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 (Jakobet 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 (Bliss 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

- 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 x 10^6 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.

EXPERIMENTAL SETUP

- All investigations were carried out in a 1080 L quartz-glass reactor in synthetic air (296 ± 3 K and 1013 mbar) (Mihalopoulos et al., 1992).
- A White type multiple reflection mirror system (248.7 ± 0.8 m cm coupled to an FTIR spectrometer was used for reactant and reference monitoring.
- IR spectra were recorded at a spectral resolution of 0.5 cm^-1 using a Nicolet NEXUS FT-IR spectrometer.

REVIEWS

- 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 in 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 dimethyl-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.

- Dimethyl-1,4-benzoquinone have a rate coefficient 2-3 times smaller than other 1,4-dicarboxylic acids (3-hexene-2,5-dione, Z-buttersial; Z and E-4-oxo-2-pentenal; 3H-furan-2-one) (Bierbach et al., 1994).

LITERATURE

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