



Mechanistic aspects of the nucleophilic substitution of pectin. On the formation of chloromethane



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HIGHLIGHTS

- Abiotic formation of chloromethane from pectin and alkali chlorides.
- Pseudo first-order nucleophilic attack of chloride ion on methyl ester in pectin.
- Apparent lack of influence of alkali metal cations.

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ABSTRACT

Chloromethane, accounting for approximately 16% of the tropospheric chlorine, is mainly coming from natural sources. However anthropogenic activities, such as combustion of biomass may contribute significantly as well. The present study focuses on the thermal solid state reaction between pectin, an important constituent of biomass, and chloride ions as found in alkali metal chlorides. The formation of chloromethane is evident with the amount formed being linear with respect to chloride if pectin is in great excess. Thus the reaction is explained as a pseudo first order S_N2 reaction between the chloride ion and the methyl ester moiety in pectin. It is suggested that the polymeric nature of pectin plays an active role by an enhanced transport of halides along the carbohydrate chain. Optimal reaction temperature is around 210 °C. At higher temperatures the yield of chloromethane decreases due to a thermal decomposition of the pectin. The possible influence of the type of cation is discussed.

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1. Introduction

Chloromethane (CH_3Cl) is the most abundant natural chlorine-containing compound in the atmosphere the contribution being 16% of the total tropospheric chlorine (WMO, 2010). The global average mixing ratio of CH_3Cl in the troposphere has been estimated to be 550 ± 30 parts per trillion per volume (Lee-Taylor et al., 2001). Chloromethane has been reported predominantly to originate from natural sources (Butler et al., 1999).

According to the emission data provided by the Reactive Chlorine Emission Inventory (RCEI) conducted under the International Global Atmospheric Chemistry (IGAC) Global Emission Activity (GEIA) project, known sources such as biomass burning, ocean, incineration/industrial sources contribute 910 (650–1120), 650 (40–950) and 162 (30–294) Gg (10^9 g) yr^{-1} , respectively (Keene

et al., 1999; Khalil et al., 1999; Lobert et al., 1999; McCulloch et al., 1999). Further emissions from certain wood rotting fungi have been estimated to contribute 156 (35–385) Gg yr^{-1} (Watling and Harper, 1998; Khalil et al., 1999; Lee-Taylor et al., 2001). Further, Rhew and Mazéas (2010) estimated an annual global release of 170 (65–440) Gg of CH_3Cl from salt marshes and Varner et al. (1999) calculated a global flux of 48 Gg yr^{-1} from wetlands. Keppler et al. (2005), Yoshida et al. (2006), as well as Saito and Yokouchi (2008) provide strong support for the proposal that the largest source of atmospheric chloromethane (1800–2500 Gg yr^{-1} and 1500–3500 Gg yr^{-1} , respectively) is the abiotic methylation of chloride in terrestrial ecosystems, primarily located in tropical and subtropical areas where turnover of biomass is highest. Furthermore, Keppler et al. (2005) indicates that the microbial soil sink for chloromethane is likely to be much larger (>1000 Gg yr^{-1}).

The major removal process for CH_3Cl in the atmosphere is apparently caused by oxidation by OH radicals, accounting for a

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removal of 3.5 (2.8–4.6) Tg (10^{12} g) per year (Koppmann et al., 1993).

Conversion of chloride to chloromethane occurs readily in plant material with the ubiquitous plant component pectin acting as the methyl donor (Hamilton et al., 2003). Plant derived C_1 volatile organic compounds are depleted in ^{13}C in comparison with higher VOCs. This supports that the plant 'methoxy pool' is a predominant source of biospheric C_1 compounds (Keppler et al., 2004). Apparently, the reaction is nucleophilic in nature as the release of methyl halides are further observed by heating pectin with other halide and pseudohalide ions (Hamilton et al., 2003). It was suggested that vegetation is the bulk source of chloromethane released into the atmosphere by using a stable carbon isotope ratios. Carbon isotope ratios measured for chloromethane may be expected to reflect the combined effect of both production and loss processes (Keppler et al., 2005). Pyrolysis of the almond shell sample impregnated with cobalt chloride yields chloromethane at elevated temperature (Conesa et al., 1997).

The appearance of chloromethane may be of high importance in energy production from biomass, especially regarding thermal processes. The role of chlorine in gasification and combustion is generally classified as an inorganic aspect, e.g., associated with deposits or ash quality within the field of bioenergy. It appears 40% of the chlorine preliminarily may be released as chloromethane during the thermal processes.

The objective of the investigations presented in the present paper has been to study the formation of chloromethane under abiotic conditions using alkali metal chlorides and a pectin, to study the possible influence of cations on the chloromethane formation, to establish the reaction order and improve the understanding of mechanistic aspects of the reaction. Hence, studies on the formation of chloromethane from pectin, at different temperatures and reaction times are reported. In the present study large excess of pectin relative to chloride was consequently used to force the reaction into a pseudo first order domain thus facilitating data analyses as well as increasing yields of chloromethane.

2. Experimental

2.1. Reactants

Pectin (apple) (CAS No. 9000-69-5) was obtained from Sigma-Aldrich (Germany) with specifications: Mw 30–100 kDa, degree of esterification 70–75%, water content < 10 wt% and ash content 6 wt%.

Chloromethane was purchased from Gerling Holz (Germany). Chloromethane (99.8%) has a vapour pressure of 49 bar (20 °C), bp -24.2 °C and mp -98 °C (BOC, 2003).

Galacturonic acid methyl ester (CAS No. 1048-08-1) was obtained from Carbosynth Ltd., (UK).

Glucuronic acid methyl ester was synthesized on location by dissolving glucuronic acid γ -lactone in methanol with a trace of methanolate. The product was characterized by ESI-MS/MS.

2.2. Sample preparation

Pectin, 10.00 g, was placed in a 200 mL volumetric flask and dissolved with 150 mL distilled water by gentle shaking at 85 °C for 5 h. Subsequently water was added to 200 mL.

Stock solutions of LiCl, NaCl, KCl, RbCl, and CsCl, respectively, were prepared at a concentration 0.134 M in 100 mL volumetric flasks and subsequently diluted into 0.0134 M working solutions.

2.3. Experiments with uronic acids

Pectin, 2.5 g, was dissolved in 50 mL MilliQ water at 85 °C and 0.2 g of the uronic acid methyl ester of choice was dissolved in 20 mL MilliQ water. For the chloromethane experiments 2 mL of the uronic acid methyl ester solution and 1 mL pectin solution were placed into pear shaped flasks. 1 mL 0.0134 M KCl solution was added to all flasks and the mixtures were lyophilized. The dried samples were subsequently heated at 210 °C for 20 min, followed by cooling to ambient temperature. The head space was sampled with a gas syringe. All analyses were carried out in duplicate.

Standard mixtures of chloromethane were volumetrically prepared.

2.4. Instrumentation

Gas analyses were performed using a Varian 3400 gas chromatograph interfaced to a Saturn II ion trap mass spectrometer. Samples of 0.5 mL were injected manually using a Pressure-Lok[®] syringe (VICI Precision Sampling, Inc., USA), and introduced in split mode (approximately 1:50) at a temperature of 150 °C. For both the GC to MS transfer line and the manifold of the mass spectrometer the temperature was kept at 200 °C. Separation was achieved using a 0.32 mm i.d. \times 25 m fused silica column packed with 10 μ m CP-Pora PLOT U (Varian Inc., USA). Appropriate separations were achieved isothermally at 80 °C. Full mass spectra were recorded every 0.5 s (mass range m/z 35– m/z 100).

The application of GCMS has in the present context been regarded as state-of-the-art providing the desirable high sensitivity of mass spectrometry and high separation power of capillary gas chromatography. In addition, through the mass spectrometric analysis the $^{37}Cl/^{35}Cl$ isotope pattern unambiguously disclosed the presence of one chlorine atom in the reaction product.

2.5. Temperature influence

To study the temperature influence on the chloromethane formation, a series of experiments was carried out at temperatures 190, 200, 210, 220 and 230 °C, respectively. Samples of 1 mL of the pectin and 1 mL of KCl working solutions were added to 5 flasks, mixed and lyophilized. After drying, the closed flasks were heated for 20 min at the pre-selected temperatures. Following cooling to ambient temperature, the head space of the single flasks was sampled by gas syringe and analyzed by GC/MS. All analyses were carried out in duplicate. The relatively narrow temperature range applied in the temperature study was solely to identify the optimal temperature for the reaction.

2.6. Time influence

To study time influence on chloromethane formation, a series of experiments was carried out using reaction times 10, 20, 30 and 40 min., respectively, at a temperature 210 °C, respectively. Samples of 1 mL of the pectin and 1 mL of KCl working solutions were added to 4 flasks, mixed and lyophilized. After drying, the closed flasks were heated for the pre-selected time. Following cooling to ambient temperature, the head space of the single flasks was sampled by gas syringe and analyzed by GC/MS. All analyses were carried out in duplicate.

2.7. Cation influence

To study the possible influence of cations on abiotic chloromethane formation, a series of alkali metal chlorides were chosen, i.e., LiCl, NaCl, KCl, RbCl, CsCl. Concentration of all working

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