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Research paper

Gas-phase oxidation of aromatic hydrocarbons: A kinetic study of the OH reaction with methoxybenzenes at atmospheric conditions

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ABSTRACT

Rate coefficients for methoxybenzene, 1,2,3-trimethoxybenzene, 1,2,4-trimethoxybenzene and 1,3,5-trimethoxybenzene reacting with hydroxyl radicals have been studied in a 1080 L chamber at atmospheric conditions using the relative kinetic method. The following rate coefficients (cm^3 molecules^{-1} s^{-1}) were determined at (298 ± 2) K: $(2.86 \pm 0.12) \times 10^{-11}$ for methoxybenzene, $(7.70 \pm 0.36) \times 10^{-11}$ for 1,2,3-trimethoxybenzene, $(1.29 \pm 0.56) \times 10^{-10}$ for 1,2,4-trimethoxybenzene and $(1.56 \pm 0.69) \times 10^{-10}$ for 1,3,5-trimethoxybenzene. This work constitutes the first kinetic study for the three isomers of trimethoxybenzene. Differences in reactivity are discussed. Atmospheric lifetimes and implications are presented.

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1. Introduction

Aromatic hydrocarbons play a key role in urban air pollution events, contributing significantly to photo-oxidant and secondary organic aerosols formation in the troposphere [1].

Methoxybenzenes are widely used in industrial activities, such as pharmaceuticals [2,3], cosmetics [4] and agricultural pest control (formulating insect attractants) [5,6]. They were also identified among the oxygenated aromatic compounds emitted during biomass burning in both the gas and aerosol phases [7–9]. Furthermore, trimethoxybenzene based compounds are potentially toxic in nature and cause numerous health problems. They are found in many hazardous waste dumps, which have been included in the national priority list proposed by the U.S. environmental protection agency [10,11].

Oxygenated aromatic compounds like methoxybenzenes have been shown to be highly reactive in the atmosphere and it is expected that the main degradation process in the gas phase is the reaction with OH radicals, resulting in a considerable contribution to photo-oxidant and secondary organic aerosol formation in the atmosphere [1].

The rate coefficient of the OH radical reaction with methoxybenzene has been studied as a function of temperature by Perry et al. [12], and more recently at 298 K by Coeur-Tourneur [13] et al. and Lauraguais et al. [14]. In order to obtain information about its atmospheric degradation during night-time, the reaction of NO_3 radicals with methoxybenzene was investigated at 298 K
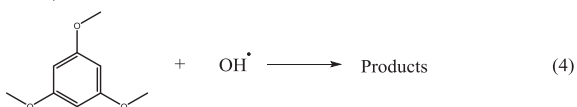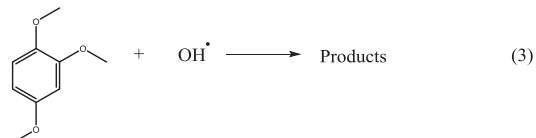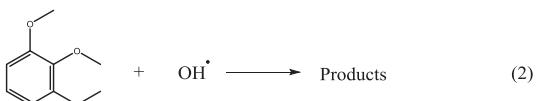
using relative rate methods [15–17]. In addition, using the relative kinetic method and simulation chambers, the rate constant for the reaction with chlorine atoms was determined by Lauraguais et al. [18] Reaction mechanisms and rate constants where also studied with ozone molecules by computational calculations by Sun et al. [19] From these studies it could be concluded that methoxybenzene removal by reaction with NO_3, O_3 molecules and Cl atoms radicals are negligible compared to other processes such as the reaction with OH radicals. With respect to the reaction of OH radicals with the different dimethoxybenzene isomers, only 1,2-dimethoxybenzene has been studied at atmospheric conditions using a relative rate technique [20]. Regarding night-time chemistry, the reactions of 1,2-, 1,3-, and 1,4-dimethoxybenzene towards NO_3 radicals were investigated using a relative rate method [17]. Other than monomethoxylated benzene, the night-time loss of the dimethoxybenzenes via reaction with NO_3 contributes considerably to their atmospheric removal process [1].

In contrast to methoxylated benzenes with one or two $-OCH_3$ substituents, there is a lack of knowledge about the reactivity and degradation mechanisms of benzenes with a higher number of oxygenated substituents at the ring, such as the trimethoxybenzene isomers. Accordingly, and because to the atmospheric implications mentioned above, it seemed necessary to study the reaction of OH radicals with these compounds and to derive their reactivity in the atmosphere. By extending the gas phase kinetic database for oxygenated aromatic compounds, it helps to improve the Master Chemical Mechanism (MCM) and to understand in more detail how these compounds may affect the oxidizing capacity of the atmosphere and air quality.

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The present work provides a new determination of the rate coefficient for the reaction of OH radicals with methoxybenzene and for the first time with 1,2,3-trimethoxybenzene, 1,2,4-trimethoxybenzene and 1,3,5-trimethoxybenzene under simulated atmospheric conditions:

$$\text{(benzene-OCH}_3\text{)} + OH^\bullet \longrightarrow \text{Products} \qquad (1)$$

$$\text{(1,2,3-trimethoxybenzene)} + OH^\bullet \longrightarrow \text{Products} \qquad (2)$$

$$\text{(1,2,4-trimethoxybenzene)} + OH^\bullet \longrightarrow \text{Products} \qquad (3)$$

$$\text{(1,3,5-trimethoxybenzene)} + OH^\bullet \longrightarrow \text{Products} \qquad (4)$$

In addition, one of the objectives of this work was to study the potential impact of the position of the substituents at the aromatic ring towards the reaction with OH radicals, to analyze the effects of their spatial distribution, electronegativity and the stability of the possible reaction intermediates formed. Furthermore, atmospheric implications of these compounds are explained in terms of their atmospheric lifetimes considering the measured rate coefficients.

2. Experimental

All experiments were performed in a 1080 L quartz-glass reaction chamber at (298 ± 2) K and a total pressure of (760 ± 10) Torr of synthetic air (760 Torr = 101.325 kPa). A pumping system consisting of a turbo-molecular pump backed by a double stage rotary fore pump was used to evacuate the reactor to 10^{-3} Torr. Three magnetically coupled Teflon mixing fans are mounted inside the chamber to ensure homogeneous mixing of the reactants. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40 W: 320–480 nm, $\lambda_{max} = 360$ nm) and 32 low-pressure mercury vapour lamps (Philips TUV 40 W; $\lambda_{max} = 254$ nm), which are spaced evenly around the reaction vessel. The lamps are wired in parallel and can be switched individually, which allows variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber. The chamber is equipped with a White type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive in situ long path infrared absorption monitoring of reactants and products in the spectral range 4000–700 cm^{-1}. The White system was operated at 82 traverses, giving a total optical path length of (484.7 ± 0.8) m. Infrared spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus FT-IR spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector.

OH radicals were generated by photolysis of CH$_3$ONO/NO/air mixtures at 360 nm using fluorescent lamps:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \qquad (5)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (7)$$

The initial mixing ratios of the reactants in ppmV (1 ppmV = 2.46×10^{13} molecule cm^{-3} at 298 K) were: methoxybenzene (1-3), 1,2,3-trimethoxybenzene (1-3), 1,2,4-trimethoxybenzene (2-4), 1,3,5-trimethoxybenzene (1-3), isobutene (3-5) and propene (3-5).

The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): methoxybenzene at 1253 and 1600; 1,2,3-trimethoxybenzene at 1254 and 1600; 1,2,4-trimethoxybenzene at 1515; 1,3,5-trimethoxybenzene at 1160 and 1211; isobutene at 3085 and propene at 3091.

The relative rate method was used to calculate the rate coefficients for the reactions of OH radicals with methoxybenzene, 1,2,3-trimethoxybenzene, 1,2,4 trimethoxybenzene and 1,3,5 trimethoxybenzene by comparing their decay rate with that of the corresponding decay of the two reference compounds isobutene and propene:

$$OH + OAH \rightarrow products \qquad (8)$$

$$OH + reference \rightarrow products \qquad (9)$$

Provided that the reference compound and the alcohol are lost only by reactions (8) and (9), then it can be shown that:

$$ln\left\{\frac{[OAH]_0}{[OAH]_t}\right\} = \frac{k_8}{k_9}ln\left\{\frac{[reference]_0}{[reference]_t}\right\} \qquad (I)$$

where, $[OAH]_0$, $[reference]_0$, $[OAH]_t$ and $[reference]_t$ are the concentrations of the corresponding oxygenated aromatic hydrocarbon and the reference compound at times $t = 0$ and t, and k_8 and k_9 are the rate coefficients of reactions (8) and (9), respectively.

The relative rate technique relies on the assumption that OAH and the reference compound are removed solely by reaction with OH radicals. To verify this assumption, various tests were performed to assess the loss of the reactants via secondary reactions and wall deposition in absence of the oxidant (OH radicals). These processes that could interfere with the kinetic determinations were found to be negligible for all investigated OAH and the reference compounds. The different concentration mixtures used in this work, i.e. OAH and reference compounds diluted in synthetic air, did not show any decrease in the reactant concentrations over the time span of the experiments.

3. Materials

The following chemicals, with purities as stated by the supplier, were used without further purification: synthetic air (Air Liquide, 99.999%), propene (Messer Schweiz AG, 99.5%), isobutene (Messer Griesheim, 99%), methoxybenzene (Aldrich, 99.7%), 1,2,3-trimethoxybenzene (Aldrich, 98%), 1,2,4-trimethoxybenzene (Aldrich, 97%) and 1,3,5-trimethoxybenzene (Aldrich, 99%). Methyl nitrite was prepared by the drop-wise addition of 50% sulphuric acid to a saturated solution of sodium nitrite in water and methanol. The products were carried by a stream of nitrogen gas through a saturated solution of sodium hydroxide followed by calcium chloride, to remove excess acid, and water and methanol, respectively. Methyl nitrite was collected and stored at 193 K [21].

4. Results

The losses of the studied methoxybenzenes by OH radicals are shown with different reference compounds in Figs. 1–4 plotted according to Eq. (I) for the reactions of OH radicals with the individual compounds studied measured relative to different reference compounds. They represent only one example with two references for each reaction studied for clarity. Each plot represents a minimum of 2 experiments for each reference compound. Good linear