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Reaction products and mechanisms for the reaction of n-butyl vinyl ether with the oxidants OH and Cl: Atmospheric implications

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HIGHLIGHTS

- The reaction products of butyl vinyl ether (BVE) with Cl and OH have been obtained.
- FTIR and GC-TOFMS have been used as experimental systems.
- Butyl formate, butyl chloroacetate and formyl chloride were identified with Cl.
- Butyl formate and formic acid were identified in the reaction with OH.
- Addition mechanism of Cl/OH at double bond of BVE has been proposed.

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ABSTRACT

A reaction product study for the degradation of butyl vinyl ether ($CH_3(CH_2)_3OCH{=}CH_2$) by reaction with chlorine atoms (Cl) and hydroxyl radicals (OH) has been carried out using Fourier Transform Infrared absorption spectroscopy (FTIR) and/or Gas Chromatography-Mass Spectrometry with a Time of Flight analyzer (GC-TOFMS). The rate coefficient for the reaction of butyl vinyl ether (BVE) with chlorine atoms has also been evaluated for the first time at room temperature (298 ± 2) K and atmospheric pressure (708 ± 8) Torr. The rate coefficient obtained was $(9.9 \pm 1.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and this indicates the high reactivity of butyl vinyl ether with Cl atoms. However, this value may be affected by the dark reaction of BVE with Cl_2. The results of a qualitative study of the Cl reaction show that the main oxidation products are butyl formate ($CH_3(CH_2)_3OC(O)H$), butyl chloroacetate ($CH_3(CH_2)_3OC(O)CH_2Cl$ and formyl chloride (HCOCl). Individual yields in the ranges ~16–40% and 30–70% in the absence and presence of NO_x, respectively, have been estimated for these products. In the OH reaction, butyl formate and formic acid were identified as the main products, with yields of around 50 and 20%, respectively. Based on the results of this work and a literature survey, the addition of OH radicals and Cl atoms at the terminal C atom of the double bond in $CH_3(CH_2)_3OCH{=}CH_2$ has been proposed as the first step in the reaction mechanism for both of the studied oxidants. The tropospheric lifetime of butyl vinyl ether is very short and, as a consequence, it will be rapidly degraded and will only be involved in tropospheric chemistry at a local level. The degradation products of these reactions should be considered when evaluating the atmospheric impact.

1. Introduction

Oxygenated volatile organic compounds (OVOCs) are present in the atmosphere and they arise from different types of biogenic and anthropogenic sources. Ethers, and particularly vinyl ethers ($ROCH{=}CH_2$), are widely used in manufacturing industries as solvents and motor oil additives (George et al., 2005). Moreover, butyl

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vinyl ether is used in the manufacture of adhesives and coatings (Ash and Ash, 2007).

The main gas phase removal processes for this type of ether involve reactions with OH, NO_3, and O_3. Kinetic data concerning the gas phase reactivity of vinyl ethers have been published in recent years (Scarfogliero et al., 2006; Thiault and Mellouki, 2006; Zhou et al., 2006; Peirone et al., 2011). The published kinetic data for ethyl, propyl, and butyl vinyl ethers are around 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for OH radicals, $1–2 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for NO_3 radicals, and $\sim 2 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} for ozone. To date, only kinetic data for the reactions of ethyl and propyl vinyl ethers with chlorine atoms have been published (Wang et al., 2009). The rate coefficients reported (2.43×10^{-10} and 4.23×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for ethyl vinyl ether and propyl vinyl ether, respectively) are comparable to the values reported for other saturated ethers (Notario et al., 2000).

It is known that the oxidation of ethers with OH and NO_3 radicals proceeds through an H-atom abstraction mechanism, mainly from the C–H bonds on the carbon atoms adjacent to the ether group (Atkinson, 1994). However, vinyl ethers can also react by double bond addition due to the presence of the vinyl group ($RC{=}CH_2$). One experimental study on the reaction of butyl vinyl ether with the nitrate radical is available in the literature (Scarfogliero et al., 2006) and it was concluded that the main degradation products for a double bond addition on the vinyl group were an alkyl formate and formaldehyde.

In order to complete the published data for the tropospheric reactivity of butyl vinyl ether (hereafter referred to as BVE), the work presented here involved a kinetic and product study of the reaction of BVE with chlorine atoms and a product determination for the reaction with OH radicals. It is known that hydroxyl radicals are the main degradation route for most of the OVOCs in the troposphere during daytime. However, the recent observation of nitryl chloride derived from anthropogenic sources (Mielke et al., 2011) and the significant mixing ratios observed over continental Europe (Phillips et al., 2012) were associated with air masses that were influenced by sea salt and also anthropogenic NO_x emissions, thus indicating that early morning production rates of Cl atoms could significantly exceed the production of OH. Therefore, the role of Cl in initiating the oxidation of VOCs may be widespread and could be more significant than previously thought.

The results obtained will improve our understanding of the degradation mechanisms of vinyl ethers in the atmosphere and the possible environmental implications of the generated products.

2. Experimental section

Kinetic and product studies were performed by employing two experimental set-ups: (1) a 50 L Pyrex® glass reaction chamber in conjunction with Fourier Transform Infrared absorption spectroscopy (FTIR-Nicolet) as a detection technique. Typically, for each spectrum, 60 interferograms were co-added over 60 s and approximately 15–20 spectra were recorded per experiment. The glass chamber contained a multireflection White cell that allowed a long pathlength of 200 m to be used in these experiments. (2) a 200 L Teflon® bag and a Solid Phase Micro Extraction fiber (SPME) as a pre-concentration sample method, followed by analysis on a Gas Chromatography-Mass Spectrometry system with a Time of Flight analyzer (SPME-GC-TOFMS) (AccuTOF GCv Jeol).

Chlorine atoms were obtained by photolysis of Cl_2 at a wavelength of 360 nm using 8 actinic lamps. Methyl nitrite (CH_3ONO) was generated in the laboratory as described elsewhere (Taylor et al., 1980) and was used in the presence of air and NO to generate OH radicals by photolysis according to the following reactions:

$$CH_3ONO + h\nu \rightarrow CH_3O\cdot + NO \tag{1}$$

$$CH_3O\cdot + O_2 \rightarrow HO_2 + HCHO \tag{2}$$

$$HO_2 + NO \rightarrow NO_2 + OH\cdot \tag{3}$$

Radiation with a maximum at around 360 nm was supplied by appropriate lamps.

The rate coefficients for the reactions of BVE with chlorine atoms were determined by comparing the rates of decay of the reactant relative to that of a selected reference compound:

$$BVE + Cl \rightarrow P \quad k_S \tag{4}$$

$$Reference + Cl \rightarrow P \quad k_R \tag{5}$$

On the assumption that the substrate and the reference compound are only consumed by reaction with chlorine atoms, the kinetic treatment for the reactions expressed by equations (4) and (5) yields the following relationship:

$$\ln\left(\frac{[BVE]_0}{[BVE]_t}\right) = \frac{k_S}{k_R}\ln\left(\frac{[R]_0}{[R]_t}\right) \tag{I}$$

where $[BVE]_0$, $[R]_0$, $[BVE]_t$, and $[R]_t$ are the initial concentrations and those at time t for butyl vinyl ether and the reference compound, respectively.

Two references were used (2-methylpropene and 1-butene) to ensure that the reference compound did not have an influence on the global rate coefficient. These reference compounds were selected because both compounds have an IR absorption band that can be easily monitored during the reaction and that does not overlap with the IR spectrum of BVE and reaction products. Furthermore, these compounds provide a suitable rate coefficient that allows the decays of the studied compound and each reference compound to be followed at the same time.

A plot of $\{\ln([BVE]_0/[BVE]_t)\}$ versus $\{\ln([R]_0/[R]_t)\}$ should be a straight line that passes through the origin. The slope of this line gives the ratio of rate coefficients k_S/k_R. The value of k_S can therefore be obtained if the rate coefficient k_R of the reference compound is known.

Changes in concentrations of substrate (BVE) and the reference compounds throughout the reaction were assessed by monitoring a characteristic IR absorption band for each compound (1209 cm^{-1} for BVE, 890 cm^{-1} for 2-methylpropene, and 912 cm^{-1} for 1-butene). A spectral subtraction procedure was used to derive the concentrations of substrate and reference compounds at time $t = 0$ and time t. The experimental set up and methodology were described in greater detail in previous publications (Colmenar et al., 2012, 2014).

The product evaluation was carried out using the same procedure as for the kinetic FTIR experiments, but in this case without a reference compound, at a pressure of (700 ± 1) Torr of synthetic air and a temperature of ≈298 K. The substrate and the appropriate precursors of chlorine atoms or OH radicals were introduced into the chamber (glass cell). The decay of BVE and the presence of new IR bands due to generated products were observed for 20–30 min during the reaction. The same set of experiments was performed in the presence of NO_x. The products detected in the FTIR experiments were also confirmed by Gas Chromatography-Mass Spectrometry (GC–MS). The GC–MS experiments were carried out in a 200 L Teflon® bag and a 50/30 mm DVB/CAR/PDMS Solid Phase Micro Extraction fiber (SPME) was used to obtain samples. Each sample