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Methyl chavicol reactions with ozone, OH and NO_3 radicals: Rate constants and gas-phase products

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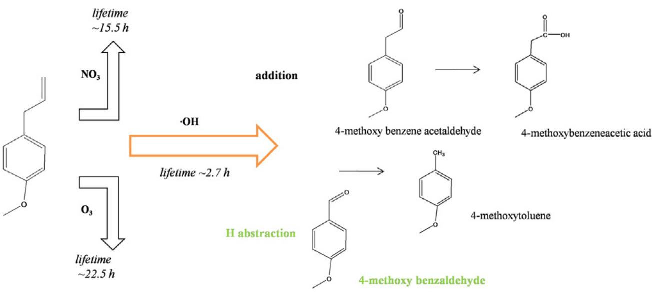
HIGHLIGHTS

- Reaction rate constants for methyl chavicol with OH, NO_3 and O_3 were determined.
- Atmospheric lifetimes of methyl chavicol were estimated.
- Major gas phase products of methyl chavicol with OH were analyzed.
- Possible formation mechanism for the main products was also proposed.
- Methyl chavicol could play an important role in regional atmospheric chemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

The rate constants for methyl chavicol reactions with OH and NO_3 radicals and O_3 have been measured using the relative rate method at (298 ± 1) K and atmospheric pressure. The constants are $k_{\text{methyl chavicol+OH}} = (5.20 \pm 0.78) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{\text{methyl chavicol+NO}_3} = (3.58 \pm 0.67) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_{\text{methyl chavicol+O}_3} = (1.03 \pm 0.23) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. To more clearly understand the main atmospheric degradation mechanism of methyl chavicol, the products of the methyl chavicol + OH reaction were also investigated by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). The identified products were 4-methoxytoluene, 4-methoxybenzaldehyde, 4-methoxy benzene acetaldehyde and 4-methoxybenzeneacetic acid. A possible formation mechanism for the main products is also proposed. The results indicate that methyl chavicol could have an impact on atmospheric chemistry at the regional scale and could also contribute to the production of secondary organic aerosol.

1. Introduction

It is now well recognized that biogenic volatile organic compound (BVOC) emissions are the dominant source of reduced organic gases to the atmosphere, even larger than the emissions from anthropogenic activities and biomass burning (Guenther et al., 1995). BVOCs emissions are naturally involved in the formation of tropospheric ozone and secondary organic aerosol (SOA), and thus cause important effect on atmospheric chemistry and climate, from local to regional and global areas (Andreae and Crutzen, 1997; Fuentes et al., 2000). This effect may now be even more significant, with increasing emission rates in response to warming and global change (Peñuelas and Staudt, 2010).

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With the continuing development and improvement of analytical instrumentation, more and more BVOCs have been measured in the atmosphere in recent years (Schade and Goldstein, 2001; Helmig et al., 2007; Matsunaga et al., 2008), and the list of specific BVOCs included in emission inventories and atmospheric chemistry models is growing (Sakulyanontvittaya et al., 2008; Matsunaga et al., 2012). Methyl chavicol ($C_{10}H_{12}O$) is just one of these BVOCs, and the growing interest of this compound in the atmospheric science community has been relatively recent. Methyl chavicol is an oxygenated aromatic BVOC, and could be produced by a variety of plants (Bouvier-Brown and Goldstein, 2009). For example, it is a major essential oil component of many common herbs found worldwide, even high up to 90% in some cases (Ciccio, 2004; Kaya et al., 2007). It is also a known attractant of the African oil palm weevil (Elaeidobius kamerunicus), which pollinates oil palms (Hussein et al., 1989).

Methyl chavicol is volatile enough to be readily emitted from vegetation to the atmosphere, however, only little about its atmospheric behavior and impact has been investigated until now. Bouvier-Brown and Goldstein (2009) recently reported the measurements of methyl chavicol emission rate and ambient concentrations from ponderosa pine forest and highlighted the importance this compound might have for atmospheric chemistry. Misztal et al. measured a global estimate of methyl chavicol emissions from oil palm plantations of about 0.5 Tg y^{-1} (Misztal et al., 2010). Lee et al. (2006a,b) reported a high SOA yield (40%) from the photooxidation reaction of methyl chavicol and some unidentified products with high molecular weight, further demonstrating its important impacts in the atmosphere. But methyl chavicol is normally not included in atmospheric models of biogenic emissions and atmospheric chemistry despite its relatively high potential for SOA formation from photooxidation. In this work, in order to better understand the reaction kinetics and mechanism of methyl chavicol in the atmosphere, the rate constants of methyl chavicol reactions with O_3, OH and NO_3 radicals were first measured using relative rate method. Some products from OH reaction were also identified using TD-GC-MS.

2. Experimental

2.1. Experimental methods

Experiments to measure the OH, NO_3 radicals and O_3 reaction rate constants were conducted in a 150 L Teflon reaction chamber. A detailed description of the chamber can be found elsewhere (Gai et al., 2011a).

The rate constants for the reactions of methyl chavicol with OH, NO_3 radicals and O_3 were measured using relative rate method in which the relative disappearance rates of methyl chavicol and a reference compound, whose reaction rate coefficient was reliably known, were monitored synchronously in the presence of OH, NO_3 radicals or O_3 (denoted as X):

$$\text{Methyl chavicol} + \text{X} \xrightarrow{k_M} \text{products} \tag{1}$$

$$\text{Reference} + \text{X} \xrightarrow{k_R} \text{products} \tag{2}$$

The rate equations for reactions (1) and (2) are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\text{methyl chavicol}]_{t_0}}{[\text{methyl chavicol}]_t}\right) = \frac{k_M}{k_R}\ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) \tag{3}$$

where $[\text{methyl chavicol}]_{t_0}$, $[\text{methyl chavicol}]_t$ and $[\text{reference}]_{t_0}$, $[\text{reference}]_t$ are the concentrations of methyl chavicol and the reference compound at time 0 and t, respectively. If reaction with X (OH, NO_3 radicals or O_3) is the only removal mechanism for methyl chavicol and reference compound and none of them are reformed in any process, then a plot of $\ln\left([\text{methyl chavicol}]_{t_0}/[\text{methyl chavicol}]_t\right)$ against $\ln\left([\text{reference}]_{t_0}/[\text{reference}]_t\right)$ should be straight line with zero intercept and slope of $k_M k_R^{-1}$. So multiplying the slope of this linear plot by k_R yields k_M, which is $k_{\text{methyl chavicol}+\text{OH}}$, $k_{\text{methyl chavicol}+\text{O}_3}$, or $k_{\text{methyl chavicol}+\text{NO}_3}$ in this experiment.

During the kinetic experiment, the disappearance of methyl chavicol and reference compounds were monitored by a gas chromatograph equipped with a flame ionization detector (GC/FID, GC6820, Agilent Technologies). Gas samples were collected from the chamber by a gastight syringe and introduced via a 1 cm^3 stainless steel loop and gas sampling valve onto a capillary column (DB-624, 60 m length × 0.53 mm i.d., 3 μm film thickness, Agilent Technologies). The GC oven parameters were as follows: 80 °C for 5 min then 70 °C min^{-1} to 220 °C, and then held for 11 min, and N_2 was used as the carrier gas. During the experiments, to avoid the absorption of the gas samples on the valve, the steel tube was changed to Teflon tube, and the valve was heated to 430 K.

The reaction products were sampled using a set of Tenax-TA absorption tubes (150 mm length × 6 mm O.D., 0.2 g sorbent), and subsequently desorbed and analyzed by thermal desorption–gas chromatography–mass spectrometry (TD-GC-MS, 6890A-5975C, Agilent Technologies). A thermal desorption unit from Beijing Tashi Electronics Co., Ltd. (AutoTDS-III) was used. Compound separation was achieved by a HP-5ms capillary column (30 m length × 0.25 mm i.d., 0.25 μm film thickness, Agilent Technologies) and the following GC oven parameters: 50 °C for 1 min then 20 °C min^{-1} to 130 °C, and then 5 °C min^{-1} to 200 °C and held for 5 min.

The identification of the products was made by analysis of the mass spectrum and by comparison with the spectra of NIST library. When possible, the identification was also performed by comparing the retention time of the detected product with a commercial sample. When this identification was not possible, a tentative assignment was proposed.

2.2. Chemicals

The chemicals used and their stated purities were as follows: Methyl chavicol (98%), Alfa Aesar; Cyclohexane (99%), Beijing Beihua Fine Chemcials Co., Ltd.; 4-Methoxybenzaldehyde (99%), J&K Chemical; 4-Methoxyphenylacetaldehyde (98%), China Langchem Inc.. The following gases were supplied by Beijing Tailong Electronics Company: nitrogen (99.999%), propene (1%, N_2 as bath gas), 1-butene (1%, N_2 as bath gas), NO (0.5%, N_2 as bath gas) and NO_2 (0.5%, N_2 as bath gas). A zero air generator (model 111, Thermo scientific) was used to generate clean compressed air which mainly contains O_2 and N_2. Analysis of this treated compressed air by GC revealed that if contaminants were present they would be below the part per billion range. All experiments were carried out at 298 ± 1 K and 1.01 × 10^5 Pa with clean air as bath gas.

OH radicals were generated from the photolysis of methyl nitrite (CH_3ONO) in the presence of NO. CH_3ONO was synthesized and purified using the method in the literature (Atkinson et al., 1981; Pan et al., 2012). A set of six ultraviolet light lamps (Model F40T8BL, Beijing Light Research Institute) fixed on the interior wall of the chamber box were used as the light source of the photolysis. These light lamps provide ultraviolet light with a central wavelength of 365 nm.

Ozone was produced via electrical discharge by flowing oxygen through an ozone generator (BGF-YQ, Beijing Ozone, China). The NO_3 radicals were produced by the thermal decomposition of N_2O_5,