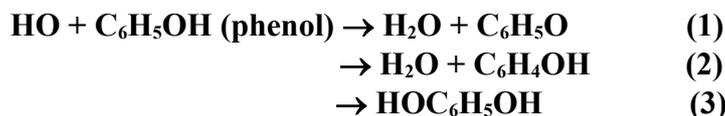


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_AROM6

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.

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



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.83 \pm 0.57) \times 10^{-11}$	296	Rinke and Zetzsch, 1984	FP-RF (a)
$k_1 + k_2 = (0 \pm 0.5) \times 10^{-12}$	300	Knispel et al., 1990	FP-RF (b)
$k_3 = (2.9 \pm 0.3) \times 10^{-11}$	300		
$k_1 + k_2 = (0 \pm 0.5) \times 10^{-12}$	308		
$k_3 = (2.6 \pm 0.3) \times 10^{-11}$	308		
$k_1 + k_2 = (3.4 \pm 0.5) \times 10^{-12}$	323		
$k_3 = (1.9 \pm 0.2) \times 10^{-11}$	323		
$k_1 + k_2 = (4.6 \pm 0.5) \times 10^{-12}$	339		
$k_3 = (1.4 \pm 0.2) \times 10^{-11}$	339		
$k_1 + k_2 = (4.6 \pm 0.4) \times 10^{-12}$	354		
$k_3 = (1.3 \pm 0.2) \times 10^{-11}$	354		
$k_1 + k_2 = (5.1 \pm 0.4) \times 10^{-12}$	374		
$k_3 = (1.2 \pm 0.2) \times 10^{-11}$	374		
<i>Relative Rate Coefficients</i>			
$1.35 \times 10^{-11}$	1032	He et al., 1988	RR (c)
$2.66 \times 10^{-13} \exp[(1376.5 \pm 282.5)/T]$	301-373	Semadeni et al., 1995	RR (d)
$(2.56 \pm 0.27) \times 10^{-11}$	301		
$(2.41 \pm 0.21) \times 10^{-11}$	301	Semadeni et al., 1995	RR (e)
$(2.07 \pm 0.18) \times 10^{-11}$	314		

## Comments

- (a) Rate coefficients were measured over the pressure range 5-733 mbar (3.75-550 Torr) of He diluent, with no effect of pressure on the rate coefficient being observed at pressures  $\geq 43$  mbar (32 Torr). The cited rate coefficient is at 133 mbar pressure.
- (b) Rate coefficients  $k_1$  and  $k_2$  were derived from fitting the observed non-exponential HO radical decays, measured at a total pressure of 133 mbar of Ar, to reactions (1) plus (2), (3), the back-decomposition of the HO-phenol adducts and accounting for diffusive and background losses of HO radicals and the HO-phenol adducts. Using the rate coefficient of He et al. (1988) at 1032 K and the expression  $(k_1 + k_2) = C T^2 \exp(-D/T)$ , a global fit to the experimental data resulted in rate coefficients  $(k_1 + k_2)$  of  $(3.97 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , essentially independent of temperature, over the range 300-374 K.
- (c) Based on the effect of added CO on shocked 2,2,3,3-tetramethylbutane-phenol-Ar mixtures. The derived rate coefficient ratio  $k(\text{HO} + \text{phenol})/k(\text{HO} + \text{CO}) = 33.2$  (from the listed rate expressions)

is placed on an absolute basis by use of  $k(\text{HO} + \text{CO}) = 4.08 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 1032 K and  $3.75 \pm 1.25$  bar pressure (Atkinson, 2003). From comparison of their rate coefficient at 1032 K with those of Tully et al. (1981) for HO + benzene at ~1000 K, He et al. (1988) concluded that channel (1) was the dominant reaction pathway.

- (d) HO radicals generated by the photolysis of  $\text{CH}_3\text{ONO}$  in air at atmospheric pressure in a ~200 L Teflon chamber. Phenol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + \text{phenol})/k(\text{HO} + 1,3\text{-butadiene}) = 0.018 \exp[(925.5 \pm 282.5)/T]$  over the temperature range 301-373 K is placed on an absolute basis using a rate coefficient of  $k(\text{HO} + 1,3\text{-butadiene}) = 1.48 \times 10^{-11} \exp(448/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003).
- (e) HO radicals generated by the photolysis of  $\text{CH}_3\text{ONO}$  in air at atmospheric pressure in a ~200 L Teflon chamber. Phenol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratios  $k(\text{HO} + \text{phenol})/k(\text{HO} + \textit{o}\text{-cresol}) = 0.60 \pm 0.05$  at 301 K and  $0.59 \pm 0.05$  at 314 K are placed on an absolute basis using a rate coefficient of  $k(\text{HO} + \textit{o}\text{-cresol}) = 1.6 \times 10^{-12} \exp(970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k = 4.7 \times 10^{-13} \exp(1220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 290-350 K.

$k = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  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 phenol 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-phenol adduct,  $\text{HOC}_6\text{H}_5\text{OH}$ , being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (Rinke and Zetzsch, 1984). At temperatures >400-450 K, decomposition of the HO-phenol adduct back to reactants is sufficiently rapid that measured rate coefficients are then those for pathways (1) and/or (2). At temperatures in the range ~325-450 K, decomposition of the HO-phenol adduct is significant and the measured rate coefficients depend on the experimental conditions.

The preferred values of  $k$  at  $\leq 350$  K are based on the absolute rate coefficients of Rinke and Zetzsch (1984) and Knispel et al. (1990) and the rate coefficients measured by Semadeni et al. (1995) relative to 1,3-butadiene. The rate coefficients measured by Semadeni et al. (1995) relative to *o*-cresol at 301 K and 314 K are in good agreement with the preferred values, indicating that the preferred values for HO + phenol and HO + *o*-cresol (IUPAC, current recommendation) are internally self-consistent. Note that no rate coefficients have been measured below 296 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-phenol adducts, and hence the preferred rate expression should not be used below ~290 K.

An Arrhenius fit to the relative rate coefficient of He et al. (1988) at 1032 K (which is subject to significant uncertainty, in part due to uncertainties in the rate coefficient for the reaction of HO radicals with CO, the reference compound used) and the values of  $(k_1 + k_2)$  derived by Knispel et al. (1990) from HO radical decay curves at 323 K, 339 K, 354 K and 374 K results in  $(k_1 + k_2) \sim 2.4 \times 10^{-11} \exp(-590/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The values of  $(k_1 + k_2)$  obtained by Knispel et al. (1990) at ~350 K are a factor of ~200 higher than the rate coefficient for H-atom abstraction from the ring C-H bonds in

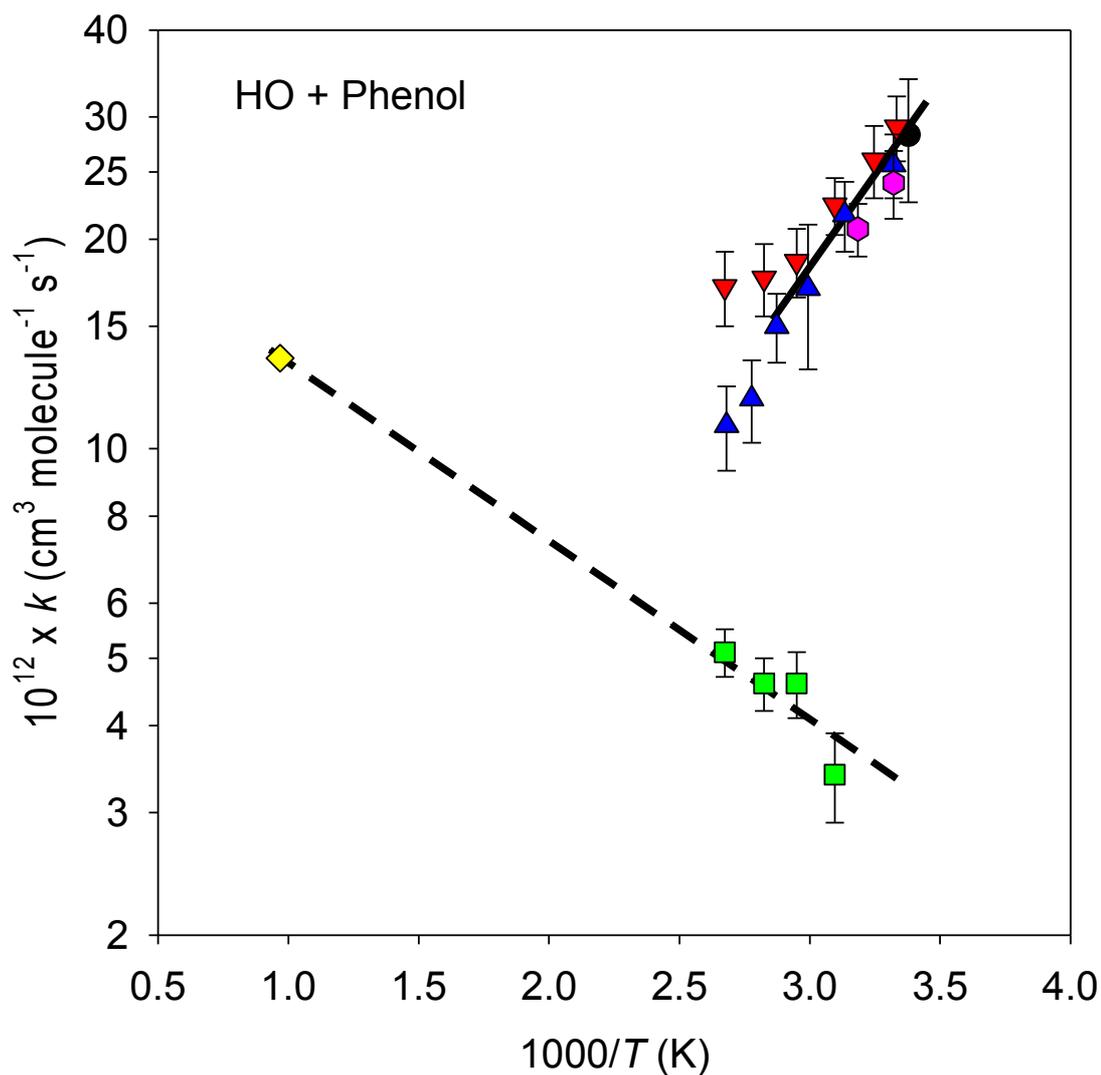
benzene (Knispel et al., 1990; IUPAC, 2008), indicating that for HO + phenol channel (1) dominates over channel (2) (i.e.,  $k_1 \gg k_2$ ). Hence, as also concluded by He et al. (1988), channel (2) is of no importance and can be neglected at temperatures  $< 1100$  K.

At atmospherically-relevant temperatures, the reaction proceeds almost entirely by channels (1) and (3), with channel (1) being estimated to account for  $\sim 12\%$  of the overall reaction of HO radicals with phenol at 298 K, and for less at lower temperatures. In the presence of  $\text{NO}_x$ , Atkinson et al. (1992) and Olariu et al. (2002) measured 2-nitrophenol formation yields from the OH radical-initiated reaction of phenol to be  $6.7 \pm 1.5\%$  at  $296 \pm 2$  K and  $5.8 \pm 1.0\%$  at  $298 \pm 2$  K, respectively. Since 2-nitrophenol formation is attributed to the reaction of phenoxy radicals with  $\text{NO}_2$ , these observations indicate that at room temperature channel (1) accounts for least 6% of the overall reaction, consistent with the kinetic data.

## References

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- Recommendation
- - - Arrhenius fit to values of  $k_1 + k_2$
- Rinke and Zetzsch (1984)
- ▼ Knispel et al. (1990)
- Knispel et al. (1990),  $k_1 + k_2$
- ◆ He et al. (1988)
- ▲ Semadeni et al. (1995), relative to 1,3-butadiene
- ◆ Semadeni et al. (1995), relative to *o*-cresol



- Recommendation
- Rinke and Zetzsch (1984)
- ▼ Knispel et al. (1990)
- Semadeni et al. (1995), relative to 1,3-butadiene
- ◆ Semadeni et al. (1995), relative to *o*-cresol

