IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_AROM2

$$HO + C_6H_5CH_3 \text{ (Toluene)} \rightarrow H_2O + C_6H_5CH_2 \qquad (1)$$
$$\rightarrow HOC_6H_5CH_3 \qquad (2)$$
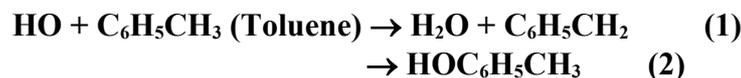
Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.11 \pm 0.40) \times 10^{-12}$	298	Davis et al., 1975	FP-RF (a)
$(5.78 \pm 0.58) \times 10^{-12}$	298	Hansen et al., 1975	FP-RF (b)
$(6.40 \pm 0.64) \times 10^{-12}$	297.9	Perry et al., 1977	FP-RF (c)
$(4.90 \pm 0.6) \times 10^{-12}$	323.7		
$(1.49 \pm 0.22) \times 10^{-12}$	379.2		
$(1.58 \pm 0.24) \times 10^{-12}$	394.2		
$(1.69 \pm 0.25) \times 10^{-12}$	408.7		
$(1.76 \pm 0.18) \times 10^{-12}$	424.4		
$(1.71 \pm 0.20) \times 10^{-12}$	472.7		
$3.8 \times 10^{-12} \exp[(180 \pm 170)/T]$	213-298	Tully et al., 1981	FP-RF (d)
$(8.20 \pm 0.54) \times 10^{-12}$	213		
$(8.73 \pm 0.39) \times 10^{-12}$	231		
$(7.97 \pm 0.56) \times 10^{-12}$	250		
$(8.53 \pm 0.37) \times 10^{-12}$	260		
$(7.44 \pm 0.55) \times 10^{-12}$	270		
$(6.36 \pm 0.69) \times 10^{-12}$	298		
$(2.16 \pm 0.08) \times 10^{-12}$	504		
$(2.45 \pm 0.05) \times 10^{-12}$	568		
$(2.49 \pm 0.12) \times 10^{-12}$	568		
$(3.26 \pm 0.29) \times 10^{-12}$	666		
$(3.58 \pm 0.16) \times 10^{-12}$	694		
$(4.67 \pm 0.19) \times 10^{-12}$	793		
$(5.54 \pm 0.27) \times 10^{-12}$	868		
$(6.87 \pm 0.23) \times 10^{-12}$	958		
$(9.5 \pm 1.0) \times 10^{-12}$	1046		
$k_1 = (0 \pm 2.0) \times 10^{-13}$	299	Knispel et al., 1990	FP-RF (e)
$k_2 = (7.0 \pm 2.1) \times 10^{-12}$	299		
$k_1 = (4.5 \pm 2.1) \times 10^{-13}$	311		
$k_2 = (5.6 \pm 0.4) \times 10^{-12}$	311		
$k_1 = (5.0 \pm 0.6) \times 10^{-13}$	323		
$k_2 = (5.0 \pm 0.3) \times 10^{-12}$	323		
$k_1 = (6.2 \pm 0.9) \times 10^{-13}$	340		
$k_2 = (3.8 \pm 0.9) \times 10^{-12}$	340		
$(6.4 \pm 0.7) \times 10^{-12}$	338	Markert and Pagsberg, 1993	PR-UVA (f)
$(5.60 \pm 0.14) \times 10^{-12}$	299 ± 2	Bohn, 2001	PLP-UVA (g)
$(5.70 \pm 0.19) \times 10^{-12}$	299 ± 2		
Relative Rate Cofficients			

$(3.4 \pm 1.5) \times 10^{-12}$	304 ± 1	Doyle et al., 1975	RR (h)
7.6×10^{-12}	300	Cox et al., 1980	RR (i)
$(5.62 \pm 0.16) \times 10^{-12}$	~298	Ohta and Ohyama, 1985	RR (j)
$(5.07 \pm 0.52) \times 10^{-12}$	297	Edney et al., 1986	RR (k)
$(5.48 \pm 0.16) \times 10^{-12}$	296 ± 2	Atkinson and Aschmann, 1989	RR (l)
$(6.35 \pm 1.50) \times 10^{-12}$	297 ± 2	Sommerlade et al., 1993	RR (m)
$(5.56 \pm 0.26) \times 10^{-12}$	298	Finlayson-Pitts et al., 1993	RR (n)
$2.09 \times 10^{-18}\ T^2$ $\exp[(207.4 \pm 113.5)/T]$	284-363	Semadeni et al., 1995	RR (o)
$(5.62 \pm 0.29) \times 10^{-12}$	299		
$(5.39 \pm 0.07) \times 10^{-12}$	276	Anderson and Hites, 1996	RR (p,q)
$(5.84 \pm 0.07) \times 10^{-12}$	285		
$(5.58 \pm 0.14) \times 10^{-12}$	285		
$(5.34 \pm 0.07) \times 10^{-12}$	293		
$(5.61 \pm 0.08) \times 10^{-12}$	303		
$(5.47 \pm 0.08) \times 10^{-12}$	310		
$(5.43 \pm 0.16) \times 10^{-12}$	323		
$(5.13 \pm 0.16) \times 10^{-12}$	323		
$(5.05 \pm 0.08) \times 10^{-12}$	323		
$(5.22 \pm 0.16) \times 10^{-12}$	324		
$(5.07 \pm 0.08) \times 10^{-12}$	324		
$(4.96 \pm 0.17) \times 10^{-12}$	344		
$(4.77 \pm 0.09) \times 10^{-12}$	363		
$(3.36 \pm 0.19) \times 10^{-12}$	371		
$(2.94 \pm 0.19) \times 10^{-12}$	383		
$(5.61 \pm 0.56) \times 10^{-12}$	296	Anderson and Hites, 1996	RR (p,r)
$(5.35 \pm 0.21) \times 10^{-12}$	297		
$(5.28 \pm 0.42) \times 10^{-12}$	297		
$(5.21 \pm 0.21) \times 10^{-12}$	297		
$(4.82 \pm 0.08) \times 10^{-12}$	323		
$(5.21 \pm 0.16) \times 10^{-12}$	323		
$(4.67 \pm 0.16) \times 10^{-12}$	323		
$(4.90 \pm 0.08) \times 10^{-12}$	323		
$(4.61 \pm 0.16) \times 10^{-12}$	324		
$(4.60 \pm 0.09) \times 10^{-12}$	363		
$(4.51 \pm 0.09) \times 10^{-12}$	363		
$(4.60 \pm 0.27) \times 10^{-12}$	363		
$(4.51 \pm 0.09) \times 10^{-12}$	363		
$(4.42 \pm 0.98) \times 10^{-12}$	363		
$(4.42 \pm 0.09) \times 10^{-12}$	363		
$(5.55 \pm 0.07) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,t)
$(5.15 \pm 0.11) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,t)
$(5.77 \pm 0.07) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,u)
$(5.36 \pm 0.08) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,v)

Branching Ratios

$k_1/k = 0.728\ 0.082$	298 ± 2	Atkinson et al., 1989	(w)
$k_1/k_2 < 0.022$	299	Knispel et al., 1990	FP-RF (e)

$k_1/k_2 = 0.08 \pm 0.04$	311		
$k_1/k_2 = 0.10 \pm 0.02$	323		
$k_1/k_2 = 0.16 \pm 0.05$	340		
$k_1/k = 0.11 \pm 0.02$	338	Markert and Pagsberg, 1993	PR-UVA (x)
$k_1/k = 0.067 \pm 0.07$	298	Smith et al., 1998	(y)
$k_1/k = 0.065 \pm 0.09$	~298	Klotz et al., 1998	(z)

Comments

(a) At 100 Torr (133 mbar) of He diluent. Lower rate coefficients were measured at 3 and 20 Torr (4 and 27 mbar) of He diluent.

(b) Measured rate coefficient was independent of the pressure of Ar diluent over the range 100-619 Torr (133-825 mbar).

(c) Non-exponential HO radical decays were observed at temperatures between 325 K and 379 K. No effect of increasing the total pressure at 325 K, 378 K or 424 K from 100 Torr to 200 Torr (133-267 mbar) of argon diluent was observed on the measured rate coefficients (at 325 K and 378 K these were derived from the initial HO radical decay rates).

(d) Experiments were generally carried out at 100 Torr (133 mbar) pressure of Ar diluent. At 298 K, the rate coefficient was measured as a function of total pressure over the ranges 20-100 Torr (27-133 mbar) of He, 25-100 Torr (33-133 mbar) of Ar, and at 100 Torr (133 mbar) of SF_6, and the 298 K rate coefficient appeared to reach the high-pressure value at ~100 Torr pressure. Non-exponential HO radical decays were observed at temperatures between 320 K and 380 K.

(e) Rate coefficients k_1 and k_2 were derived from fitting the observed non-exponential HO radical decays, measured over time periods at a total pressure of 133 mbar of Ar, to reactions (1), (2), the back-decomposition of the HO-toluene adduct and accounting for diffusive and background losses of HO radicals and the HO-toluene adduct. Using the rate coefficients of Tully et al. (1981) at 500-1000 K and the expression $k_1 = C\,T^2\,\exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients k_1 of 4.3×10^{-13} cm^3 molecule^{-1} s^{-1} at 299 K, 4.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 311 K, 5.3×10^{-13} cm^3 molecule^{-1} s^{-1} at 323 K and 6.1×10^{-13} cm^3 molecule^{-1} s^{-1} at 340 K.

(f) k was determined from the formation kinetics of the HO-toluene adduct monitored by UV absorption at 300 nm.

(g) Experiments were carried out in N_2 and O_2 diluent at a total pressure of 750 Torr (1 bar), with rate coefficients of $(5.70 \pm 0.19) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in N_2 and $(5.60 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in O_2.

(h) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of toluene and n-butane (the reference compound) by GC. The measured rate coefficient ratio k(HO + toluene)/k(HO + n-butane) = 1.4 $\pm$ 0.6 is placed on an absolute basis using a rate coefficient of k(HO + n-butane) = 2.41×10^{-12} cm^3 molecule^{-1} s^{-1} at 304 K (IUPAC, current recommendation).

(i) HO radicals generated by the photolysis of HONO at 300-450 nm in air at atmospheric pressure. Toluene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + ethene) is placed on an absolute basis using a rate coefficient of k(HO + ethene) = 8.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(j) HO radicals generated by the photolysis of H_2O_2 at 254 nm at atmospheric pressure. Experiments were carried out at room temperature (the specific temperature not being noted). Toluene and n-hexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + n-hexane) = 1.08 $\pm$ 0.03 is placed on an absolute basis using a 298 K rate coefficient of k(HO + n-hexane) = 5.20×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(k) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and cyclohexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + cyclohexane) is placed on an absolute basis using a rate coefficient of k(HO + cyclohexane) = 6.95×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 297 K (Atkinson and Arey, 2003).

(l) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and propene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + propene) = 0.206 ± 0.006 is placed on an absolute basis using a rate coefficient of k(HO + propene) = 2.66×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(m) HO radicals generated by the photolysis of NO_x in the presence of organics in air at 70 Torr (93 mbar) pressure. Toluene and n-hexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio k(HO + toluene)/k(HO + n-hexane) is placed on an absolute basis using a rate coefficient of k(HO + n-hexane) = 5.17×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 297 K (Atkinson and Arey, 2003).

(n) HO radicals were generated from the dark reactions of O_3 with toluene and n-hexane (the reference compound) in O_2 diluent at 14.1-19.4 Torr (19-26 mbar) pressure. Toluene and n-hexane were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + n-hexane) = 1.07 $\pm$ 0.05 is placed on an absolute basis using a rate coefficient of k(HO + n-hexane) = 5.20×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Atkinson and Arey, 2003).

(o) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and 2,3-dimethylbutane (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + 2,3-dimethylbutane) = 0.126 exp[$(614.4 \pm 113.5)/T$] over the temperature range 294-363 K is placed on an absolute basis using a rate coefficient of k(HO + 2,3-dimethylbutane) = 1.66×10^{-17} T^2 exp($407/T$) cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003). Rate coefficients were also measured at 258 K, 264 K and 269 K but were not used by Semadeni et al. (1995) in their derivation of the Arrhenius expression.

(p) HO radicals generated by the photolysis of O_3 in the presence of water vapor at 254 nm in $N_2 + O_2$ or He diluent at atmospheric pressure. Toluene and cyclohexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio k(HO + toluene)/k(HO + cyclohexane) are placed on an absolute basis using a rate coefficient of k(HO + cyclohexane) = 3.26×10^{-17} T^2 exp($262/T$) cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(q) In He diluent.

(r) In $N_2 + O_2$ diluent.

(s) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and 1,3-butadiene, propene or cyclohexane (the reference compounds) were monitored by GC, and the measured rate coefficient ratios k(HO + toluene)/k(HO + reference compound) are placed on an absolute basis using rate coefficients at 296 K and atmospheric pressure of air of k(HO + 1,3-butadiene) = 6.72×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003), k(HO + propene) = 2.66×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003) and k(HO + cyclohexane) = 6.92×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(t) Relative to 1,3-butadiene.

(u) Relative to propene.

(v) Relative to cyclohexane.

(w) Derived from the measured yields of benzaldehyde [C_6H_5CHO] plus benzyl nitrate [$C_6H_5CH_2ONO_2$] in irradiated CH_3ONO-NO-toluene-air mixtures at 298 ± 2 K and ~740 Torr of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1).

(x) Pulse radiolysis study. Benzyl radicals were monitored at 253 nm and the derived benzyl radical concentration (calibrated using the Cl + toluene reaction to generate known concentrations of

benzyl) were compared to the initial concentration of HO radicals generated in the reactions from the pulse radiolysis of Ar in the presence of H_2O.

(y) Derived from the measured yield of benzaldehyde [C_6H_5CHO] plus an estimated benzyl nitrate [$C_6H_5CH_2ONO_2$] yield in irradiated CH_3ONO-NO-toluene-air mixtures at 298 K and atmospheric pressure of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1), and the benzyl nitrate yield is estimated using a yield ratio of benzyl nitrate/benzaldehyde = 0.12 (Hoshino et al., 1978; Atkinson et al., 1989).

(z) Derived from the measured yield of benzaldehyde [C_6H_5CHO] plus an estimated benzyl nitrate [$C_6H_5CH_2ONO_2$] yield in irradiated NO_x-toluene-air mixtures at ~298 K and atmospheric pressure of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1), and the benzyl nitrate yield is estimated using a yield ratio of benzyl nitrate/benzaldehyde = 0.12 (Hoshino et al., 1978; Atkinson et al., 1989).

Preferred Values

$k = 1.8 \times 10^{-12} \exp(340/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-350 K.
$k = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 2.5 \times 10^{-11} \exp(-1270/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 310-1050 K.
$k_1 = 3.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta\log k = \pm 0.10$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta\log k_1 = \pm 0.20$ at 298 K.
$\Delta(E_1/R) = \pm 200$ K.

Comments on Preferred Values

Absolute rate studies show that the reaction of HO radicals with toluene can be considered as comprising three temperature regimes (Perry et al., 1977; Tully et al., 1981). At temperatures <325-350 K the reaction proceeds by channels (1) and (2), with pathway (2) dominating and with the HO-toluene adducts, $HOC_6H_5CH_3$, being thermally stable against back-decomposition to reactants at total pressures above ~100 Torr. At total pressures <100 Torr, channel (2) is in the fall-off regime (Davis et al., 1975; Tully et al., 1981; Bourmada et al., 1988a,b), with a limiting low-pressure rate coefficient at 295 ± 2 K of k_o(He) = 4.0 x 10^{-28} cm^6 molecule^{-2} s^{-1} (Bourmada et al., 1988a,b). At temperatures >450 K, decomposition of the HO-toluene adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1). At temperatures in the range ~325-450 K, decomposition of the HO-toluene adducts is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies non-exponential HO radical decays are generally observed.

The >450 K rate coefficients of Perry et al. (1977) and Tully et al. (1981), which are attributed to those for pathway (1), and the values of k_1 derived by Knispel et al. (1990) from HO radical decay curves at 299-340 K indicate that an Arrhenius fit is adequate. The preferred values of k_1 are obtained from a least-squares fit of the >450 K rate coefficients of Perry et al. (1977) and Tully et al. (1981) and the rate coefficients k_1 of Knispel et al. (1990) at 323 K and 340 K (their rate coefficients k_1 at 299 K and 311 K have high associated uncertainties and are not used in the evaluation of k_1). The preferred values of k at ≤350 K are based on the absolute rate coefficients of Hansen et al. (1975), Perry et al. (1977), Tully et al. (1981), Knispel et al. (1990) [omitting the 299 K rate coefficient which has a high associated uncertainty] and Bohn (2001) and the relative rate studies of Edney et al. (1986), Atkinson and Aschmann (1989), Finlayson-Pitts et al. (1993), Semadeni et al. (1995), Anderson and Hites (1996)

and Kramp and Paulson (1998). The rate coefficient ratio k_1/k derived from the preferred values (0.063 at 298 K) is in excellent agreement with the branching ratios obtained from product studies (Atkinson et al., 1989; Smith et al., 1998; Klotz et al., 1998).

References

Anderson, P. N. and Hites, R. A. : Environ. Sci. Technol., 30, 301, 1996.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 21, 355, 1989.
Atkinson, R., Aschmann, S. M., Arey, J. and Carter, W. P. L.: Int. J. Chem. Kinet., 21, 801, 1989.
Bohn, B.: J. Phys. Chem. A, 105, 6092, 2001.
Bourmada, M., Devolder, P. and Sochet, L.-R.: Chem. Phys. Lett., 149, 329, 1988a.
Bourmada, M., Carlier, M., Pauwels, J.-F. and Devolder, P.: J. Chim. Phys., 95, 881, 1988b.
Cox, R. A., Derwent, R. G. and Williams, M. R.: Environ. Sci. Technol., 14, 57, 1980.
Davis, D. D., Bollinger, W. and Fischer, S.: J. Phys. Chem., 79, 293, 1975.
Doyle, G. J., Lloyd, A. C., Darnall, K. R., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 9, 237, 1975.
Edney, E. O., Kleindienst, T. E. and Corse, E. W.: Int. J. Chem. Kinet., 18, 1355, 1986.
Finlayson-Pitts, B. J., Hernandez, S. K. and Berko, H. N.: J. Phys. Chem., 97, 1172, 1993,
Hansen, D. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 79, 1763, 1975.
Hoshino, M., Akimoto, H. and Okuda, M.: J. Chem. Soc. Jpn., 51, 718, 1978.
IUPAC,: http://iupac.pole-ether.fr (2013).
Klotz, B., Sørensen, S., Barnes, I., Becker, K. H., Etzkorn, T., Volkamer, R., Platt, U., Wirtz, K. and Martín-Reviejo, M.: J. Phys. Chem. A, 102, 10289, 1998.
Kramp, F. and Paulson, S. E. : J. Phys. Chem. A, 102, 2685, 1998.
Knispel, R., Koch, R., Siese, M. and Zetzsch, C.: Ber. Bunsenges. Phys. Chem., 94, 1375, 1990.
Markert, F. and Pagsberg, P.: Chem. Phys. Lett., 209, 445, 1993.
Ohta, T. and Ohyama, T.: Bull. Chem. Soc. Jpn., 58, 3029, 1985.
Perry, R. A., Atkinson, R. and Pitts Jr., J. N.: J. Phys. Chem., 81, 296, 1977.
Semadeni, M., Stocker, D. W. and Kerr, J. A.: Int. J. Chem. Kinet., 27, 287, 1995.
Smith, D. F., McIver, C. D. and Kleindienst, T. E.: J. Atmos. Chem., 30, 209, 1998.
Sommerlade, R., Parlar, H., Wrobel, D. and Kochs, P.: Environ. Sci. Technol., 27, 2435, 1993
Tully, F. P., Ravishankara, A. R., Thompson, R. L., Nicovich, J. M., Shah, R. C., Kreutter, N. M. and Wine, P. H.: J. Phys. Chem., 85, 2262, 1981.