



PRODUCT AND KINETIC INVESTIGATIONS ON THE GAS PHASE CHEMISTRY OF DIMETHYLATED-1,4-BENZOQUINONES

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INTRODUCTION

- Aromatic hydrocarbons are significant constituents of lead-free gasoline.
- The oxidation of alkylated-hydroxylated aromatic compounds is now known to lead to the formation of alkylated benzenediols and benzoquinones (Olariu et al., 2002; Berndt and Boege, 2002).
- 1,4-Benzoquinones are present in the vehicle gas and particle exhaust emissions (Jakober et al., 2007).
- 1,4-Benzoquinones were found to be significant products in the phenol oxidation mechanism (Olariu et al., 2002; Berndt and Boege, 2002).
- The latest version of the Master Chemical Mechanism (MCMv3.1) indicates that the formation of benzoquinone type compounds in the gas phase degradation of aromatic hydrocarbons is likely to be quite significant (Bloss et al., 2005). Investigation of the chemistry of these compounds is required, so their photooxidation can be correctly represented in mechanisms such as the MCM.
- The available information on the atmospheric chemistry of benzoquinones, and in particular, alkylated benzoquinones, is very limited (Olariu et al., 2000).
- As part of a systematic study of the gas-phase atmospheric chemistry of aromatic hydrocarbons, we have investigated the reactions of the dimethyl-1,4-benzoquinones (DMBQ) isomers with OH radicals.

RESULTS

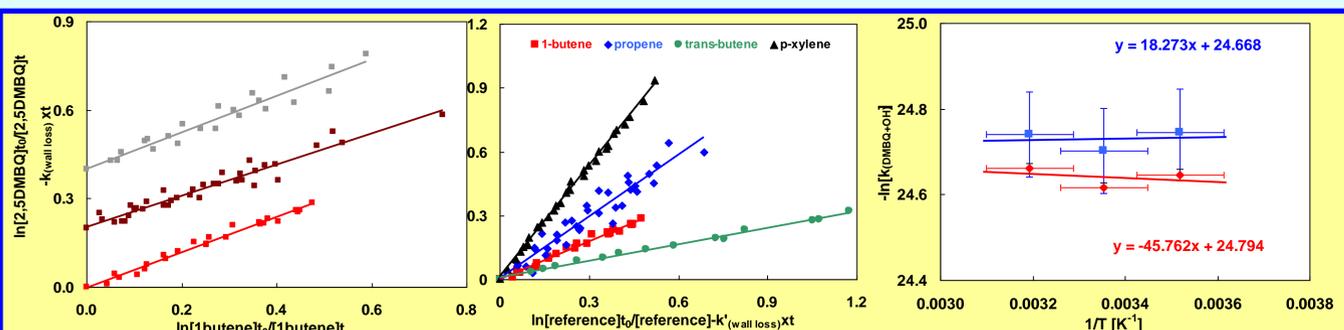


Fig. 1: Plot of the kinetic data for the reaction of 2,5DMBQ with OH radicals at three different temperature (11°C, 25°C, 40°C).
Fig. 2: Plot of the kinetic data for the reaction of 2,5DMBQ with OH radicals using 4 different reference hydrocarbons.
Fig. 3: Arrhenius plots of the rate coefficients determined for 2,5DMBQ+OH and 2,6DMBQ+OH in the temperature range 284 – 313K.

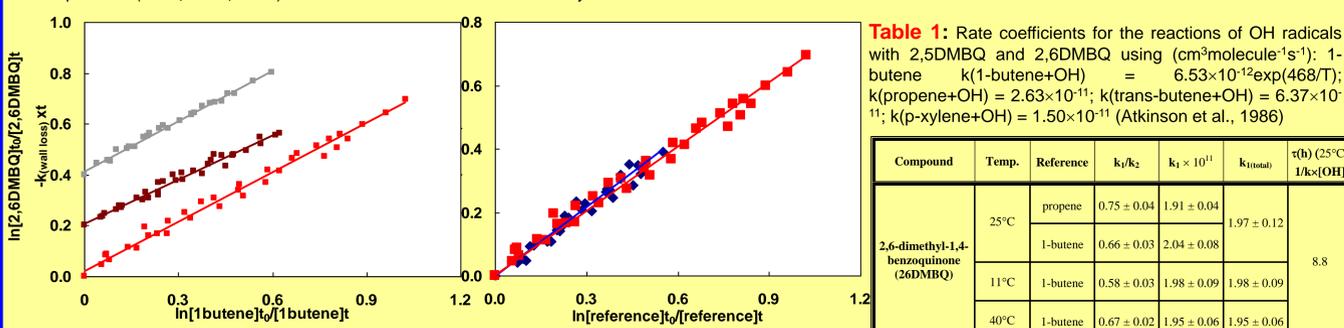


Fig. 4: Plot of the kinetic data for the reaction of 2,6DMBQ with OH radicals at three different temperature (11°C, 25°C, 40°C).
Fig. 5: Plot of the kinetic data for the reaction of 2,5DMBQ with OH radicals using (■) 1-butene and (♦) propene as reference hydrocarbons.

- All the plots show good linearity considering the difficulties which arise in using solid compounds;
- Using the kinetic data obtained in the present study in combination with a daytime average tropospheric OH radicals concentration of $1.6 \times 10^6 \text{ cm}^{-3}$, residence times have been calculated (Table 1.);
- The quoted errors are the 2σ statistical errors from the linear regression analyses.
- A very small temperature dependence was found for the rate constants

Table 1: Rate coefficients for the reactions of OH radicals with 2,5DMBQ and 2,6DMBQ using ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): 1-butene $k(1\text{-butene}+\text{OH}) = 6.53 \times 10^{-12} \exp(468/T)$; $k(\text{propene}+\text{OH}) = 2.63 \times 10^{-11}$; $k(\text{trans-butene}+\text{OH}) = 6.37 \times 10^{-11}$; $k(\text{p-xylene}+\text{OH}) = 1.50 \times 10^{-11}$ (Atkinson et al., 1986)

Compound	Temp.	Reference	k_1/k_2	$k_1 \times 10^{11}$	$k_{1(\text{wall})}$	$\tau(\text{h}) (25^\circ\text{C})$ $1/k_1[\text{OH}]$
2,6-dimethyl-1,4-benzoquinone (2,6DMBQ)	25°C	propene	0.75 ± 0.04	1.91 ± 0.04		8.8
		1-butene	0.66 ± 0.03	2.04 ± 0.08	1.97 ± 0.12	
	11°C	1-butene	0.58 ± 0.03	1.98 ± 0.09	1.98 ± 0.09	
	40°C	1-butene	0.67 ± 0.02	1.95 ± 0.06	1.95 ± 0.06	
2,5-dimethyl-1,4-benzoquinone (2,5DMBQ)	25°C	p-xylene	1.76 ± 0.03	2.62 ± 0.09		8.0
		trans-butene	0.26 ± 0.01	1.68 ± 0.07	2.18 ± 0.46	
		propene	0.97 ± 0.08	2.55 ± 0.22		
	11°C	1-butene	0.60 ± 0.03	1.87 ± 0.09		
		1-butene	0.53 ± 0.04	1.79 ± 0.13	1.79 ± 0.13	
		40°C	1-butene	0.62 ± 0.07	1.80 ± 0.19	
1,4-benzoquinone (Olariu et al., 2002)				0.46×10^{-11}	37	
methyl-1,4-benzoquinone (Olariu et al., 2002)				2.35×10^{-11}	7.4	

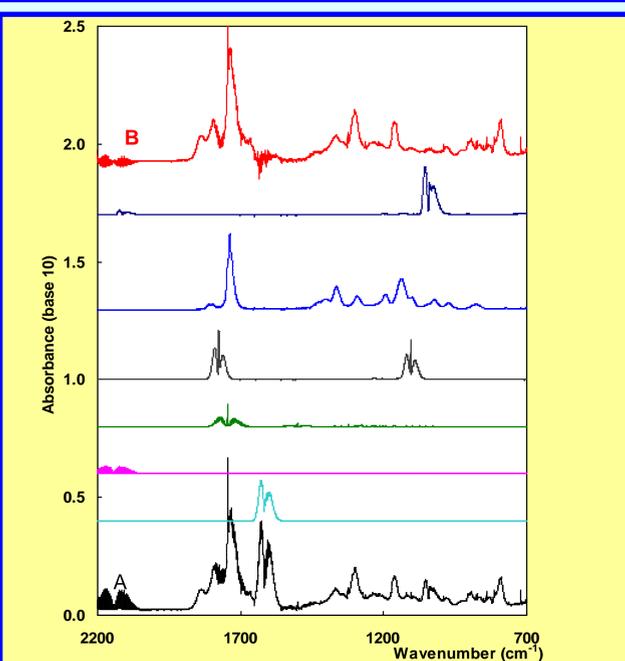


Fig. 6: Search for possible products in the reaction system 2,5DMBQ/air/NO/CH₃ONO. Spectrum (A) is a product spectrum. Comparison with reference spectra show that NO₂, CO, O₃, formaldehyde and formic acid are formed in the system. A possible triketobutan formation may be identified reported to the triketopentan reference spectrum. Spectrum (B) is the residual spectrum after the subtraction of known products.

- Gas phase products identified in the reaction of OH with 2,5-dimethyl-1,4-benzoquinone include: CO, formaldehyde, formic acid and O₃ (Figure 6).
- The most prominent absorption feature in the IR residual spectra (Figure 6 (B)) is a carbonyl band around 1700 cm⁻¹.
- In the residual spectrum (Figure 5 (B)) the product(s) giving rise to the absorption features at 794.4 cm⁻¹, 1163.4 cm⁻¹, 1304.2 cm⁻¹, 1368 cm⁻¹, 1735-1737 cm⁻¹, 1795.8 cm⁻¹ and 1839.6 cm⁻¹ still have to be identified.
- Based on the residual product spectrum we propose that the main reaction channel is an addition of OH followed by reaction with O₂ to produce 3-methyl-3-hepten-1,2,5,6 tetraketone. Further reaction of this compound could result in formation of butan-1,2,3 triketone.
- Absorption attributable to a -C(O)-C=C-C(O)- is present in the residual spectrum.
- Carboxylic acid anhydride may be responsible for the absorption at 1795.8 cm⁻¹ and 1839.6 cm⁻¹.

LITERATURE

- Atkinson, R., *Chem. Rev.*, **86**, 1986
- Berndt, T. and O. Böge, *Phys. Chem. Chem. Phys.*, **5**, 342, 2003
- Bierbach, A., I. Barnes, K.H. Becker; E. Wiesen, *Environ. Sci. Technol.*, **28**, 715, 1994
- Bloss, C., V. Wagner, M. E. Jenkin, R. Volkamer, W. J. Bloss, J. D. Lee, D. E. Heard, K. Wirtz, M. Martin-Reviejo, G. Rea, J. C. Wenger, and M. J. Pilling *Atmos. Chem. Phys.*, **5**, 641, 2005
- Jakober, C.A., S.G. Riddle, M.A. Robert, H. Destailats, M.J. Charles, P.G. Green, and M.J. Kleeman, *Environ. Sci. Technol.*, **41**, 4548, 2007
- Mihalopoulos, N., Barnes, I., Becker, K.H., *Atmos Environ.*, **26**, 807, 1992
- Olariu, R.I., Klotz, B., Barnes, I., Becker, K. H., Mocanu, R., *Atmos Environ.*, **36**, 3685, 2002
- Olariu, R.I., Barnes, I., Becker, K. H., Klotz, B., *Int. J. Chem. Kin.*, **32**, 696, 2000

EXPERIMENTAL SETUP

- All investigations were carried out in a 1080 L quartz-glass photoreactor in synthetic air (296 ± 3 K and 1013 mbar) (Mihalopoulos et al., 1992)
- A White type multiple reflection mirror system (484.7 ± 0.8) m coupled to an FTIR spectrometer was used for reactant and reference monitoring
- IR spectra were recorded at a spectral resolution of 1 cm⁻¹ using a Nicolet NEXUS FT-IR spectrometer

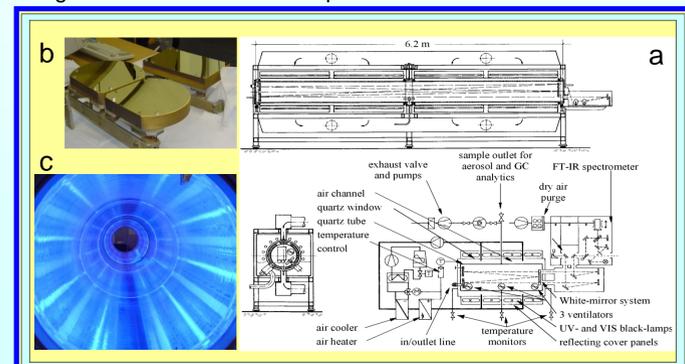
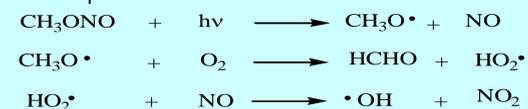


Figure 2: a) Experimental setup of the Wuppertal's reactor; b) White-type multiple reflection mirrors; c) Inner view of the tubular 1080L quartz glass reactor

- Gaseous compounds (CH₃ONO, 1-butene, trans-butene, propene) and liquid compound (p-xylene) were injected using calibrated syringes; the solid compounds (dimethyl-1,4-benzoquinone) were introduced into the chamber in air flow by using a special inlet system and the reactor under reduced pressure;
- The initial reactant concentrations were (in molecules cm⁻³ units): dimethyl-1,4-benzoquinones, < 4.8×10^{13} ; CH₃ONO, 5×10^{13} ; C₃H₆, trans-C₄H₈, 1-C₄H₈, $(4 - 6) \times 10^{13}$; p-xylene, 2×10^{14}
- The photolysis of CH₃ONO with 32 super-actinic fluorescent lamps in the presence of air was used as the OH radical source:



- The experimental data are plotted in Fig.1. according to an expression for the analysis of kinetic data by the relative technique:

$$\text{reactant} + \text{OH} \longrightarrow \text{products} \quad (k_1)$$

$$\text{reference} + \text{OH} \longrightarrow \text{products} \quad (k_2)$$

$$\text{reactant} (+\text{wall loss, hv}) \longrightarrow \text{products} \quad (k_3)$$

$$\ln \frac{[\text{reactant}]_0}{[\text{reactant}]_t} - k_3(t - t_0) = \frac{k_1}{k_2} \ln \frac{[\text{reference}]_0}{[\text{reference}]_t} \quad (1)$$

REMARKS

- This work represents the first reported experimental kinetic study of the reaction of OH radicals with dimethylated 1,4-benzoquinones at room temperature and first preliminary results on the temperature dependence investigation on the rate coefficients;
- Within the experimental error limits, the rate coefficients for 2,5-dimethyl-1,4-benzoquinone and 2,6-dimethyl-1,4-benzoquinone are almost the same. This is expected because the number of possible addition sites for the OH radical is the same for both compounds and in both compounds the number of additional methyl groups to the double bonds is the same.
- Considering their residence times presented into Table 1 it can be suggested that the dimethylated-1,4-benzoquinone have a lifetime of around 8 hours during daytime and probably this could have an influence on atmospheric chemistry processes on a regional scale.

- The dimethylated 1,4-benzoquinones are 4-5 times more reactive than 1,4-benzoquinone. This indicates that the electron-donating effect of the methyl groups counteract the strong deactivating effect of -C(O)- functional group.

- Dimethylated 1,4-benzoquinones have a rate coefficient 2-3 times smaller than other 1,4-dicarbonyls (3-hexene-2,5-dione; Z-butendial; Z and E-4-oxo-2-pentenal; 3H-furan-2-one) (Bierbach et al., 1994).

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