IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_AROM3

This data sheet last evaluated August 2008; last change in preferred values August 2008.

HO + *m*-$CH_3C_6H_4OH$ (*m*-cresol) → H_2O + $CH_3C_6H_4O$ (1)
→ H_2O + $CH_2C_6H_4OH$ (2)
→ $CH_3C_6H_4(OH)_2$ (3)

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(5.77 \pm 0.33) \times 10^{-11}$	300 ± 1	Atkinson et al., 1978	RR (a)
$(6.78 \pm 0.43) \times 10^{-11}$	296 ± 2	Atkinson and Aschmann, 1990	RR (b)
$3.97 \times 10^{-12} \exp[(775.4 \pm 230.9)/T]$	299-373	Semadeni et al., 1995	RR (c)
$(5.42 \pm 0.54) \times 10^{-11}$	299		
$(5.78 \pm 0.91) \times 10^{-11}$	294 ± 2	Coeur-Tourneur et al., 2006	RR (d)

Comments

(a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *m*-cresol and *o*-cresol (the reference organics) were measured by GC. The measured rate coefficient ratio k(HO + *m*-cresol)/k(HO + *o*-cresol) = 1.42 ± 0.08 is placed on an absolute basis using a rate coefficient at 300 K of k(HO + *o*-cresol) = 4.06×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(b) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. The concentrations of *m*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + *m*-cresol)/k(HO + propene) = 2.55 ± 0.15 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).

(c) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *m*-Cresol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + *m*-cresol)/k(HO + *o*-cresol) = $2.482 \exp[-(194.6 \pm 230.9)/T]$ over the temperature range 299-373 K is placed on an absolute basis using a rate coefficient of k(HO + *o*-cresol) = $1.6 \times 10^{-12} \exp(970/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(d) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *m*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios k(HO + *m*-cresol)/k(HO + 1,3,5-trimethylbenzene) = 1.02 ± 0.16 is placed on an absolute basis using a rate coefficient of k(HO + 1,3,5-trimethylbenzene) = 5.67×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

$k = 2.3 \times 10^{-12} \exp(965/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290-350 K.
$k = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

As for the reactions of HO radicals with benzene, toluene, phenol and *o*-cresol (IUPAC, 2008), the reaction of HO radicals with *m*-cresol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2008)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions.

The available rate coefficients (Atkinson et al., 1978; Atkinson and Aschmann, 1990; Semadeni et al., 1995; Coeur-Tourneur et al., 2006) are all from relative rate studies, with only one study being carried out as a function of temperature (Semadeni et al., 1995). At room temperature, the relative rate data of Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in reasonable agreement. The preferred temperature dependence is obtained from a least-squares analysis of the rate coefficients of Semadeni et al. (1995) at temperatures <350 K. The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) and Coeur-Tourneur et al. (2006), using the preferred temperature dependence to correct the measured rate coefficients to 298 K. The pre-exponential factor is adjusted to fit the 298 K preferred value. Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K

By analogy with the HO + *o*-cresol reaction (Perry et al., 1977; IUPAC, 2008), at atmospherically-relevant temperatures the HO + *m*-cresol reaction is expected to proceed almost entirely by channels (1) and (3), with channel (1) accounting for a minor fraction (~4%) of the overall reaction at 298 K and for less at lower temperatures. In the presence of NO_x, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 5-methyl-2-nitrophenol plus 3-methyl-2-nitrophenol formation yields from the OH radical-initiated reaction of *m*-cresol to be 3.2 ± 1.5% at 296 ± 2 K, 7.7 ± 2.2% at 298 ± 2 K, and 2.9 ± 0.5% at 294 ± 2 K, respectively. Since 3- and 5-methyl-2-nitrophenol formation is attributed to the reaction of 3-methylphenoxy radicals with NO_2, these observations indicate that at room temperature channel (1) accounts for least 3% of the overall reaction, consistent with the kinetic data.

References

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