# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AROM_RAD4

$$HOC_7H_8 + O_2 \rightarrow o\text{-}C_7H_7OH \ (o\text{-cresol}) + HO_2 \quad (1)$$
$$\rightarrow m\text{-}C_7H_7OH \ (m\text{-cresol}) + HO_2 \quad (2)$$
$$\rightarrow p\text{-}C_7H_7OH \ (p\text{-cresol}) + HO_2 \quad (3)$$
$$\rightarrow \text{other products} \quad (4)$$
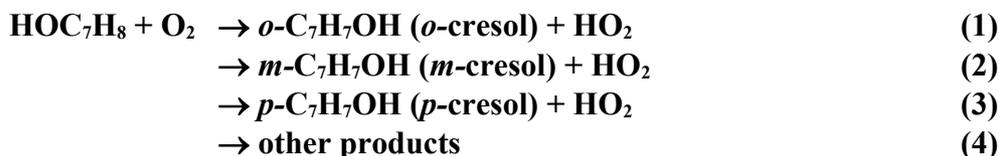
## Rate coefficient data

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(6.0 \pm 0.4) \times 10^{-16}$ | 299 | Bohn, 2001 | PLP-AS (a) |
| $(5.6 \pm 1.5) \times 10^{-16}$ | 299 | Koch et al., 2007 | FP-RF (b) |
| $(5.6 \pm 0.6) \times 10^{-16}$ | 321 | | |
| $(5.6 \pm 0.6) \times 10^{-16}$ | 339 | | |
| $(5.3 \pm 0.7) \times 10^{-16}$ | 347 | | |
| $(5.9 \pm 0.8) \times 10^{-16}$ | 354 | | |
| *Branching ratios* | | | |
| $k_1/k = (0.130 \pm 0.023)$ | 296 | Atkinson and Aschmann, 1994 | (c,d) |
| $k_1/k = (0.131 \pm 0.013)$ | 298 | Smith et al., 1998 | (c,e) |
| $k_2/k = (0.028 \pm 0.003)$ | | | |
| $k_3/k = (0.032 \pm 0.003)$ | | | |
| $k_1/k = (0.128 \pm 0.015)$ | 298* | Klotz et al., 1998 | (c,f) |
| $k_2/k = (0.029 \pm 0.007)$ | | | |
| $k_3/k = (0.034 \pm 0.006)$ | | | |

## Comments

(a) Photolysis of $H_2O_2$-toluene-$O_2$-$N_2$ mixtures at 248 nm (1 bar total pressure). Time-resolved continuous-wave UV-laser long-path (100 m) absorption was used to monitor the concentration of the $HOC_7H_8$ adduct in the system (-0.0045 nm off the $Q_1(2)$ rotational line of $A^2\Sigma^+ \leftarrow X^2\Pi$ transition for HO at 307.995 nm), the initial concentrations of which were of the order of $10^{11}$ molecule cm$^{-3}$. A rapid equilibrium between $HOC_7H_8$ and $HOC_7H_8O_2$ was characterised from experiments in which $[O_2]$ was varied over the range 1.0 x $10^{17}$ molecule cm$^{-3}$ to 2.4 x $10^{19}$ molecule cm$^{-3}$. A value of the equilibrium constant, $K = (3.25 \pm 0.33) \times 10^{-19}$ cm$^3$ molecule$^{-1}$, and an estimate of the rate coefficient of the forward reaction, $k_f = (3 \pm 2) \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, were reported. The listed value of $k$ represents the total measured loss from the $HOC_7H_8/O_2/HOC_7H_8O_2$ equilibrium system, either via an additional irreversible reaction of $HOC_7H_8$ with $O_2$, or via unimolecular loss of $HOC_7H_8O_2$.

(b) Re-analysis of the earlier results of Knispel et al. (1990), using improved software tools developed by Koch (1992). Vacuum-UV photolysis of $H_2O$-toluene-$O_2$-Ar mixtures (at 133 mbar total pressure) to produce low concentrations of HO ($<10^{10}$ molecule cm$^{-3}$), the decay of which was monitored by resonance-fluorescence. Kinetics determined from perturbation of the equilibrium between HO and $HOC_7H_8$ when systematically-varied low concentrations of $O_2$

were added. $k$ was determined from analytical solution of a six reaction mechanism in which potentially competing losses for HO and $HOC_7H_8$ were represented, as characterised from experiments in the absence of $O_2$.

(c) Branching ratios are based on yields of the cresol isomers from the HO-initiated oxidation of toluene in studies performed with zero or low concentrations of NOx and at close to atmospheric pressure. The reported yields have been adjusted here by a factor of 1/0.937, where 0.937 is the recommended yield of $HOC_7H_8$ from the HO + toluene reaction (see datasheet HOx_AROM2).

(d) HO-initiated oxidation of toluene in air in 7900 L Teflon chamber at 296 K and 980 mbar total pressure. HO radicals generated in the absence of NOx from the reaction of propene or $\alpha$–pinene with $O_3$; and in the presence of NOx by UV irradiation of $CH_3ONO/NO/NO_2$/toluene/air mixtures. Yield of $o$-cresol, measured by GC-FID, was found to increase from $0.123 \pm 0.022$ in the absence of NOx to $0.160 \pm 0.008$ in the presence of 1.7 x $10^{14}$ molecule $cm^{-3}$ $NO_2$.

(e) UV irradiation of $CH_3ONO/NO$/toluene/air mixtures in a 1L bulbous flow reactor with sub ppm levels of NOx (typically 200 – 800 ppb). Reactants pumped from a darkened Teflon bag at atmospheric pressure. Residence times set such that 4-10% conversion of toluene occurred. The following species were detected and quantified, and reported as primary products, using GC, GC-MS, HPLC and IC: benzaldehyde, $o$-cresol, $m$-cresol, $p$-cresol, 4-oxo-2-pentenal, 5-methyl-3H-furan-2-one, glyoxal and methylglyoxal.

(f) Based on the results of chamber photo-oxidation studies of toluene-NOx-air mixtures at atmospheric pressure in the 187 $m^3$ EUPHORE chamber at CEAM, Valencia, Spain. Chemistry initiated with natural sunlight, with species detection and quantification using DOAS. Yields reported for benzaldehyde, $o$-cresol, $m$-cresol and $p$-cresol, which were independent of NOx mixing ratio over the range 3 – 300 ppb. The yields were based on product formation during the early stages of the irradiation, and were optimised through numerical simulation of the system using a chemical mechanism for the HO + toluene system in which product removal through reaction with OH was represented. Evidence for additional, unrepresented loss of the cresol isomers was apparent at longer irradiations, which was interpreted in terms of $NO_3$-initiated chemistry.

**Preferred Values**

| Parameter | Value | T/K |
|---|---|---|
| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | 5.8 x 10$^{-16}$ | 298 |
| $k_1/k$ | 0.13 | 298 |
| $k_2/k$ | 0.028 | 298 |
| $k_3/k$ | 0.033 | 298 |
| *Reliability* | | |
| $\Delta \log k$ | $\pm 0.2$ | 298 |
| $\Delta k_1/k$ | $\pm 0.03$ | 298 |
| $\Delta k_2/k$ | $\pm 0.01$ | 298 |
| $\Delta k_3/k$ | $\pm 0.01$ | 298 |

*Comments on Preferred Values*

The values of $k$, which are appropriate for describing toluene oxidation under lower tropospheric conditions, represent loss from the $HOC_7H_8/O_2/HOC_7H_8O_2$ equilibrium system,

either via an additional irreversible reaction of $HOC_7H_8$ with $O_2$, or via unimolecular loss of $HOC_7H_8O_2$. The values reported by Bohn (2001) and Koch et al. (2007) are in good agreement, and the preferred value at 298 K is based on their average (it is also noted that Johnson et al. (2005) cite a consistent unpublished value of $k = 6 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, determined using PLP-AS). The results of Koch et al. (2007) suggest that $k$ is independent of temperature up to about 350 K, but confirmatory studies are required before a recommendation for the temperature dependence can be made.

The values of $k_1/k$, $k_2/k$ and $k_3/k$ are based on the reported yields of the respective cresol isomers from the HO-initiated oxidation of toluene, corrected to account for the yield of $HOC_7H_8$ formed from the reaction of HO with toluene (see comment (c)). The preferred 298 K value of $k_1/k$ is based on the mean of the values reported by Atkinson and Aschmann (1994), Smith et al. (1998) and Klotz et al. (1998), with $k_2/k$ and $k_3/k$ based on the mean of the values reported by Smith et al. (1998) and Klotz et al. (1998). The cresol yields in these studies were derived from experiments with low or zero levels of NOx, performed at close to atmospheric pressure, and are in excellent agreement. It is noted that, in contrast to phenol formation in the benzene system, the presence of ppm levels of $NO_2$ tends to lead to an increase in the cresol yields, e.g., as demonstrated systematically for $o$-cresol in the study of Atkinson and Aschmann (1994). This suggests that the reactions of the $HOC_7H_8$ isomers with $NO_2$ have channels forming the corresponding cresol and HONO, and that the cresol yields are greater than those from the $HOC_7H_8 + O_2$ reactions.

As discussed in numerous studies, formation of the cresol isomers and $HO_2$ via channels (1)-(3) may proceed via either a direct abstraction of hydrogen from the appropriate isomers of $HOC_7H_8$, or from isomerisation and decomposition of the appropriate isomers of $HOC_7H_8O_2$ (e.g., Calvert et al. (2002), and references therein). Under atmospheric conditions, the remainder of the reaction (represented by channel (4) above) is generally believed to be dominated by ring-closure of $HOC_7H_8O_2$ to form a set of isomeric peroxide-bridged bicyclic radicals, for example:
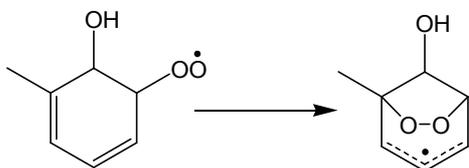


Under atmospheric conditions, the major fate of the peroxide-bridged radicals has been calculated to be reaction with $O_2$ to form stabilised peroxy radicals (Suh et al., 2003). The subsequent reactions of the peroxy radicals (e.g., as described on page 103 of Calvert et al., 2002) can rationalise the formation of the $\alpha$–dicarbonyl products, glyoxal and methyl glyoxal, which have been observed as major primary products in a number of studies, and co-products such as 1,3-butendial and 4-oxo-2-pentenal (e.g., Smith et al., 1998; Gómez Alvarez et al., 2007; Arey et al., 2009). However, it is recognised that other channels also potentially contribute, and further studies are required to elucidate the full details of the oxidation mechanism.

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