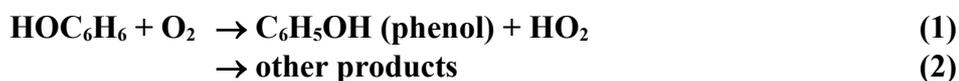


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet AROM_RAD_1

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. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>. This data sheet last evaluated: September 2009; last change in preferred values: September 2009.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.2) \times 10^{-16}$	297	Bohn and Zetzsch, 1999	PLP-AS (a,b)
$(5.5 \pm 3.0) \times 10^{-16}$	265-320	Johnson et al., 2002	PLP-AS (a,c)
$(2.52 \pm 0.39) \times 10^{-16}$	295	Raoult et al., 2004	PLP-AS (a,d)
$(1.6 \pm 0.6) \times 10^{-16}$	299	Koch et al., 2007	FP-RF (e)
$(2.1 \pm 0.4) \times 10^{-16}$	313		
$(3.0 \pm 0.3) \times 10^{-16}$	333		
$(3.7 \pm 0.4) \times 10^{-16}$	354		
<i>Branching ratios</i>			
$k_1/k = (0.531 \pm 0.066)$	287-307	Volkamer et al., 2002	P-AS/FTIR (f,g)
$k_1/k = (0.61 \pm 0.07)$	295	Berndt and Böge, 2006	F-AS/FTIR (f,h)

Comments

- The listed value of k represents the total measured loss from the $\text{HOC}_6\text{H}_6/\text{O}_2/\text{HOC}_6\text{H}_6\text{O}_2$ equilibrium system, either via an additional irreversible reaction of HOC_6H_6 with O_2 , or via unimolecular loss of $\text{HOC}_6\text{H}_6\text{O}_2$.
- Photolysis of H_2O_2 -benzene- 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_6H_6 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 $10^{11} \text{ molecule cm}^{-3}$. A rapid equilibrium between HOC_6H_6 and $\text{HOC}_6\text{H}_6\text{O}_2$ was characterised from experiments in which $[\text{O}_2]$ was varied over the range $7 \times 10^{16} \text{ molecule cm}^{-3}$ to $2.5 \times 10^{19} \text{ molecule cm}^{-3}$. A value of the equilibrium constant, $K = (2.7 \pm 0.4) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$, and an estimate of the rate coefficient of the forward reaction, $k_f = (2 \pm 1) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, were reported.
- Photolysis of H_2O_2 -benzene- O_2 - N_2 mixtures at 248 nm (1 bar total pressure). Time-resolved absorption spectroscopy (deuterium lamp source) in the range 300-320 nm was used to monitor the concentration of the HOC_6H_6 adduct in the system, the initial concentrations of which were typically in the range $(1-4) \times 10^{13} \text{ molecule cm}^{-3}$. A rapid equilibrium between HOC_6H_6 and $\text{HOC}_6\text{H}_6\text{O}_2$ was characterised over the temperature range 265-345 K, from experiments in which $[\text{O}_2]$ was present at pressures up to about 0.8 bar. Equilibrium and rate coefficients were determined from simulation of the system, using a 13 reaction mechanism which also considered interferences from radical-radical reactions involving HOC_6H_6 , $\text{HOC}_6\text{H}_6\text{O}_2$ and HO_2 . The equilibrium constant K was reported to vary from $7 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ at 265 K to $9 \times 10^{-21} \text{ cm}^3 \text{ molecule}^{-1}$ at 345 K, with a value of $(1.15 \pm 0.6) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ at 295 K.

- (d) As in comment (c), but with improved detection of HOC_6H_6 achieved through use of a dual-pass beam from a high pressure xenon lamp as the monitoring light source. This allowed initial concentrations of HOC_6H_6 a factor of five lower to be employed, decreasing interference from radical-radical reactions. The equilibrium between HOC_6H_6 and $\text{HOC}_6\text{H}_6\text{O}_2$ was characterised, leading to reported values of the equilibrium constant, $K = (2.62 \pm 0.24) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$, and of the rate coefficient for the forward reaction, $k_f = (1.31 \pm 0.12) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K.
- (e) 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 -benzene- O_2 -Ar mixtures (at 133 mbar total pressure) to produce low concentrations of HO ($<10^{10} \text{ molecule cm}^{-3}$), the decay of which was monitored by resonance-fluorescence. Kinetics determined from perturbation of the equilibrium between HO and HOC_6H_6 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_6H_6 were represented, as characterised from experiments in the absence of O_2 .
- (f) Reported as a yield of phenol from the HO-initiated oxidation of benzene.
- (g) Based on the results of chamber photo-oxidation studies of benzene- NO_x -air mixtures at atmospheric pressure in two facilities: the 187 m^3 EUPHORE chamber at CEAM, Valencia, Spain; and a 6 m^3 indoor chamber at NIES, Tsukuba, Japan. The EUPHORE experiments used natural sunlight to initiate the chemistry, with phenol and benzene quantified using both DOAS and FTIR spectroscopy. The light source in the NIES experiments was a series of xenon arc lamps with pyrex filters to remove wavelengths $< 290 \text{ nm}$. Phenol and benzene were quantified using FTIR spectroscopy. Six different types of HO-radical sources were employed, and initial concentrations for benzene and NO_x were varied by about a factor of 400 and four orders of magnitude, respectively. The quoted phenol yield was based on the results of experiments low NO_x mixing ratios typical of tropospheric conditions, and was found to remain essentially constant for NO_x levels of up to several tens of ppb. A progressive reduction in the phenol yield was observed at levels greater than 100 ppb (about $2.5 \times 10^{12} \text{ molecule cm}^{-3}$). Variation of the prevailing temperature over the given range had no significant effect on the yield.
- (h) HO-initiated oxidation of benzene in air in a flow tube at 950 mbar and $295 \pm 2 \text{ K}$. HO radicals generated in the absence of NO from the reaction of O_3 with 2,3-dimethyl-but-2-ene, and in the presence of NO from the photolysis of CH_3ONO . Phenol formation measured using FTIR and UV-AS. The quoted phenol yield was found to be independent of initial NO concentration over the range from zero to $1.3 \times 10^{12} \text{ molecule cm}^{-3}$.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.1×10^{-16}	298
k_1/k	0.57	298
$\Delta \log k$	± 0.2	298
$\Delta k_1/k$	± 0.1	298

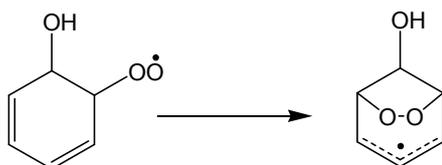
Comments on Preferred Values

The values of k , which are appropriate for describing benzene oxidation under lower tropospheric conditions, represent loss from the $\text{HOC}_6\text{H}_6/\text{O}_2/\text{HOC}_6\text{H}_6\text{O}_2$ equilibrium system, either via an additional irreversible reaction of HOC_6H_6 with O_2 , or via unimolecular loss of

$\text{HOC}_6\text{H}_6\text{O}_2$. There is reasonable agreement in the reported values of k , and the preferred value at 298 K is based on the average of the values from the studies of Bohn and Zetzsch (1999), Raoult et al. (2004) and Koch et al. (2007). The value of k of Johnson et al. (2002) is about a factor of two higher than the consensus, and is taken to be superseded by that of Raoult et al. (2004) from the same laboratory (see comment (d)). The results of Koch et al. (2007) suggest that k increases notably with temperature, whereas Johnson et al. (2002) found no evidence for a significant temperature dependence. Additional studies are required before a recommendation for the temperature dependence can be made.

The values of k_1/k are based on reported yields of phenol from the HO-initiated oxidation of benzene, and the assumption is made here that the reaction of HO with benzene proceeds exclusively to form the HOC_6H_6 adduct. As discussed in the datasheet for the reaction of HO with benzene (HOx_ AROM1), this is a reasonable assumption for temperatures near 298 K, where H atom abstraction is believed to account for < 1% of the reaction. The preferred 298 K value of k_1/k is based on the mean of the values reported by Volkamer et al. (2002) and Berndt and Böge (2006), with these values being derived from experiments at low or zero levels of NOx, performed at close to atmospheric pressure. It is noted that substantially lower phenol yields from benzene oxidation have previously been reported at temperatures near 298 K by Atkinson et al. (1989), 0.236 ± 0.044 , and Berndt et al. (1999), 0.23 ± 0.07 . As discussed by Volkamer et al. (2002), these can be rationalised by the operation of competing loss processes from the $\text{HOC}_6\text{H}_6/\text{O}_2/\text{HOC}_6\text{H}_6\text{O}_2$ equilibrium system under the experimental conditions employed, such that the reported yield cannot be used here as a direct measure of k_1/k . The competing loss likely results from the presence of ppm levels of NOx (Atkinson et al., 1989) or the use very high radical concentrations (Berndt et al., 1999), leading to additional reactions for HOC_6H_6 and/or $\text{HOC}_6\text{H}_6\text{O}_2$. The role of NOx in reducing phenol yields has subsequently been characterised systematically and in some detail by Klotz et al. (2002).

As discussed in numerous studies, formation of phenol and HO_2 via channel (1) may proceed via either a direct abstraction of hydrogen from HOC_6H_6 , or from isomerisation and decomposition of $\text{HOC}_6\text{H}_6\text{O}_2$ (e.g., Glowacki et al., 2009 and references therein). Under atmospheric conditions, the remainder of the reaction (represented by channel (2) above) is generally believed to be dominated by ring-closure of $\text{HOC}_6\text{H}_6\text{O}_2$ to form a peroxide-bridged bicyclic radical:



At atmospheric pressure, the major fate of the peroxide-bridged radical has been calculated to be reaction with O_2 to form a stabilised peroxy radical (Glowacki et al., 2009). The subsequent reactions of the peroxy radical (e.g., as described generically for aromatics on page 103 of Calvert et al., 2002) can rationalise the formation of the ring-opened products, glyoxal and butenedial, which have been observed as major primary products in a number of studies (e.g., Volkamer et al., 2001; 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.

References

- Arey, J., Obermeyer, G., Aschmann, S. M., Chattopadhyay, S., Cusick, R. D. and Atkinson R.: Environ. Sci. Technol., 43 (3), 683, 2009.
- Atkinson, R., Aschmann, S. M., Arey, J. and Carter, W. P. L.: Int. J. Chem. Kinet., 21, 801, 1989.
- Berndt, T. and Böge, O.: Phys. Chem. Chem. Phys., 8, 1205, 2006.

Berndt, T., Böge, O. and Herrmann, H.: Chem. Phys. Lett., 314, 435, 1999.

Bohn, B. and Zetzsch, C.: Phys. Chem. Chem. Phys., 1, 5097, 1999.

Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G. (2002). The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press.

Glowacki, D. R., Wang, L. and Pilling, M. J.: J. Phys. Chem. A., 113, 5385, 2009.

Gómez Alvarez, E.; Viidanoja, J.; Munõz, A.; Wirtz, K.; Hjorth, J.: Environ. Sci. Technol., 41, 8362, 2007.

Johnson, D., Raoult, S., Rayez, M.-T., Rayez, J.-C. and Lesclaux, R.: Phys. Chem. Chem. Phys., 4, 4678, 2002.

Klotz, B., Volkamer, R., Hurley, M. D., Andersen, M. P. S., Nielsen, O. J., Barnes, I., Imamura, T., Wirtz, K., Becker, K.H., Platt, U., Wallington, T. J. and Washida, N.: Phys. Chem. Chem. Phys., 4, 4399, 2002.

Knispel, R., Koch, R., Siese, M., and Zetzsch, C.: Adduct formation of OH radicals with benzene, toluene, and phenol and consecutive reactions of the adducts with NO_x and O₂, Ber. Bunsenges. Phys. Chem., 94, 1375, 1990.

Koch, R.: PhD thesis, University of Hannover, 1992.

Koch, R., Knispel, R., Elend, M., Siese, M. and Zetzsch, C.: Atmos. Chem. Phys., 7, 2057, 2007.

Raoult, S., Rayez, M.-T., Rayez, J.-C. and Lesclaux, R. : Phys. Chem. Chem. Phys., 6, 2245, 2004.

Volkamer, R., Platt, U. and Wirtz, K.: J. Phys. Chem. A, 105, 7865, 2001.

Volkamer, R., Klotz, B., Barnes, I., Imamura, T., Wirtz, K., Washida, N., Becker, K. H. and Platt, U.: Phys. Chem. Chem. Phys., 4, 1598, 2002.