http://dx.doi.org/10.5012/bkcs.2013.34.2.649

Formation of Methoxybenzenes from Cellulose in the Presence of Tetramethylammonium Hydroxide by Pyrolysis

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Received September 12, 2012, Accepted November 19, 2012

Key Words : Pyrolysis-GC/MS, Cellulose, TMAH, Methoxybenzene derivatives

Pyrolysis-gas chromatography/mass spectrometry (Pyrolysis-GC/MS)[1,2] has been extensively used for characterizing the structural information of various macromolecules such as humic substances,[3,4] woods,[5,6] and synthetic polymers.[7] Challinor improved the technique by introducing simultaneous pyrolysis and methylation with tetramethylammonium hydroxide (TMAH).[8] As the technique offers a number of advantages over conventional pyrolysis, it has been used widely for the characterization of a wide variety of macro-organic molecules such as polysaccharides.[9] Thermally assisted hydrolysis and methylation of carbohydrates by TMAH has been investigated.[10,11] This approach has improved the separation by methylation of acidic functional group. Several researchers have demonstrated that the role of TMAH is not only the methylation of the pyrolysis products but also assisting in bond cleavage.[12-15] Because TMAH possesses a strong basicity, highly basic conditions are likely to induce a variety of reactions.[16] Pyrolysis technique using TMAH renders polar pyrolysis products volatile enough to be eluted from the GC column by subsequent on-line methylation.[17]

Carbohydrates are one of the major groups of organic substances on the earth with a simple chemical structure based on various monosaccharides. They are widespread in plant tissue and can make up about 80% of its dry mass. Recently the pyrolytic characterization of carbohydrates has gained more and more attention. Analytical pyrolysis has been used extensively to study the structure of those macro-biomolecules and some studies have dealt with the pyrolytic characterization of carbohydrates.[18-20] Pyrolysis of carbohydrates is known to produce many kinds of products and has already been described by many researchers.[21-29] But the information deals with the limitative area of derivatives from carbohydrates. Anhydrosugars, furans, and benzene derivatives are known to be the major pyrolysis products.

Cellulose consists of a linear polysaccharide with α-1,4 linkages of D-glucopyranose monomers. The top and bottom of cellulose chains are essentially completely hydrophobic. The sides of cellulose chains are hydrophilic and capable of hydrogen bonding, because all the aliphatic hydrogen atoms are in axial positions, and the polar hydroxyl groups are in equatorial positions. The degree of polymerization of cellulose is approximately 1.0×10^4 to 1.5×10^4 glucopyranose monomer units in wood and cotton, respectively.[30] Cellulose pyrolysis is a technique for biofuels production that transforms cellulose materials like switchgrass, corn stover, or cellulose wastes into chemicals that can be further processed to yield fuels suitable for motor vehicle use.[31] Pyrolysis of pure cellulose produces mainly levoglucosan in yields of up to 60%.[22]

In this study, pyrolysis products of cellulose in the presence of TMAH were analyzed using GC/MS. We focused on the formation of mono-, di-, tri-, and tetramethoxybenzenes. Cellulose pyrolysis is a complicated process involving multiphase reactions, complex chemical pathways, and highly unstable intermediates.[32] Lojewski *et al.*[33] reported that furan and furfural were major decomposed products of paper. Besides furfural, benzene derivatives such as phenol, methylphenol, and methoxyphenol were produced by pyrolysis of biomass.[34,35] Adama *et al.*[35] pyrolyzed biomass in the presence of Al-MCM-41 type catalysts and reported that large methoxyphenols were increased by the catalysts. MCM-41 (mobile crystalline material) is a silicate obtained by a templating mechanism.[36-38] Rice husk and rice straw contain silica about 11-19 and 5-8 wt %, respectively.[39,40] Cellulose mixed with silica was also pyrolyzed to investigate the influence of silica on the formation of methoxybenzenes.

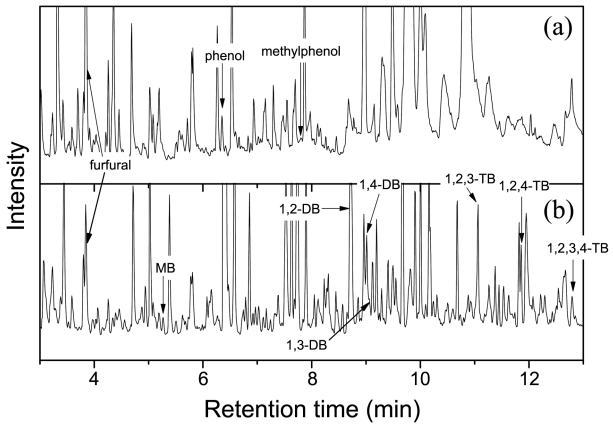
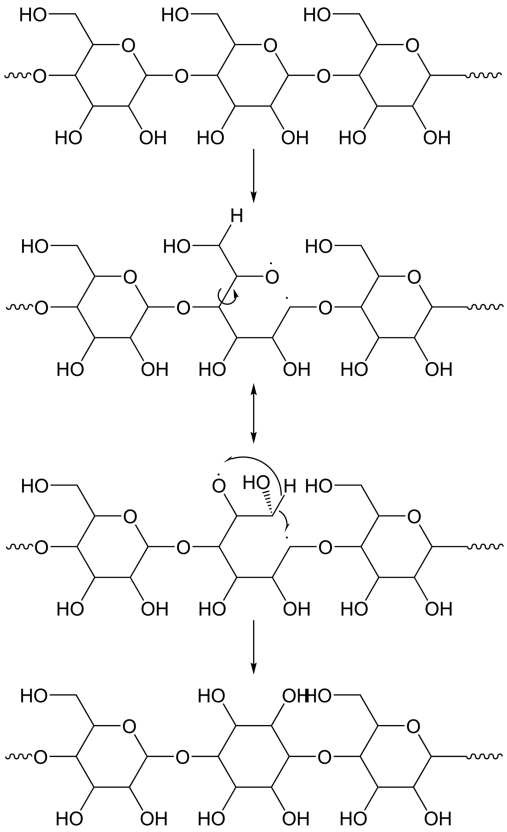


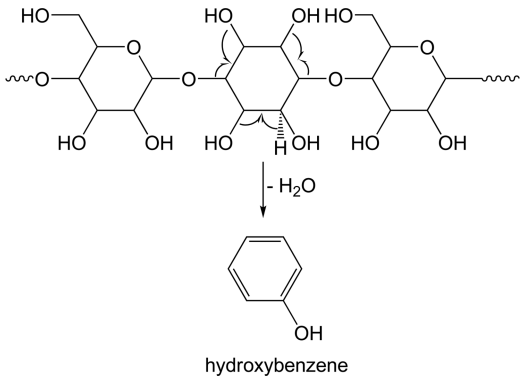
Figure 1. Pyrolysis-GC/MS TIC chromatograms of cellulose without (a) and with (b) TMAH. MB, 1,2-DB, 1,4-DB, 1,3-DB, 1,2,3-TB, 1,2,4-TB, and 1,2,3,4-TB mean methoxybenzene, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, 1,3-dimethoxybenzene, 1,2,3-trimethoxybenzene, 1,2,4-trimethoxybenzene, and 1,2,3,4-tetramethoxybenzene, respectively.

Figure 1 shows pyrolysis-GC/MS TIC chromatograms of pyrolysis products obtained from cellulose without and with TMAH. Lots of pyrolysis products were observed. Furfural (3.84 min) was observed in high abundance irrespective of TMAH. For the pyrolysis products of cellulose without TMAH, phenol and methyl phenol (6.35 and 7.80 min, respectively) as phenol derivatives were observed. For the pyrolysis of cellulose with TMAH, phenol was not observed but its methylated product, methoxybenzene (MB, 5.27 min) was observed. Methyl phenol and its methylated product, methoxytoluene (6.92 min) was also observed. Di-, tri-, and tetrahydroxybenzenes were not observed in the pyrolysis-GC/MS TIC chromatogram of cellulose without TMAH, but their methylated products, di-, tri-, and tetramethoxybenzenes were formed in the pyrolysis products of cellulose with TMAH. 1,2-Dimethoxybenzene (1,2-DB, 8.70 min), 1,4-dimethoxybenzene (1,4-DB, 9.02 min), 1,3-dimethoxybenzene (1,3-DB, 9.07 min), 1,2,3-trimethoxybenzene (1,2,3-TB, 11.06 min), 1,2,4-trimethoxybenzene (1,2,4-TB, 11.81 min), and 1,2,3,4-tetramethoxybenzene (1,2,3,4-TB, 12.81 min) were observed.

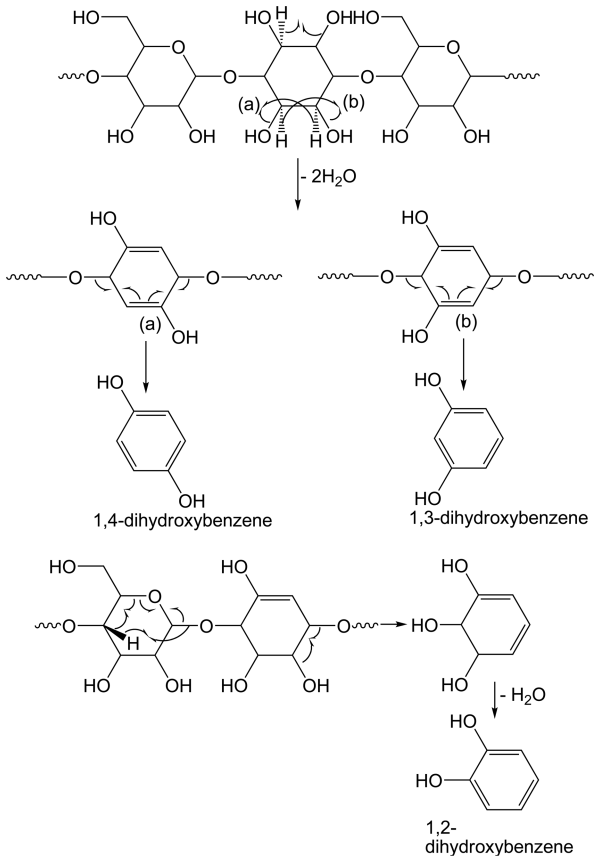
It is possible to separate and detect dihydroxybenzenes using GC/MS. Thus, no detection of di-, tri-, and tetrahydroxybenzenes in the pyrolysis products of cellulose without TMAH suggests that they are not generated from cellulose by pyrolysis. The formation of di-, tri-, and tetrahydroxybenzenes from cellulose by pyrolysis has not been reported. By adding TMAH to cellulose, fully methylated products of di-, tri-, and tetrahydroxybenzenes (di-, tri-, and tetramethoxybenzenes, respectively) were generated. This implies that TMAH played the role of assisting in bond cleavage as well as methylation of the pyrolysis products.[12-15] The formation mechanisms of pre-methylated pyrolysis products of mono-, di-, tri-, and tetramethoxybenzenes are suggested in Schemes 1-5. Fundamentally, the cellulose pyrolysis products are formed *via* a free radical mechanism.[41,42] First of all, to form a benzene ring, a glucose unit has to be transformed to a cyclohexane ring. A cyclohexane ring can be formed by cleavage of the ether linkage between C1 and C5 of a glucose unit and following rearrangement to



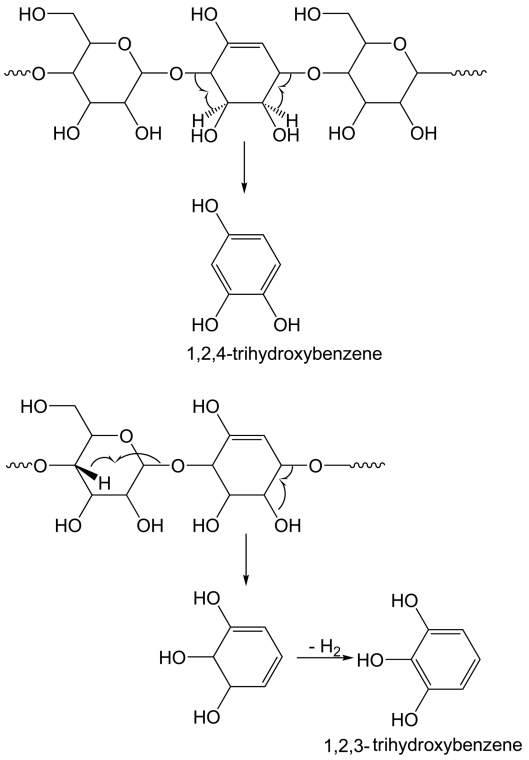
Scheme 1. Plausible mechanism for the formation of cyclohexane ring from a glucose unit.



Scheme 2. Plausible mechanism for the formation of hydroxybenzene (phenol) from cellulose.



Scheme 3. Plausible mechanism for the formation of dihydroxybenzenes from cellulose.

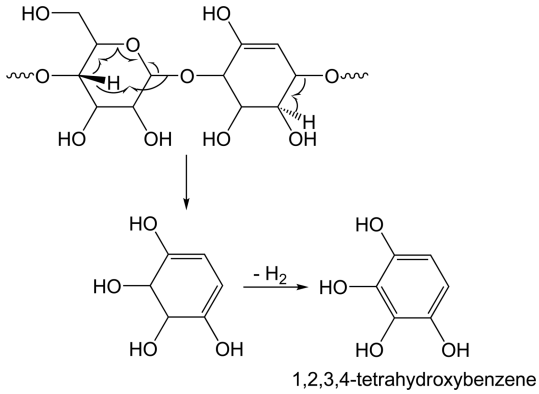


Scheme 4. Plausible mechanism for the formation of trihydroxybenzenes from cellulose.

form a tetrahydroxycyclohexane (THCH) unit as shown in Scheme 1.

Hydroxybenzene (phenol) can be formed from the THCH unit by rearrangement including two hydroxyl groups and loss of a water molecule as shown in Scheme 2. 1,3-Dihydroxybenzene and 1,4-dihydroxybenzene can be formed from the THCH unit by loss of two water molecules and following rearrangements as shown in Scheme 3. 1,2-Dihydroxybenzene can be formed from the THCH unit by rearrangement including the neighboring glucose unit and loss of a water molecule as shown in Scheme 3. 1,2,4-Trihydroxybenzene can be formed from the THCH unit by rearrangement including two hydrogen atoms, while 1,2,3-trihydroxybenzene can be formed from the THCH unit by rearrangement including the neighboring glucose unit and loss of a hydrogen molecule as shown in Scheme 4. 1,2,3,4-Tetrahydroxybenzene can also be formed from the THCH unit by rearrangement including the neighboring glucose unit and loss of a hydrogen molecule as shown in Scheme 5.

From the experimental results, we believe that the OH^- of TMAH assists cleavage of the ether linkage of cellulose to form di-, tri-, and tetrahydroxybenzenes and the $N(CH_3)_4^+$ of TMAH does methylation of the benzene derivatives. The relative abundances of methoxybenzenes were compared to investigate the influence of TMAH content and silica on the formation of benzene derivatives. The peak area of furfural was employed as the reference, because furfural is one of the abundant pyrolysis products and it can be considered a marker of the degradation progress of cellulose. The relative abundances of methoxybenzenes notably increased at high



Scheme 5. Plausible mechanism for formation of 1,2,3,4-tetrahydroxybenzene from cellulose.

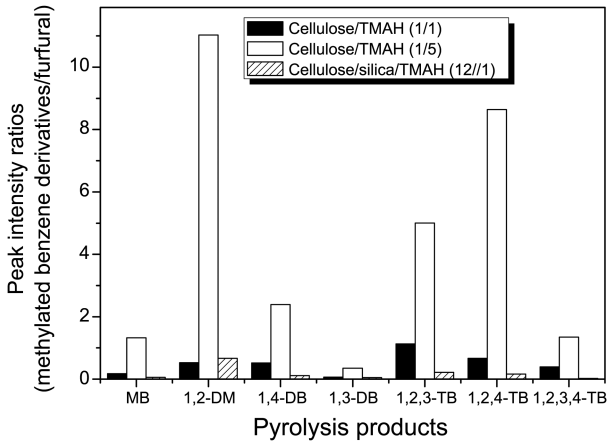


Figure 2. Peak area ratios of methylated benzene derivatives/furfural. Solid, open, and striped symbols stand for cellulose with TMAH (1:1), cellulose with TMAH (1:5), and cellulose with silica and TMAH (1:2:1), respectively. MB, 1,2-DB, 1,4-DB, 1,3-DB, 1,2,3-TB, 1,2,4-TB, and 1,2,3,4-TB mean methoxybenzene, 1,2-dimethoxybenzene, 1,4-dimethoxybenzene, 1,3-dimethoxybenzene, 1,2,3-trimethoxybenzene, 1,2,4-trimethoxybenzene, and 1,2,3,4-tetramethoxybenzene, respectively.

TMAH content as shown in Figure 2. Thus, this can lead to a conclusion that TMAH assists to generate the methoxybenzenes from cellulose by pyrolysis. By adding silica, the peak intensity ratios tended to decrease except 1,2-DB. This may be due to reactions between silica and TMAH. The acidic silanol groups (-Si-OH) can react with the OH^- of TMAH because silica has lots of silanol groups on the silica surface. Reactions of TMAH with silica will lead to decrease in reactions of TMAH with cellulose.

Experimental Section

Cellulose was purchased from Sigma-Aldrich Co. and silica was purchased from Merck Chemicals Co. Silica was baked at 120 °C for 24 h in a convection oven before use to remove moisture. Tetramethylammonium hydroxide (TMAH) in methanol (25%) was purchased from Lancaster Synthesis Inc. TMAH was added to the raw cellulose with the molar ratio of cellulose (glucose unit):TMAH = 1:1 and 1:5. The

molar ratio of cellulose (glucose unit) and silica (SiO_2) was 1:2. Approximately 0.3-0.5 mg of the mixture sample was used for pyrolysis.

Pyrolysis-GC/MS was carried out by using a pyroprobe 2000 system with a CDS 1500 interface (Chemical Data System, Oxford, USA) coupled to an Agilent 6890 gas chromatograph equipped with a 5973 mass spectrometer of Agilent Technology Inc. (USA). A DB-1 capillary column (30 m length, 0.32 mm inner diameter, 0.25 μm film thickness) of Agilent Technology Inc. was used. The following analysis conditions were used: pyrolysis temperature and time, 590 °C and 5 sec; GC injector temperature, 250 °C; split ratio, 1:20; GC oven temperature program, 35 °C (held for 1 min) to 150 °C (held for 1 min) at 10 °C/min and raised up again to 250 °C (held for 3 min) at 10 °C/min; carrier gas, helium (flow rate, 1.5 mL/min); the interface temperature of GC to MS, 250 °C. The electron ionization (70 eV) was used to ionize the pyrolysis products. The MS source temperature was 230 °C.

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