzaldehyde)/k(HO + di-isopropyl ether) = 1.12 ± 0.04, k(HO + benzaldehyde)/k(HO + diethyl ether) = 0.97 ± 0.02 and k(HO + benzaldehyde)/k(HO + 1,3-dioxolane) = 1.15 ± 0.02 are placed on an absolute basis by using k(HO + di-isopropyl ether) = 1.0 × 10^{-11}, k(HO + diethyl ether) = 1.24 × 10^{-11} and k(HO + 1,3-dioxolane) = 1.0 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (Calvert et al., 2009).

(e) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in two different FEP Teflon chambers (350 L and 3910 L). The concentrations of benzaldehyde, di-n-butyl ether, tetrahydrofuran, 1,2,4-trimethylbenzene, diethyl ether and n-hexane (the reference compounds) were measured by GC-FID during the experiments. The measured rate coefficient ratios of k(HO + benzaldehyde)/k(HO + di-n-butyl ether) = 0.45 ± 0.04, k(HO + benzaldehyde)/k(HO + tetrahydrofuran) = 0.80 ± 0.02, k(HO + benzaldehyde)/k(HO + 1,2,4-trimethylbenzene) = 0.45 ± 0.06, k(HO + benzaldehyde)/k(HO + diethyl ether) = 1.05 ± 0.06 and k(HO + benzaldehyde)/k(HO + n-hexane) = 2.63 ± 0.12 are placed on an absolute basis using k(HO + di-n-butyl ether) = 2.9 × 10^{-11}, k(HO + tetrahydrofuran) = 1.7 × 10^{-11}, k(HO + diethyl ether) = 1.24 × 10^{-11} (Calvert et al., 2009), k(HO + n-hexane) = 5.48 × 10^{-12} (Calvert et al., 2008) and k(HO + 1,2,4-trimethylbenzene) = 3.25 × 10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2002) at 298 K and atmospheric pressure and 295 K.

(f) Relative to HO + ethene
(g) Relative to HO + diethyl ether
(h) Relative to HO + di-isopropyl ether
(i) Relative to HO + 1,3-dioxolane
(j) Relative to HO + di-n-butyl ether
(k) Relative to HO + tetrahydrofuran
(l) Relative to 1,2,4-trimethylbenzene
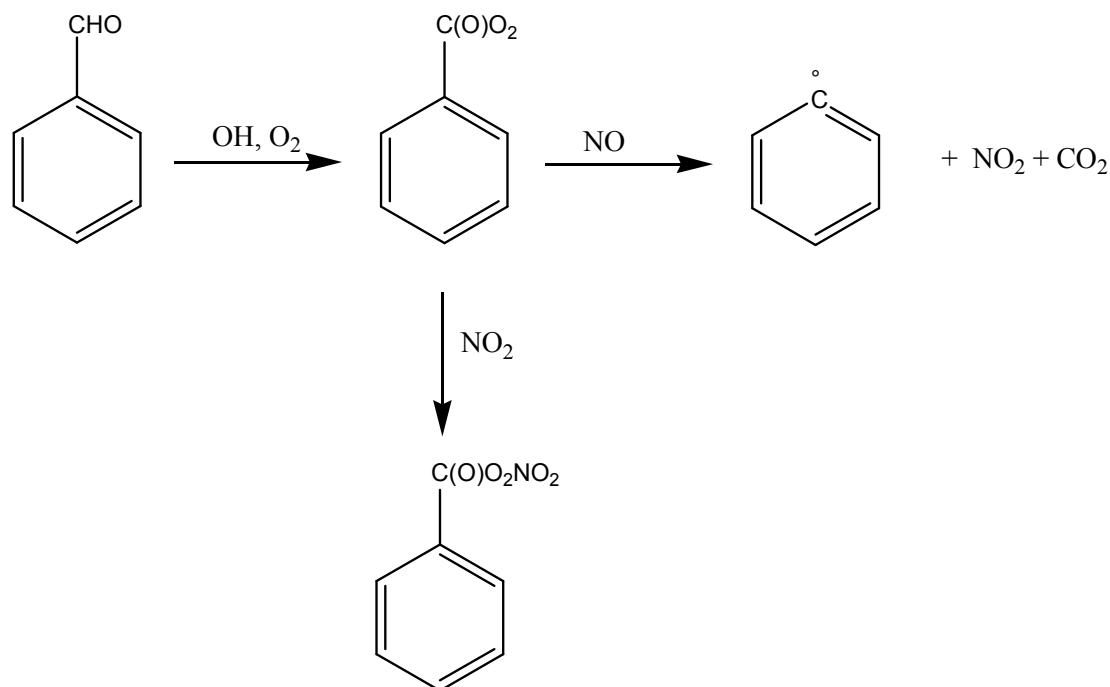(m) Relative to n-hexane

Preferred Values

Parameter	Value	T/K
k/ molecule^{-1} s^{-1}	1.26 × 10^{-11}	298
k/ cm^3 molecule^{-1} s^{-1}	5.9 × 10^{-12} exp(225/T)	290-350
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 170	

Comments on Preferred Values

The rate coefficient values reported near 298 K by different authors are in agreement within the experimental uncertainties. The preferred value at 298 K is an average of these determinations. Semadeni et al. (1995) measured the temperature dependence using a relative method in the temperature range 289-373 K but used only the data in the range 294-343 K to derive their Arrhenius expression. The preferred temperature dependence values are obtained by combining the preferred k(298) value with the sole temperature dependence of Semadeni et al. in the restricted temperature range 294-343K.

Reaction of HO with benzaldehyde proceeds mainly by abstraction of the aldehydic H-atom to form benzoyl radical which adds O_2 to form benzoyl peroxy radical. In presence of NOx, benzoyl peroxy radical reacts with NO or NO_2:

References

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