Oxidation–Reduction of Maleic Acid Induced by Argon–Hydrogen Plasma-Jet

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Plasma-jet in aqueous solutions is known to disproportionate water to give hydrogen and hydroxyl radicals. Maleic acid, which is a carbon–carbon double bond bearing dicarboxylic acid, underwent addition of hydrogen, hydrogen plus hydroxyl, hydroxyl species under an argon–hydrogen plasma-jet. Maleic acid (10 mM) yielded 42% succinic acid (dihydrogenated product) under an argon–hydrogen (1.5 and 0.5 L min^{-1}) plasma-jet. This demonstrates an effective reduction method for maleic acid by plasma-jet in aqueous solutions.

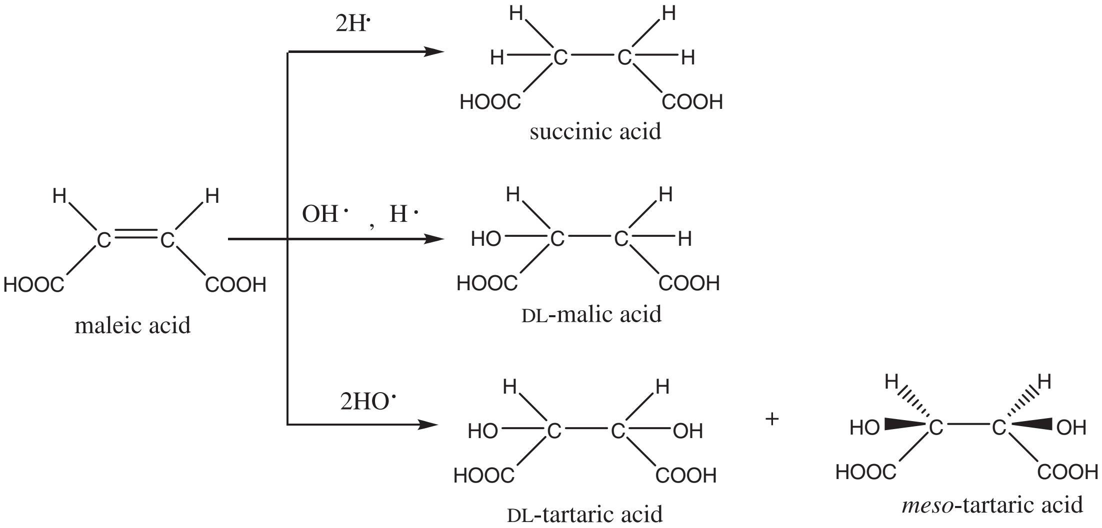
Plasma-induced reactions in gaseous, solid, and aqueous phases have been reported in the literature.[1–6] Reactions induced by plasma in aqueous solutions start with disproportionation of water molecules to hydrogen and hydroxyl radicals as shown in Scheme 1. These radicals catalyze various reactions: carbonium ion formation by hydrogen abstraction, carbon–carbon bond formation between carbon radicals, oxidation reactions by hydroxyl radicals, and so on. However, compared to glow discharge[7,8] into aqueous solutions, the reactions by hydrogen radicals have not been well investigated. This study uses argon plasma-jet[9] containing hydrogen gas in the gas mixture for the redox reaction of carbon–carbon double bonds. Maleic acid has one carbon–carbon double bond and two carboxylic groups. Therefore, as shown in Scheme 2, maleic acid can be transformed to succinic acid, malic acid, and tartaric acid by hydrogen radicals, hydrogen plus hydroxyl radicals, and hydroxyl radicals, respectively. The substrate would be useful for evaluating the effects of hydrogen and hydroxyl radicals.

Experimental

Chemicals. Maleic acid for reactions, malonic acid, and acetic acid were purchased from Wako Pure Chemical Industries. Succinic acid, L-tartaric acid, *meso*-tartaric acid, and dimethyl sulfate were purchased from Nacalai Tesque. Malic acid was received courtesy of Fuso Chemical Co., Ltd. Boron trifluoride methanol complex was purchased from Tokyo Chemical Industry Co., Ltd.

$$\mathrm{H{-}OH} \xrightarrow{\text{plasam-jet blowing}} \mathrm{H}\cdot \; + \; \cdot\mathrm{OH}$$

Scheme 1. Disproportionation of water to hydrogen and hydroxyl radicals



Scheme 2. Oxidation–reduction of maleic acid induced by hydroxyl and hydrogen radicals.

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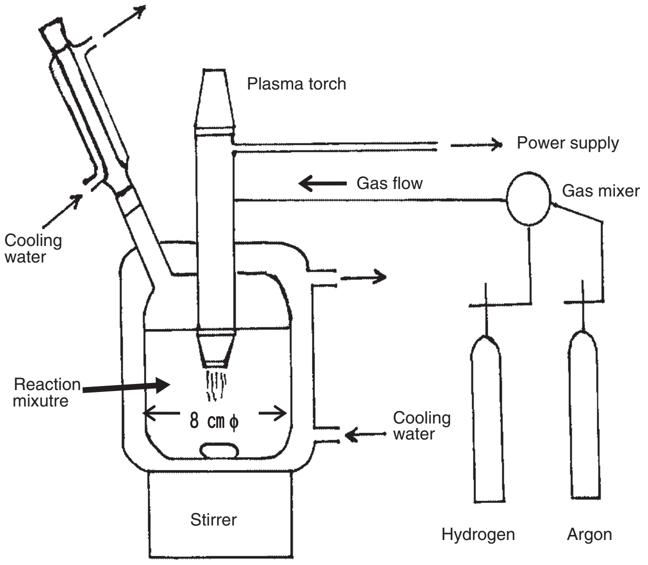


Figure 1. Apparatus for argon–hydrogen plasma-jet reactions into aqueous solutions. Volume of the reaction solution: 300 mL.

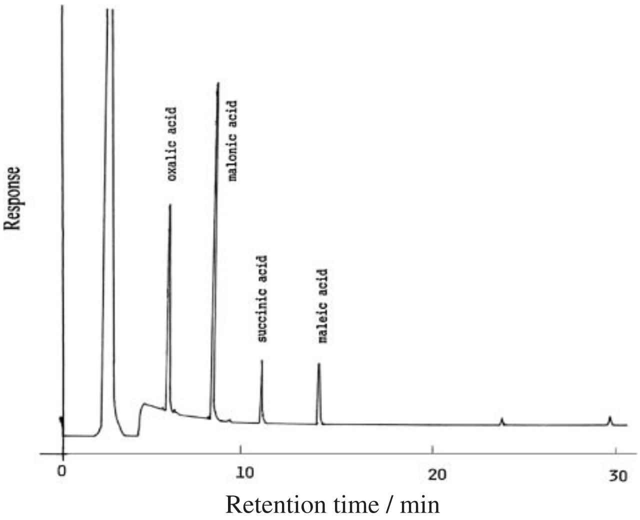


Figure 2. A typical gas chromatogram of methyl esters derived from organic acids contained in a reaction mixture. Column: FFAP glass capillary column (25 m × 0.25 mm i.d.); Temperature program: 90 to 180 °C (3 °C min^{-1}); Carrier gas: helium.

Reaction Apparatus and Reaction Conditions. The apparatus for the plasma-jet reaction is shown in Figure 1. The plasma torch was immersed into the reaction solution inside of the reaction vessel. The reaction vessel and the solution were cooled by circulating water in the outside of the vessel. The reaction apparatus has another vent leading outside of the vessel. A Liebig condenser was attached to the vent for cooling the water vapor of the reaction solution. The plasma torch was made by Nippon Welding Co., Ltd. The current and voltage were maintained at 30 A and 10 V. The total flow rate of the gas mixture introduced into the plasma torch was 2.0 L min^{-1} to mix the reaction solution.

Analysis of Maleic Acid, Malic Acid, DL-Tartaric Acid, Malonic Acid, and Acetic Acid. The solution taken from the reaction mixture was analyzed by means of reversed-phase high-performance liquid chromatography. A Jasco TRI ROTAR-V flow pump, a Jasco UVDEC-100-IV detector, and a TSK gel ODS-80TM (4.6 mm i.d. × 250 mm) column were used for analyses. The eluant (50 mM ammonium phosphate pH 2.4) flowed at a constant rate of 0.3 mL min^{-1}. The eluted solution was detected at 210 nm absorbance.

Method for Analysis of *meso*-Tartaric Acid. Sample solution (1 mL) taken from the reaction solution was lyophilized to dryness. The resulting residue was dried in a desiccator under vacuum overnight in the presence of diphosphorus pentaoxide and was followed by esterification using boron trifluoride methanol complex (0.5 mL) at 70 °C for 30 min. The reaction mixture was diluted to 5 mL using distilled water. The solution was analyzed by means of the HPLC system described above using 10% acetonitrile in water.

Analysis of Succinic Acid and Oxalic Acid. A 2 mL portion of the diluted solution described in the analysis of *meso*-tartaric acid was extracted with benzene (1 mL × 4), and the extracted benzene solution was analyzed with a Hitachi 163 gas chromatograph equipped with a 5% FFAP glass capillary column (3 mm i.d. × 3 m, GL Sciences, Inc.). Detection was carried out by a flame ionization detector. The injection port temperature was 180 °C. The column temperature was programmed from 90 to 180 °C at a rate of 3 °C min^{-1}.

Analysis of Carbon Dioxide. The gas flowing out from the reaction vessel was passed through a barium hydroxide ($Ba(OH)_2$) solution. Carbon dioxide was quantified by back titration.

Results and Discussion

Ratio of Hydrogen to Argon in the Plasma-Jet. Figure 2 shows a gas chromatogram of standard methyl esters of maleic acid, succinic acid, oxalic acid, and malonic acid. These compounds were separated completely on the gas chromatogram.

The analytical method was applied to determine the concentration of maleic and succinic acids under the plasma-jet with different ratios of hydrogen to argon (hydrogen–argon: 0, 2.0 (0%); 0.1, 1.9 (5%); 0.3, 1.7 (15%); 0.5, 1.5 L min^{-1} (25%)). The hydrogen ratio of 25% was the maximum ratio to generate a stable plasma-jet. When pure argon in the plasma-jet was used for the reaction, hydrogenated product, succinic acid reached a maximum yield (8%) in 20 min as shown in Figure 3a. On the other hand, when a mixture (25% hydrogen) of argon–hydrogen was used for the reaction, the yield of succinic acid reached 42% in 80 min as shown in Figure 3b. The substrate maleic acid disappeared by a reaction time of 60 min (argon plasma) and 80 min (argon–hydrogen mixture (25% hydrogen) plasma), respectively. The decrease of the substrate was faster under argon than argon–hydrogen plasma-jet and the increase of product was faster under argon–hydrogen than argon plasma. What caused the difference seemed to be the additional hydrogen radical provided from argon–hydrogen plasma.

Figure 4 shows the dependence of yield of succinic acid on the ratio of hydrogen to argon in the plasma-jet. The reaction time at which the yield of succinic acid achieved the maximum

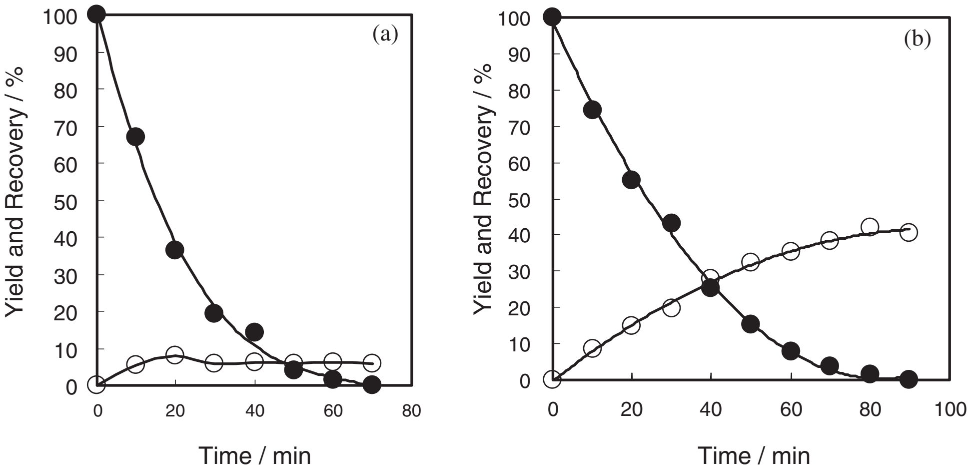


Figure 3. Yield of succinic acid (○) and recovery of maleic acid (●) in the reactions induced by pure argon plasma (a) and 75% argon–25% hydrogen plasma (b) into 10 mM maleic acid.

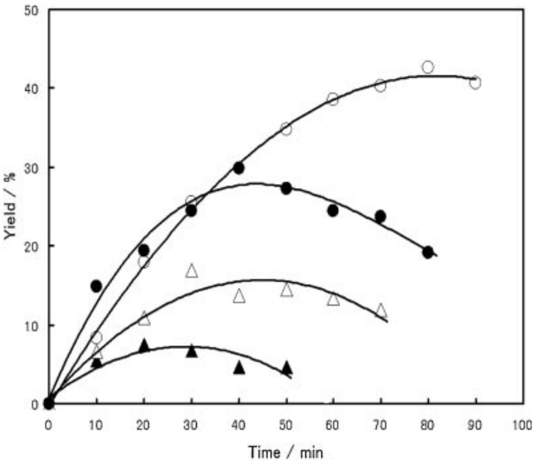


Figure 4. Succinic acid formation in 10 mM maleic acid induced by argon–hydrogen plasma at different ratios as follows: (▲), pure argon; (△), 95% argon–5% hydrogen; (●), 85% argon–15% hydrogen; (○), 75% argon–25% hydrogen.

became later with a higher rate of hydrogen to argon in the plasma-jet. In the case of 25% hydrogen plasma, the time proceeded and the maximum yields of succinic acid at the following times: 80 min, 42%; 40 min, 30%; 30 min, 15%; 20 min, 8%.

Concentration of Substrates. Figure 5 shows succinic acid formation induced by plasma-jet with mixtures of 75% argon–25% hydrogen in different concentrations of maleic acid. In all cases the yield of succinic acid increased with time, achieved maximum, and then decreased. The reaction time at which the yield of succinic acid achieved maximum became later with higher concentration of maleic acid in the plasma-jet. The maximum yield of succinic acid and the initial concentration of maleic acid are shown in Table 1 with the time maximum yield was achieved. The maximum yield of succinic acid did not depend on the initial concentration of maleic acid.

Oxidative Products. Instead of using GC for the analysis of reduction product succinic acid, oxidative products (acetic acid, tartaric acid, malic acid, and malonic acid) were analyzed by HPLC. Figure 6 shows a HPLC of standard methyl esters of maleic acid, succinic acid, oxalic acid, and malonic acid. These compounds were separated completely by HPLC. The oxidative products obtained from the reactions using argon plasma and argon–hydrogen plasma are shown in Figures 7a and 7b, respectively.

The plasma-jet using pure argon gave 13% malonic acid at 50 min as shown in Figure 7a. Malonic acid has three carbons

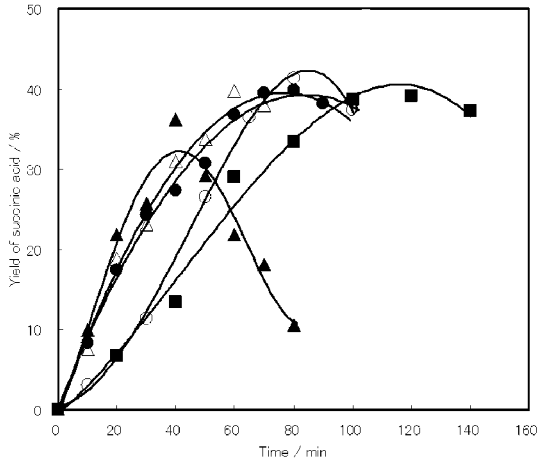


Figure 5. Succinic acid formation induced by 75% argon–25% hydrogen plasma in different concentrations of maleic acid as follows: (▲), 1; (△), 5; (●), 10; (○), 50; and (■), 100 mM.

Table 1. Maximum Yield of Succinic Acid and the Initial Concentration of Maleic Acid

Initial concentration of maleic acid/mM	Maximum yield of succinic acid/%	Time maximum yield was achieved/min
1	36	40
5	40	60
10	42	80
50	40	80
100	40	120

and seems to be formed by the oxidation of an alfa carbon of maleic acid followed by decarboxylation. Maximum yields of malic acid, DL-tartaric acid, and *meso*-tartaric acid were obtained in 5.5%, 3.0%, and 1.5% at 20 min, respectively. However, maximum yield of oxalic acid was obtained in 7.0% at 40 min. The time delay could mean that oxalic acid was formed by the oxidative degradation of malic acid, DL-tartaric acid, acetic acid, and/or *meso*-tartaric acid. Although other research[10,11] on argon plasma jet reactions has shown the pathway of oxalic acid formation through acetic acid from malonic, a detailed reaction mechanism cannot be proposed at this stage.

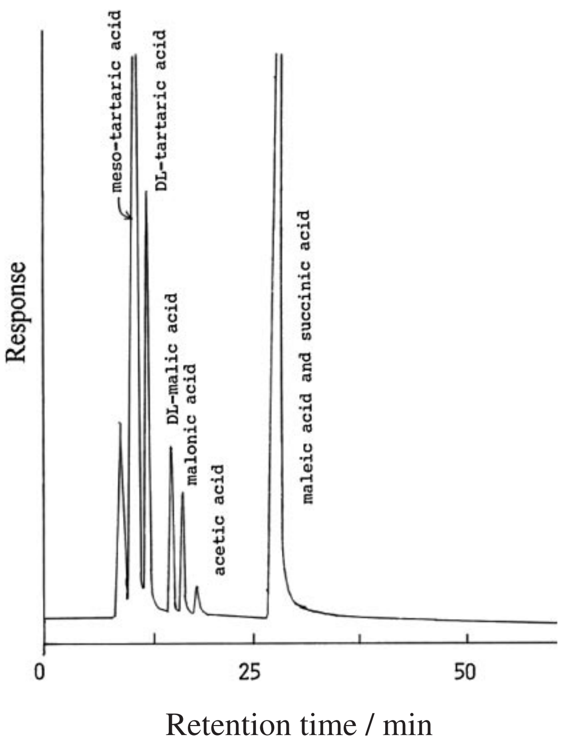


Figure 6. A reversed-phase high performance liquid chromatogram of organic acids contained in the reaction solution. Column: TSK gel ODS-80TM (250 mm × 4.6 mm i.d.); Buffer: 50 mM $NH_4H_2PO_4$; Flow rate: 0.3 mL min^{-1}; Detection: UV at 210 nm.

The plasma-jet using 25% hydrogen in argon gave little oxidative product compared with those in argon only as shown in Figure 7b. Even malic acid, the yield of which was the highest among the oxidative products, gave a maximum yield of only 5.5%. Other products were obtained in less than 2% yield. In particular, *meso*-tartaric acid was not detected under these reaction conditions. A plausible mechanism is shown in Scheme 3. The series of reactions would start with the addition of hydroxyl radical to the C–C double bond. The resulting first radical intermediate (intermediate 1) may be in equilibrium with the second radical intermediate (intermediate 2). The intermediate 1 yields DL-tartaric acid by coupling with a hydroxyl radical and also yields DL-malic acid by coupling with a hydrogen radical, respectively. Although intermediate 2 yields *meso*-tartaric acid, it can also be produced by hydrogen abstraction from DL-malic acid. In this case, there are two pathways for the formation of intermediate 2 that leads to *meso*-tartaric acid. However, *meso*-tartaric acid was not detected in the reaction using 75% argon–25% hydrogen plasma. This suggests that 75% argon–25% hydrogen plasma is not effective for the abstraction of hydrogen radical from malic acid to afford intermediate 2. Malonic acid would be formed by the hydroxylation of the intermediate 1, and the acetic acid from the decarboxylation of malonic acid. Oxalic acid was detected in lower yield than that in the reaction using pure argon plasma.

Degradation of Succinic Acid, DL-Malic Acid, and DL-Tartaric Acid. Although maleic acid can be converted into succinic acid, malic acid, and tartaric acid, these products undergo oxidative degradation to give several by-products. Degradation of succinic acid must proceed during the formation of succinic acid induced by the plasma-jet. Degradation of

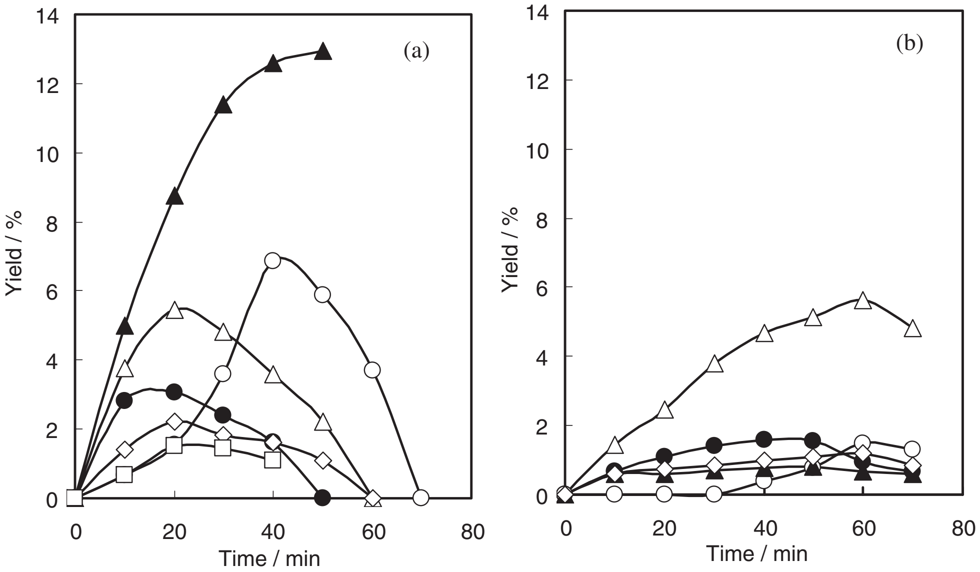
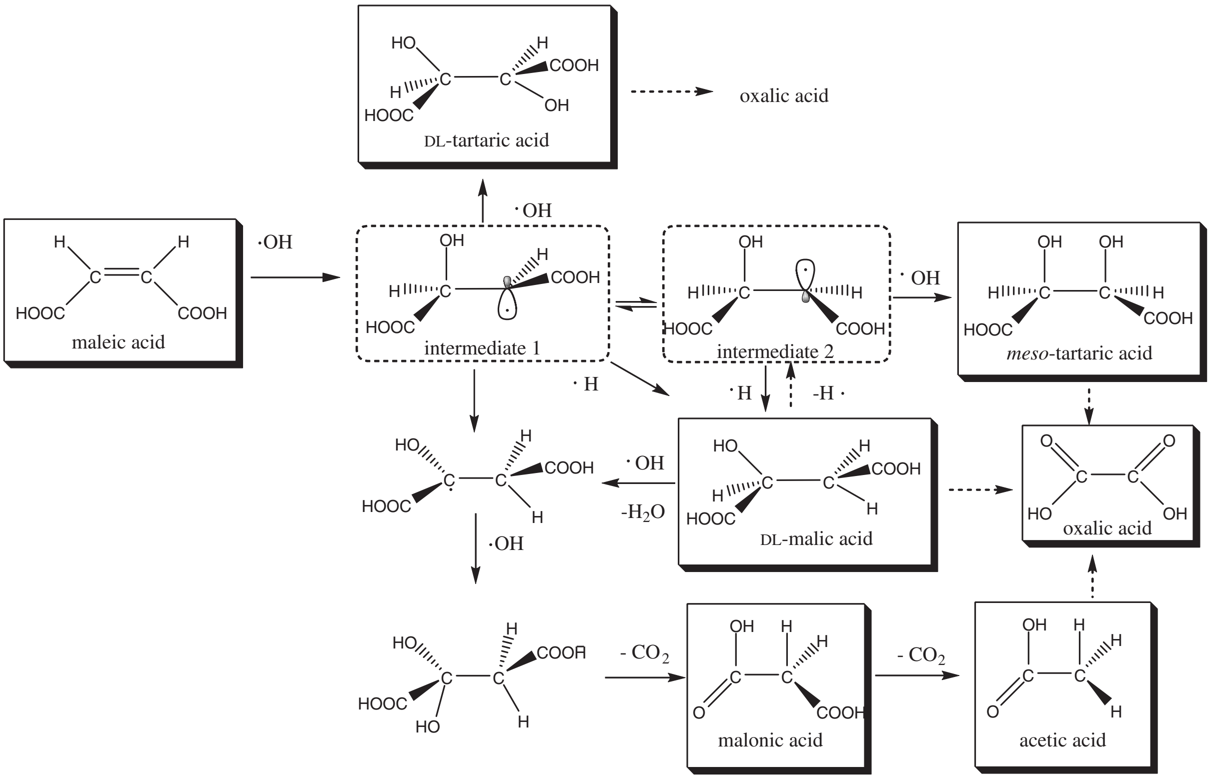


Figure 7. Oxidative products in the reaction solution of 10 mM maleic acid induced by pure argon (a) or 75% argon–25% hydrogen (b) plasma. Oxidative products are as follows: (▲), malonic acid; (△), malic acid; (○), oxalic acid; (●), DL-tartaric acid; (◇), acetic acid; and (□), *meso*-tartaric acid.



Scheme 3. Plausible mechanism for the formation of oxidative products.

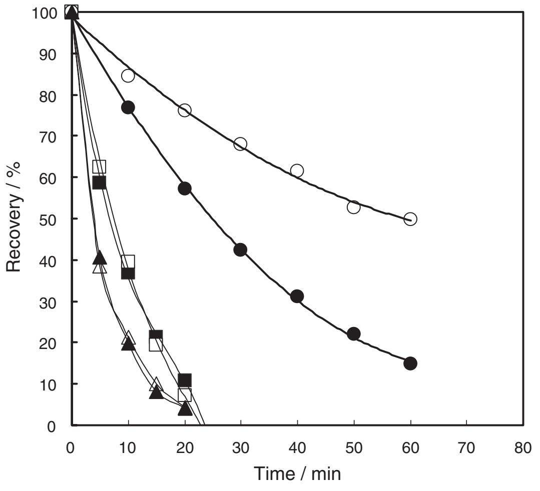


Figure 8. Degradation of succinic acid (●, ○), DL-malic acid (■, □), and DL-tartaric acid (▲, △) induced by pure argon plasma (●, ■, ▲) or 75% argon–25% hydrogen plasma (○, □, △). Concentration of substrates: 10 mM.

succinic acid (10 mM), DL-malic acid (10 mM), and DL-tartaric acid (10 mM) were examined by argon (a) or argon–hydrogen (25%) (b) plasma as shown in Figure 8. Figure 8 shows that succinic acid can be consumed slower than both malic acid and DL-tartaric acid under the plasma-jet conditions.

Conclusion

This research demonstrated that an argon–hydrogen plasma-jet in aqueous solutions of maleic acid (10 mM) gave succinic acid up to 42% as a reduction product using a plasma-jet containing 75% argon and 25% hydrogen. This shows that argon–hydrogen plasma-jets can be used to reduce carbon–carbon double bonds in good yields. This method can also cause an oxidation–reduction of carbon–carbon double bonds to give DL-malic acids by hydroxyl and hydrogen radicals as well as tartaric acid by hydroxyl radicals. This research also suggests a mechanism of oxidation–reduction of other products.

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