IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_AROM4

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

HO + *o*-$CH_3C_6H_4OH$ (*o*-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
Absolute Rate Coefficients			
$1.6 \times 10^{-12} \exp[(906 \pm 1007)/T]$	299-335	Perry et al., 1977	FP-RF (a)
$(3.41 \pm 0.68) \times 10^{-11}$	299.4		
$(2.93 \pm 0.59) \times 10^{-11}$	310.6		
$(2.98 \pm 0.60) \times 10^{-11}$	322.0		
$(2.68 \pm 0.54) \times 10^{-11}$	330.7		
$(2.55 \pm 0.51) \times 10^{-11}$	335.4		
$5.0 \times 10^{-11} \exp[-(906 \pm 1007)/T]$	400-424		
$(5.6 \pm 1.1) \times 10^{-12}$	400.6		
$(5.4 \pm 1.1) \times 10^{-12}$	407.8		
$(6.2 \pm 1.2) \times 10^{-12}$	423.1		
Relative Rate Cofficients			
$(3.85 \pm 0.33) \times 10^{-11}$	300 ± 1	Atkinson et al., 1978	RR (b)
$(4.26 \pm 0.22) \times 10^{-11}$	296 ± 2	Atkinson and Aschmann, 1990	RR (c)
$1.01 \times 10^{-12} \exp[(1155.6 \pm 246.1)/T]$	301-373	Semadeni et al., 1995	RR (d)
$(4.65 \pm 0.40) \times 10^{-11}$	301		
$(4.25 \pm 0.52) \times 10^{-11}$	294 ± 2	Coeur-Tourneur et al., 2006	RR (e)

Comments

(a) Non-exponential HO radical decays were observed at temperatures between 344 K and 393 K. The total pressure was ~100 Torr (133 mbar) of argon diluent.

(b) 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 *o*-cresol and *n*-butane and 2,2-dimethylpropane (the reference organics) were measured by GC. The measured rate coefficient ratio k(HO + *o*-cresol)/{k(HO + *n*-butane) - k(HO + 2,2-dimethylpropane)} is placed on an absolute basis using rate coefficients at 300 K of k(HO + *n*-butane) = 2.38×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) and k(HO + 2,2,-dimethylpropane)} = 8.4×10^{-13} cm^3 molecule^{-1} s^{-1} (Arey and Atkinson, 2003).

(c) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. The concentrations of *o*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + *o*-cresol)/k(HO + propene) = 1.60 ± 0.08 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).

(d) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *o*-Cresol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + *o*-cresol)/k(HO + 1,3-butadiene) = 0.068 exp[(707.6 ± 246.1)/T] over the temperature range 301-373 K is placed on an absolute basis using a rate coefficient of k(HO + 1,3-butadiene) = 1.48×10^{-11} exp(448/T) cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(e) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *o*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios k(HO + *o*-cresol)/k(HO + 1,3,5-trimethylbenzene) = 0.75 ± 0.09 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

$k = 1.6 \times 10^{-12} \exp(970/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 290-350 K.
$k = 4.1 \times 10^{-11}$ 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 and toluene (IUPAC, 2008), the reaction of HO radicals with *o*-cresol can be considered as comprising three temperature regimes (Perry et al., 1977). 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, and in absolute rate studies non-exponential HO radical decays are observed (Perry et al., 1977).

At room temperature, the absolute and relative rate data of Perry et al. (1977), Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in agreement within the experimental uncertainties. The preferred values of k at ≤350 K are based on a least-squares analysis of the absolute rate coefficients of Perry et al. (1977) and the relative rate data 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). 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 fall-off effects and/or thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K.

The rate coefficients of Perry et al. (1977) at 400-423 K suggest that H-atom abstraction, attributed to ($k_1 + k_2$), is minor at room temperature and below, accounting for ~6% of the overall reaction at 298 K to within a factor of ~2 using the Perry et al. (1977) fit to their 400-423 K data. The values of ($k_1 + k_2$) of Perry et al. (1977) at ~400 K are factors of ~200 and ~10 higher than the rate coefficients for H-atom abstraction from the ring C-H bonds in benzene and from the C-H bonds in the CH_3 substituent group in toluene, respectively (Knispel et al., 1990; IUPAC, 2008), indicating that for HO + *o*-cresol channel (1) dominates over channel (2) (i.e., $k_1 > k_2$). Moreover, the values of ($k_1 + k_2$) of Perry et al. (1977) for HO + *o*-cresol at ~400 K are similar to those of Knispel et al. (1990) for HO + phenol at 354

K and 374 K, again consistent with H-atom abstraction from the OH group dominating over H-atom abstraction from the ring C-H bonds or the C-H bonds of the CH_3 group.

At atmospherically-relevant temperatures, the reaction therefore proceeds almost entirely by channels (1) and (3), with channel (1) accounting for ~(6 $^{+6}_{-3}$)% 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 6-methyl-2-nitrophenol formation yields from the OH radical-initiated reaction of *o*-cresol to be 5.1 ± 1.5% at 296 ± 2 K, 6.8 ± 1.5% at 298 ± 2 K, and 4.7 ± 0.8% at 294 ± 2 K, respectively. Since 6-methyl-2-nitrophenol formation is attributed to the reaction of 2-methylphenoxy radicals with NO_2, these observations indicate that at room temperature channel (1) accounts for least 5% of the overall reaction, consistent with the kinetic data.

References

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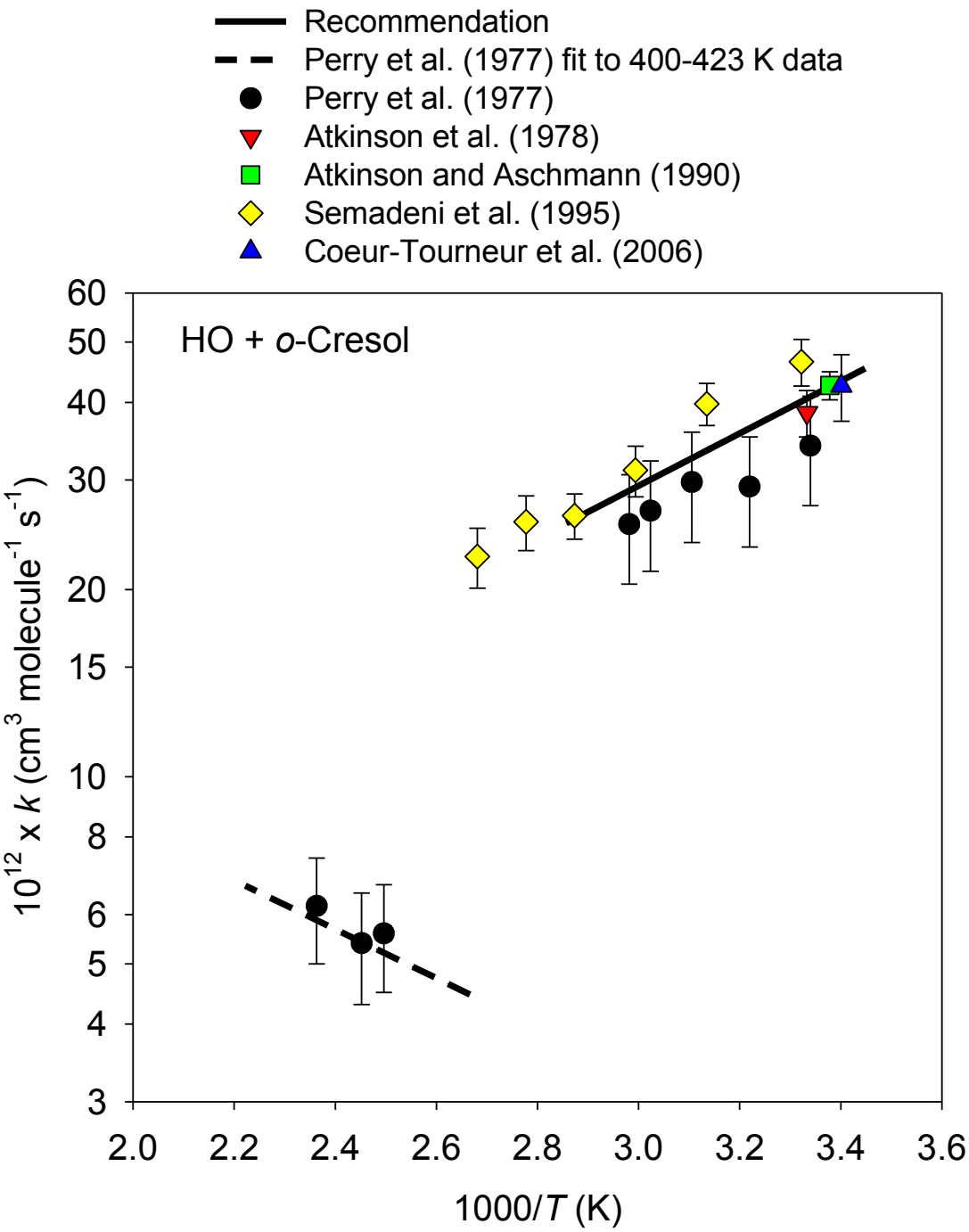
Recommendation
Perry et al. (1977) fit to 400-423 K data
Perry et al. (1977)
Atkinson et al. (1978)
Atkinson and Aschmann (1990)
Semadeni et al. (1995)
Coeur-Tourneur et al. (2006)
HO + o-Cresol
60
50
40
30
20
15
10
8
6
5
4
3
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
10^12 x k (cm^3 molecule^-1 s^-1)
1000/T (K)