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Decomposition of sugars under non-thermal dielectric barrier discharge plasma

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ABSTRACT

Solutions of ribose, glucose, and sucrose in water and phosphate buffer were treated with non-thermal plasma generated by using a dielectric barrier discharge (DBD) device and the oxidation products were characterized by ^{1}H NMR and GC–MS. Our results demonstrate that these sugars are decomposed to formic acid, glycolic acid, glyceric acid, tartronic acid, tartaric acid, acetic acid, and oxalic acid after direct exposure to DBD plasma. The concentrations of these compounds are time-dependent with plasma treatment. The decomposition mechanisms of these sugars under the DBD plasma are also proposed in this study.

1. Introduction

Dielectric barrier discharge (DBD) plasma is generated when high voltage of sinusoidal waveform or short duration pulses are applied between two electrodes, with either one electrode or both electrodes being insulated [1,2]. The plasma is formed in air or other gases at atmospheric pressure and room temperature. The insulator prevents build-up of current between the electrodes, creating electrically safe plasma without substantial gas heating.

The effects of DBD on biological systems are selective since non-thermal plasma produces little heat. When DBD is applied directly to living cells and tissues, the reactive species created in plasma can penetrate and dissolve into the liquid surface, resulting in bacteria inactivation and blood coagulation without significant heating [3,4]. DBD plasma treatment has also been demonstrated to promote cell proliferation [5], enhance cell transfection [6,7], sterilize root canals [8–10], wound healing [11], skin sterilization [3,12], etc. Although clinical application of plasma is becoming increasing clear, investigation of the chemical species generated from DBD is critical to fully understand their interaction with living cells and tissues, and to develop the clinical applications of DBD. Recently, it was observed that DBD non-thermal plasma had chemical-dependent effects on the damage of DNA in cell culture [13,14]. It is believed that DNA damage induced by DBD non-thermal plasma is initiated by production of active neutral species that induces formation of organic peroxides in cell medium. Cell culture medium is composed of amino acids, sugars, vitamins, growth factors and inorganic salts, as well as serum. Understanding of the reaction intermediates and products of these chemicals under non-thermal plasma is required to promote the development of clinical applications of non-thermal plasma.

Previous work on decomposition of organic species focused on pollution issues [15–16], little work has done on decomposition of organic chemicals related to clinical applications [17]. As an initial attempt of a series of study of these reactions and chemical species, we demonstrate in this work the decomposition products and decomposition mechanisms of glucose, ribose, and sucrose under non-thermal DBD plasma.

2. Experimental section

2.1. Chemicals

D-(−)-ribose and D-(+)-sucrose were purchased from Acros Organics. D-(+)-glucose, formic acid, acetic acid and Phosphate Buffered Saline (PBS, 0.01 M) were purchased from Fisher Scientific. PBS buffer solution was prepared immediately before plasma treatment. Deuterium oxide (D_2O), *tert*-butanol, N,O-Bis(trimethylsilyl)

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trifluoroacetamide (BSTFA) with 1% of trimethylchlorosilane, tartaric acid, and oxalic acid were purchased from Sigma-Aldrich. Glycolic acid (70% in water) and glyceric acid (20% in water) were purchased from TCI. Tartronic acid was from Alfa Aesar, and dichloromethane (DCM) of GC quality was from Pharmco-AAPER. Nitrogen and oxygen gases were obtained from Airgas.

2.2. Plasma set-up and treatment

DBD plasma was produced by using an experimental set-up as shown in Fig. 1.

Plasma was generated by applying alternating polarity pulsed (500 Hz–1.5 kHz) voltage of 20 kV magnitude (peak to peak), 10 ns pulse width and a rise time of 5 V/ns between the high voltage electrodes using a variable voltage and variable frequency power supply (FID Technology). An 1 mm thick quartz glass was used as an insulating dielectric barrier covering the 1-in. diameter copper electrode. The discharge gap between the bottom of the quartz and the treated sample surface was fixed at 1 mm. A quartz plate (87×52 mm^2) with a 1-mm deep groove (57×32 mm^2) was used as a sample holder. The parameters of the plasma set-up were set to be 11.2 kV (R=75 Ω) and 690 Hz for all the experiments. D_2O-solutions (20 mM) of D-(−)-ribose, D-(+)-glucose and D-(+)-sucrose were treated with air-, N_2- and O_2-plasma for different times.

2.3. Sample preparation for NMR and GC–MS tests

For ^{1}H NMR tests, the plasma-treated sugar solutions were tested directly without dilution. Following plasma treatment, *tert*-butanol was added to the solutions (0.2 mM) as an internal standard to quantify the concentration of chemicals in the solutions. For GC–MS, 1 mL of each plasma-treated sugar solution was evaporated to dryness at room temperature. 300 μL of BSTFA was added to these dry samples and then derivatized at 70 °C for 1 h. After derivatization the solution was diluted to 0.5 mL using CH_2Cl_2 for GC–MS. Several standard solutions of formic acid, glycolic acid, glyceric acid, tartronic acid, tartaric acid, acetic acid, and oxalic acid were also derivatized by using BSTFA with the same procedure for comparison.

2.4. Instrumentation

^{1}H NMR spectra were recorded on a Varian Gemini 500 MHz spectrometer. GC–MS analyses were performed using a GC-FID/MS (PerkinElmer Clarus 500 GC–MS) equipped with an autosampler and a split/splitless injector. Separations were accomplished using a 30-m long Elite-5 MS capillary column, 0.25 mm internal diameter (I.D.) and 0.25 μm film thickness (PerkinElmer, USA) at a constant helium flow rate of 1.2 mL/min. Samples were injected in 1.0 μL volumes with a split ratio of 25:1 at 250 °C. The column temperature was initially kept at 50 °C for 3 min, then increased from 50 to 150 °C at 10 °C/min and held for 10 min. A solvent delay of 1.0 min was selected. In full-scan mode, the electron ionization (EI) mass spectra were recorded in range of 20–550 (m/z) at 70 eV. The decomposition products of three sugars under plasma treatment were identified by comparing their mass spectra with those of National Institute of Standards and Technology (NIST) library available with instrument and by comparing the retention time with those of commercially available standards.

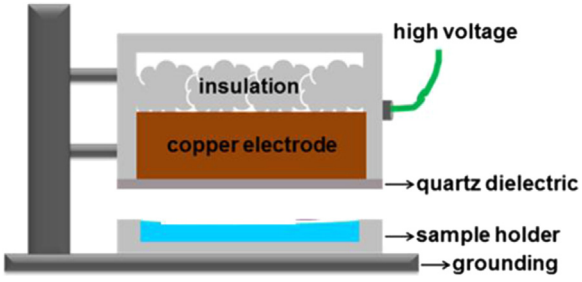

Fig. 1. Scheme of the DBD plasma set-up.

3. Results and discussion

3.1. Characterization of compounds in the air-plasma-treated sugar solutions

After treatment with DBD non-thermal plasma in the air, compounds in the D_2O solutions of ribose, glucose and sucrose were directly analyzed by using ^{1}H NMR spectroscopy. This method assured that all of the compounds remained in the solutions after the treatment so that the NMR spectra provide the full information of all the chemical species in the treated solutions. Fig. 2 shows the ^{1}H NMR spectra of ribose D_2O-solutions before and after 20 min treatment with air-plasma. Ribose totally decomposed after a 20 min air-plasma treatment. Several new peaks appeared in the ^{1}H NMR spectra of the plasma-treated ribose solution by comparing with those of the untreated ribose solution. Fig. 3 shows the GC chromatogram of 20-min plasma-treated ribose solution. Combining the NMR and GC–MS spectra, we conclude that seven compounds were produced in the solution of ribose after a 20-min air-plasma treatment. They are formic acid (1), glycolic acid (2), glyceric acid (3), tartronic acid (4), tartaric acid (5), acetic acid (6) and oxalic acid (7). Detailed analyses are summarized as follows.

3.1.1. ^{1}H NMR results

In ^{1}H NMR spectra (Fig. 2), the peak at 4.79 ppm is the solvent residual of water in D_2O. Five singlet peaks at 8.16, 5.29, 4.63, 4.15, and 2.02 ppm are assigned to formic acid, tartronic acid, tartaric acid, glycolic acid, and acetic acid, respectively. The two peaks in Fig. 2, a doublet at 3.80 ppm and a triplet at 4.31 ppm belong to glyceric acid. The assignments of these peaks were based on the reported chemical shifts, splitting patterns, and coupling constants of these chemicals [18–21]. The peak of oxalic acid is not observed in Fig. 2 because oxalic acid is not detectable in the ^{1}H NMR spectra of D_2O solutions. We also compared the ^{1}H NMR spectra right after the plasma treatment and 3 h after the plasma treatment. The two spectra are identical, suggesting that the progress of the decomposition reaction of ribose either stopped or significantly slowed down once the plasma source was removed. This may be due to the concentrations of sugars are relative high (1 mM), so all the radicals generated in plasma were consumed during the sugar decomposition process once plasma is stopped. The decomposition of ONOOH to OH and NO_2 is a fast process (within seconds) so we did not observe this change since collection of NMR data needs a time much longer than that.

3.1.2. GC–MS results

The GC chromatograms of the BSTFA-derivatized plasma-treated sample and the control sample are shown in Fig. 3. The retention time (R_t) at 1.52 min was due to the carrier solvent CH_2Cl_2, and the R_t at 1.93 and 2.67 min are attributed to the by-products of the trimethylsilyl esterification reaction and the derivatives of the residual water in the CH_2Cl_2 solution [22]. The broad peak between 3.80 and 4.30 min is from BSTFA. These peaks were observed both in the CH_2Cl_2 solution of air-plasma-treated sample and in the mixture solution of control samples. They were also shown in the GC chromatogram of pure BSTFA. By comparing