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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.

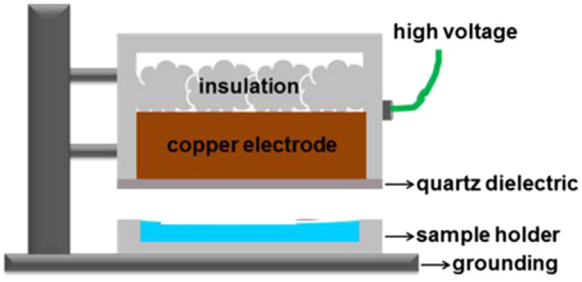

Fig. 1. Scheme of the DBD plasma set-up.

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

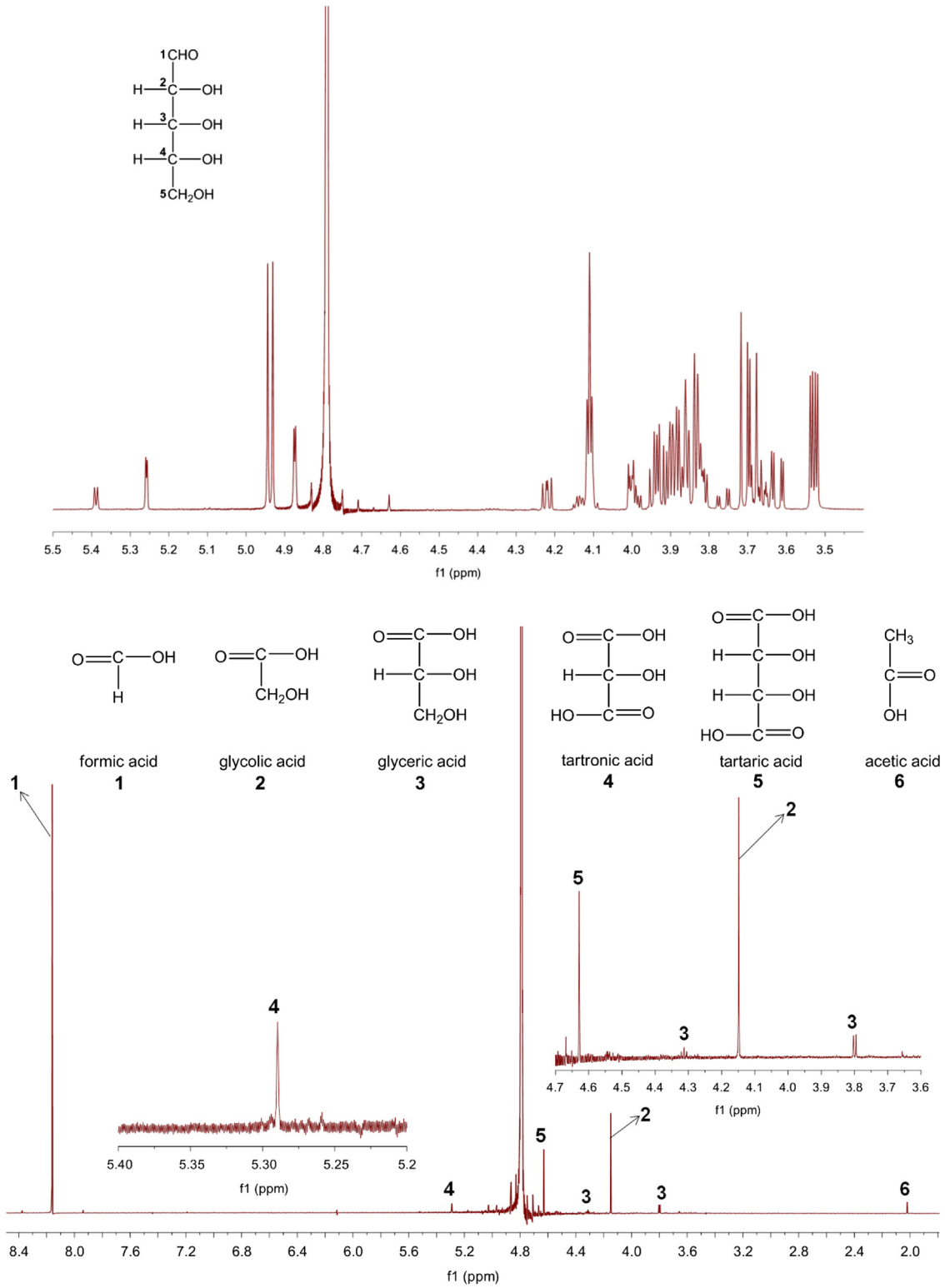

Fig. 2. ^{1}H NMR spectra of a 1-mL D_2O-solution of ribose before (top figure) and after (bottom figure) treated with air-plasma for 20 min.

the retention times and mass spectrometry characters of the plasma-treated sample (Fig. 3a) and the control sample (Fig. 3b), we concluded that the retention times at 1.81 (*m*/*z* 75, 103, 45), 2.18 (*m*/*z* 75, 117, 45), 7.92 (*m*/*z* 73, 147, 205), 8.88 (*m*/*z* 73, 147, 190, 219), 11.76 (*m*/*z* 73, 147, 189, 292), 12.55 (*m*/*z* 73, 147, 102, 292) and 17.09 min (*m*/*z* 73, 147, 292, 219) in the chromatogram of the derivatized plasma-treated sample (Fig. 3a) are attributed to the trimethylsilyl ester derivatives of formic acid, acetic acid, glycolic acid, oxalic acid, glyceric acid, tartronic acid and tartaric acid, respectively. These are largely in agreement with the NMR spectra of the plasma-treated ribose solution.

Interestingly, the NMR and GC–MS spectra of the plasma-treated samples of glucose and sucrose are similar to those of the plasma-treated ribose sample (in Supporting information), i.e. oxidation of glucose or sucrose using DBD also generates compound 1–7 as shown in NMR and GC–MS.

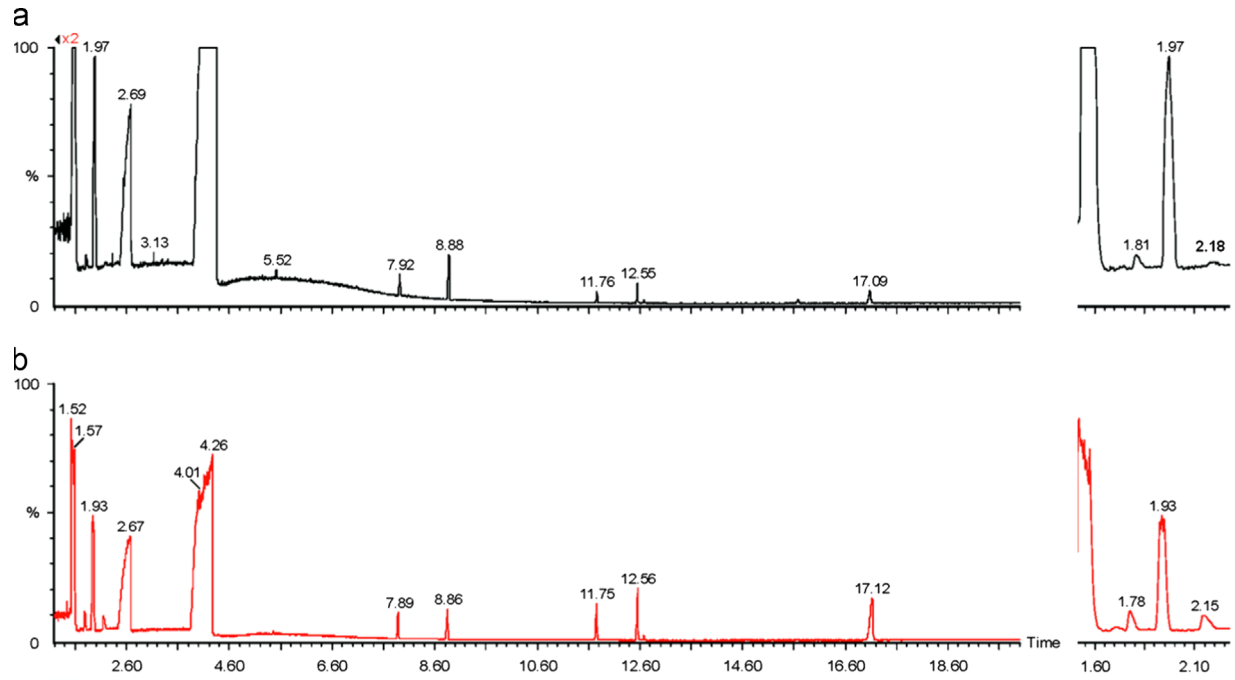

Fig. 3. GC chromatograms of the BSTFA-derivatized samples: (a) the ribose solution after a 20-min treatment with air-plasma; (b) the mixture of standards including formic acid (1.78 min), acetic acid (2.15 min), glycolic acid (7.89 min), oxalic acid (8.86 min), glyceric acid (11.75 min), tartronic acid (12.56 min) and tartaric acid (17.12 min).

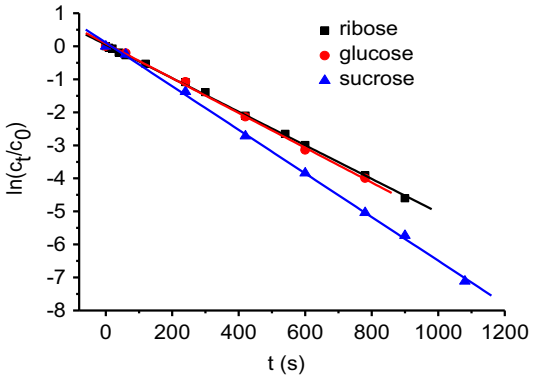

Fig. 4. First-order degradation kinetics curves of ribose, glucose, and sucrose under air-plasma treatment.

The primary reaction products further decompose on exposure to the plasma. The as-formed organic acids in the plasma-treated solutions gradually decomposed to smaller acids and eventually to CO_2 and H_2O if the exposure time is further extended. We focused on the first primary products in 3 min in this work.

3.2. Kinetics study of decomposition of ribose, glucose, and sucrose in air-plasma

The kinetics of the decomposition of ribose, glucose, and sucrose was obtained from several equal aliquots of their D_2O solutions (20 mM) that were air-plasma treated for different times. Each treated solution was immediately analyzed by using ^1H NMR to quantify the concentration of the sugars. The concentration changes of ribose, glucose, and sucrose with the air-plasma treatment time are shown in Fig. 4. All of the three curves can be well-fitted using the first-order degradation kinetics equation $\ln(c_t/c_0) = -kt$, i.e., the decomposition of ribose, glucose, and sucrose in air plasma follows the first-order kinetic law. From the slope of these plots the decomposition rate constants (k) of ribose, glucose, and sucrose under air-plasma treatment are calculated to be 5.08×10^{-3}, 5.26×10^{-3}, and $6.60 \times 10^{-3}\ s^{-1}$, respectively. The decomposition rate constants of ribose and glucose in air-plasma are comparable, while that of sucrose is slightly larger, which may be related to the structures of the sugars. Ribose ($C_5H_{10}O_5$) and glucose ($C_6H_{12}O_6$) are monosaccharides, and sucrose ($C_{12}H_{22}O_{11}$) is a disaccharide. Sucrose can readily be hydrolyzed to glucose and fructose at lower pH or under many other conditions [23–28]. In this work when sucrose was exposed to plasma, the larger kinetic constant suggests sucrose quickly decomposed to glucose and fructose first, which contributes to the overall decomposition rate of the sucrose.

3.3. Decomposition mechanisms of ribose, glucose, and sucrose under air-plasma treatment

It is known that air plasma is an ionized gas composed of UV photons, electrons, ions, electronically excited atoms and molecules, and reactive oxygen and nitrogen species (ROS and RNS), including ozone (O_3), •NO, •OH, singlet oxygen ($^1O_2$) etc [29–31]. When the solutions of ribose, glucose, and sucrose were exposed to air-plasma, hydrogen peroxide (H_2O_2), ozone (O_3), the charged species and radicals such as hydroperoxyl radicals (HO_2•), peroxynitrite ($ONOO^-$), superoxide (O_2^-), nitric oxide (•NO), and hydroxyl radicals (•OH) were generated in these solutions. Since most of the plasma-created species are strong oxidants, the sugars can be degraded via oxidation. Based on the chemicals (compounds 1–7) produced in the sugar solutions under air-plasma treatment, the reactions of the three sugars with most if not all of the plasma-created species have been examined, and as an example the reaction mechanisms of ribose under air-plasma treatment are proposed as follows.

3.3.1. Formation of formic acid, glycolic acid, glyceric acid, tartronic acid, tartaric acid, and oxalic acid

Sugars degrade via oxidation with many of the oxidative species found in plasma, such as hydroxyl radical, hydrogen peroxide, nitric acid, singlet oxygen, etc. [32–38]. With all the possible oxidations combined, Fig. 5 shows possible decomposition mechanisms of

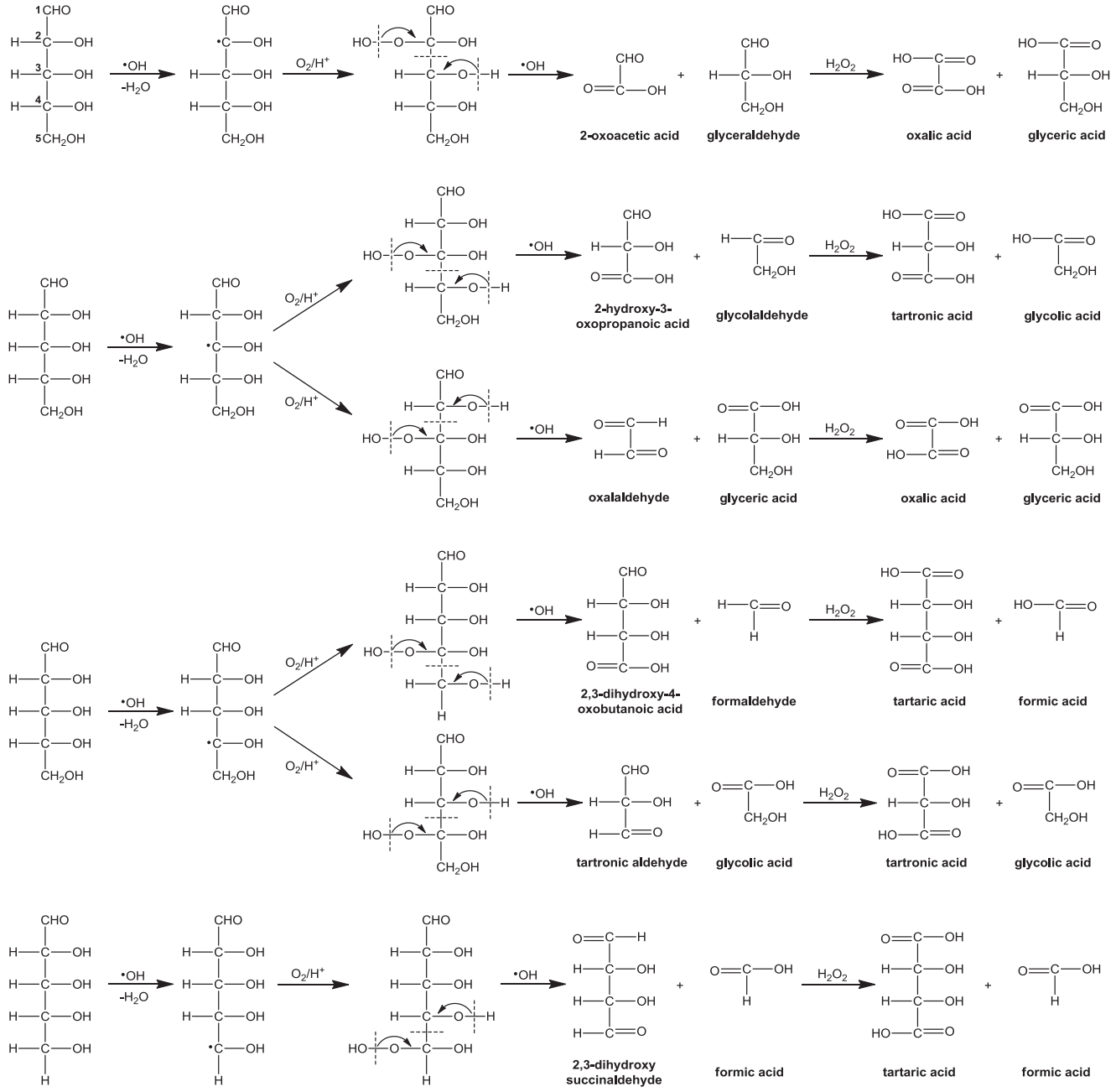

Fig. 5. Proposed mechanisms of ribose oxidized by air-plasma to form formic acid, glycolic acid, glyceric acid, tartronic acid, tartaric acid and oxalic acid.

ribose on exposure to air-plasma to form formic acid, glycolic acid, glyceric acid, tartronic acid, tartaric acid, and oxalic acid. In the presence of the oxidative species, ·OH abstracts a hydrogen atom at the C2 position of ribose to form an alkoxyl radical, followed with the addition of an oxygen to a ribose hydroperoxide. Another hydrogen abstraction occurs on the C3 position, which facilitates the homolytic cleavage of the C2–C3 bond to form a 2-oxoacetic acid and a glyceraldehyde. 2-Oxoacetic acid and glyceraldehyde are further oxidized by oxidative species in plasma such as hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) to yield oxalic acid and glyceric acid.

When the first hydrogen abstraction by a •OH occurs at the C3 position of ribose, the C3–C4 bond will break to form tartronic acid and glycolic acid via a similar mechanism; Similarly, when the first hydrogen abstraction by a ·OH occurs at the C4 position of ribose, the C4–C3 and C4–C5 bond will break to form tartaric acid, formic acid, tartronic acid and glycolic acid. The alkoxyl radical •C5, •CH(OH)CH(OH)CH(OH)CH(OH)CHO, can also be created when ribose reacts with a hydroxyl radical, which leads to the formation of tartaric acid and formic acid. The generated tartaric acid, tartronic acid, glyceric acid, oxalic acid, and glycolic acid can gradually be decomposed to smaller acids through the same mechanism, and eventually convert to CO_2 and H_2O in the presence of the oxidative species (•OH, H_2O_2 etc.) from air-plasma.

3.3.2. *Formation of acetic acid*

The NMR and GC–MS spectra show that acetic acid is a minor product of the decomposition of ribose, glucose, and sucrose under air-plasma treatment, suggesting the reactions from sugars to acetic acid are slow or through a more complicated multiple step. Hydrolysis and oxidation of sugars to formic acid, glycolic acid, and glyceric acid have been well studied [39–44], however, few has reported on the formation of acetic acid. Hayami [40] suggested that several organic acids were formed from an isomerization

process called the Lobry de Bruyn-Alberda van Ekenstein (LBAE) transformation [45], which is a series of enediol transformations. In this work when sugars are exposed to air-plasma, this mechanism seems to be used to explain the formation of acetic acid as a minor product. As an example, Fig. 6 shows the possible mechanism of acetic acid formation in the plasma-treated ribose solutions. Ribose undergoes two LBAE transformations to form 1,3,4,5-tetrahydroxypentan-2-one. The hydrogen abstraction on C3 of 1,3,4,5-tetrahydroxypentan-2-one and the following enediol transformation lead to the formation of a α-diketone (diacylcarbinol), which is isomerized into a β-diketone. The β-diketone is then cleaved into 3-hydroxy-2-oxopropanoic acid and acetic acid due to the high reactivity of diacylcarbinols.

The OH radicals seemed the major reactive species for the above proposed mechanism. The OH radicals may come from reaction of water with electrons or NO_2^+ in plasma or from decomposition of peroxynitrous acid [46–51]. Verification of the source of OH radicals will be difficult. It is highly possible that all the above mentioned sources will contribute to the formation of OH radicals. It is noteworthy that H_2O_2 may oxidize sugars. We observed that the concentration of H_2O_2 was close to 1 mM after plasma treatments for 3 min [52], however, our control experiments suggest no obvious oxidation of sugars in 1 mM H_2O_2 or 1 mM H_2O_2 and 0.07 mM HNO_2 at room temperature.

Because the produced chemicals in the three sugar solutions under air-plasma treatment are the same, the decomposition mechanisms of glucose and sucrose are expected to be quite similar to those of ribose.

3.4. Decomposition of sugars in PBS–D_2O under air-plasma treatment

The ^1H NMR spectra of the products formed in the PBS–D_2O solution of the three sugars after air-plasma treatment are the same as those of the products formed in the D_2O solution of sugars, which indicates that the decomposition mechanism of sugars under air-plasma treatment was the same in water and in buffer. However, the decomposition rates of sugars in these two solutions under air-plasma treatment show a significant difference, as shown in Table 1, since H^+ was actively involved in the reaction mechanism (Figs. 5 and 6). The most notable observation of plasma-treated solution is the decrease in pH. At 3 min of exposure to plasma, the sugar solution showed a pH around 2. It is been reported that the chemicals that contributed to acidification of aqueous solutions could be nitric acid and nitrous acid that are generated from NO_2 and NO in the plasma, respectively. HNO_2 are not detectable after 2 min treatment. Treatment of the liquid with plasma for 3 min generated approximately 5 mM of HNO_3. Our control experiments show that sugars do not react with 5 mM HNO_3 at room temperature. Thus our conclusion is that the radicals are the main contributors to the reaction mechanism, and H^+ can affect the reaction rate. PBS only slowed down the decomposition of sugars, which is due to the decrease of the concentration of H^+ in the treated PBS–D_2O solutions. The decomposition rate constant of ribose in PBS–D_2O under air-plasma treatment is $1.79 \times 10^{-3}\ s^{-1}$, estimated from the slope of the plot $\ln(c_t/c_0)$ vs t, which is approximately three times slower than that of ribose in D_2O ($k = 5.08 \times 10^{-3}\ s^{-1}$). Therefore, the decomposition rate of ribose in air-plasma displays a pH-dependence when other experimental conditions and parameters

Table 1
Decomposition rate constants (s^{-1}) of D-(−)-ribose, D-(+)-glucose, and D-(+)-sucrose in D_2O under air-, N_2- and O_2-plasma treatment and in PBS–D_2O under air-plasma treatment.

	O_2-plasma	Air-plasma	N_2-plasma	Air-plasma (PBS)
Ribose	6.24×10^{-3}	5.08×10^{-3}	3.59×10^{-3}	1.79×10^{-3}
Glucose	7.09×10^{-3}	5.26×10^{-3}	4.27×10^{-3}	2.48×10^{-3}
Sucrose	6.83×10^{-3}	6.60×10^{-3}	3.59×10^{-3}	4.39×10^{-3}

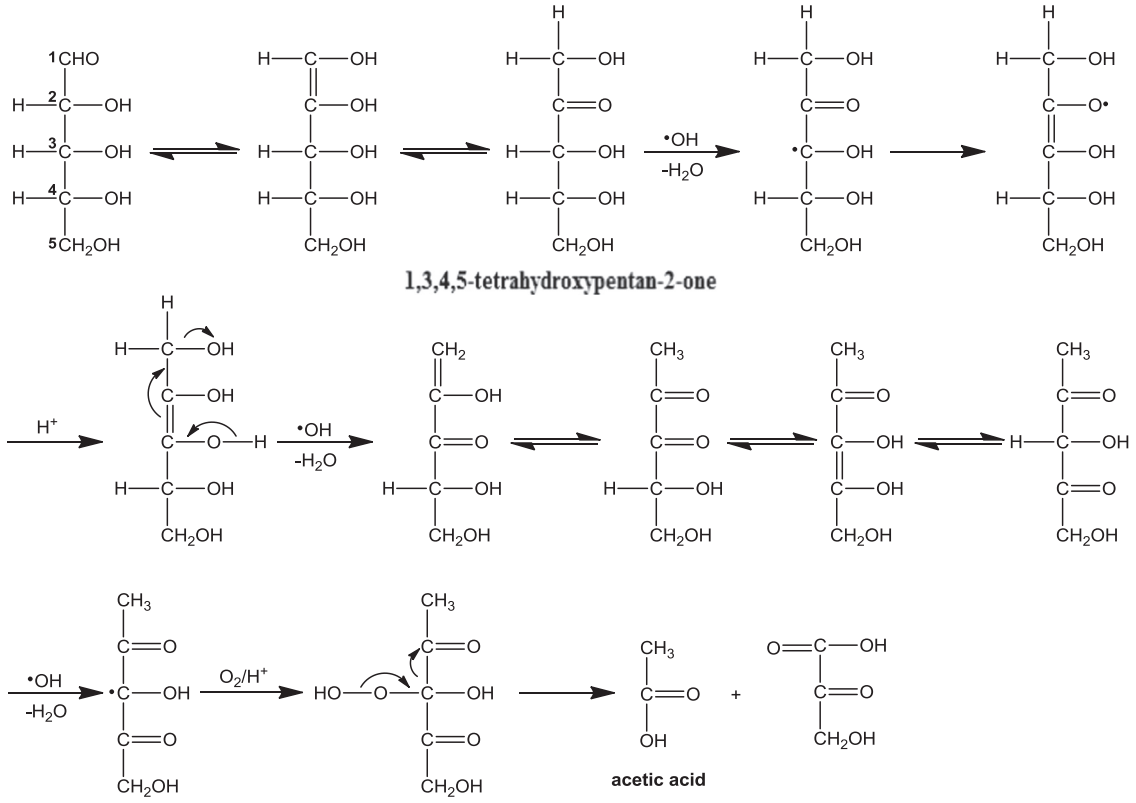

Fig. 6. Proposed mechanism of ribose decomposed by air-plasma to form acetic acid.

are the same, and the decomposition rate of ribose in air-plasma is slower in neutral buffered pH solution. Comparing the pH changes of the plasma-treated D-(−)-ribose solutions and water alone (Table 1 in the Supporting information), we concluded that the formed organic acids have little effect on the pH of the treated solutions. Since partial OH radicals may come from decomposition of peroxynitrous acid, low pH will facilitate the conversion of peroxynitrous acid to OH radicals, leading to faster kinetics of sugars in water than in buffer solutions.

The decomposition rates of glucose and sucrose in PBS–D_2O under air-plasma treatment are also slower than those in D_2O under air-plasma treatment. Table 1 summarized the decomposition rate constants.

3.5. *Decomposition of sugars under N_2-plasma and O_2-plasma treatment.*

To determine the effects of atmospheric composition on plasma treatment of D_2O solutions of sugars, samples were also treated with N_2-plasma and O_2-plasma for different times and characterized using NMR spectra after plasma treatment. The ^1H NMR spectra (in Supporting information) revealed that similar compounds were also generated when sugars solutions were treated with N_2-plasma and O_2-plasma. In O_2 or N_2 plasma, OH radicals are formed through reaction of water molecules and electrons in plasma, as shown in the following reaction.

$$H_2O \xrightarrow{e} \bullet OH + \bullet H$$

Although the products and the reaction mechanisms would be similar, detailed studies on the decomposition mechanisms of sugars in N_2-plasma and O_2-plasma are ongoing in our lab. O radicals and O_3 generated in O_2 plasma can react to form HO and HOO radicals, which are the radicals in our proposed reactions. Furthermore, the abundant O radicals and O_3 can also react with sugars, which may be the reason for faster kinetics in O_2 plasma than that in air plasma.

$$O_2 + O\bullet \rightarrow O_3$$
$$O_3 + \bullet OH \rightarrow O_2 + OOH\bullet$$
$$O_3 + \bullet H \rightarrow O_2 + OH\bullet$$

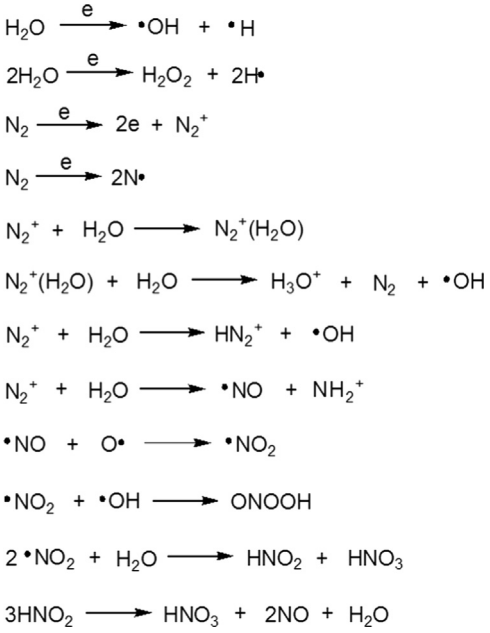

Fig. 7. Chemical reactions in water treated with N_2-plasma.

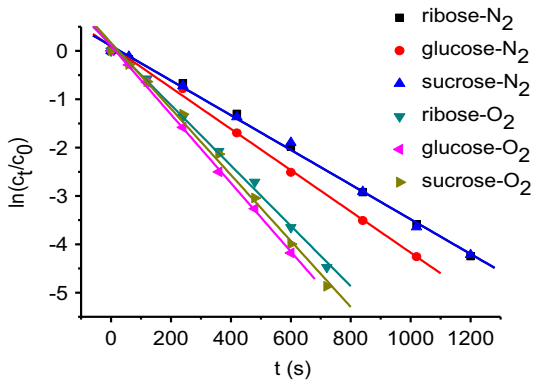

Fig. 8. First-order degradation kinetics curves of ribose, glucose, and sucrose under N_2- and O_2-plasma treatment in water.

The scheme in Fig. 7 shows possible reactions in water when water was treated with N_2-plasma. Both reactive oxygen species (OH radical and H_2O_2) and reactive nitrogen species (N, NH, NO and NO_2 radicals) are generated. OH radicals are formed through two pathways: (1) reaction of water molecules with electrons in plasma, and (2) reaction of water molecules with N_2^+ in plasma. We hypothesized that the formation of the OH radicals was the main contributor to the decomposition products of sugars, which followed the same reaction mechanisms in air plasma.

It is noteworthy that the end products discussed in our study were only main products we observed. There are indeed more chemical species in the treated solutions, which should have come from different decomposition mechanisms. However, the concentrations of those species were too low to be readily characterized now so they are neglected because of their low concentrations.

The concentration changes of sugars with time under N_2-plasma and O_2-plasma treatment also obey the first-order degradation kinetics law, as illustrated in Fig. 8. The decomposition rate constants of sugars in N_2-plasma and O_2-plasma are calculated and shown in Table 1. For all three cases, the decomposition rates of sugars in N_2-plasma are the smallest, and the rates in O_2-plasma are the highest, indicating that the reactive oxygen species play a more significant role in the decomposition of sugars under plasma treatment. The results also suggest that the nitrogen active species are less reactive than oxygen active species.

4. Conclusion

Our work provides insight on the products formed from non-thermal plasma treatment of ribose, glucose, sucrose, including formic acid, glycolic acid, glyceric acid, tartronic acid, tartaric acid, acetic acid, and oxalic acid. The decomposition mechanisms of sugars under the DBD plasma were proposed.

Reactive oxygen species play a more significant role in the decomposition of sugars under plasma treatment. In reactive oxygen species, the OH radicals seemed the major reactive species for the sugar decomposition, although peroxynitrite, O radicals, and O_3 may play a role. Our results also suggest that the nitrogen active species are less reactive than oxygen active species. Lower pH facilitate the decomposition of sugars, which may be due to further generation of reactive oxygen species, especially OH radicals under lower pH.

The results will aid in understanding the mechanisms and overall effects of the plasma acting on biological species and to expand the applications of non-thermal plasma in medicine.

Conflict of interest

All the authors worked at Drexel university, so the conflict of interest will be Drexel. No other conflict of interests related to this work.

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