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Reduction Of Mono-Alkene-Bearing Monocarboxyl And Monoamino Groups By Argon-Hydrogen Plasma Jet

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ABSTRACT

Many plasma-induced reactions which take place in gas, solution, and solid phases are reported in the literatures. Plasma-induced reactions in aqueous solutions have been investigated by Harada and coworkers. The mechanism of the plasma-induced reactions has been explained by oxidation-reduction, and by hydroxyl and hydrogen radicals formed from water molecules. Recently, oxidation-hydrogenation reactions of the carbon-carbon double bond in maleic acid to form succinic, malic, and tartaric acids have been reported. This paper describes the hydrogenation of acrylic acid, crotonic acid, vinylacetic acid, allylamine, and methionine sulfoxide induced by an argon-hydrogen plasma jet. Acrylic acid and crotonic acid were hydrogenated by the action of argon-hydrogen plasma to afford propanoic acid (48%) and 1-butanoic acid (51%), respectively.

Keywords: Plasma jet, Mono-alkene-bearing monocarboxylic acid, Reduction, Argon-hydrogen

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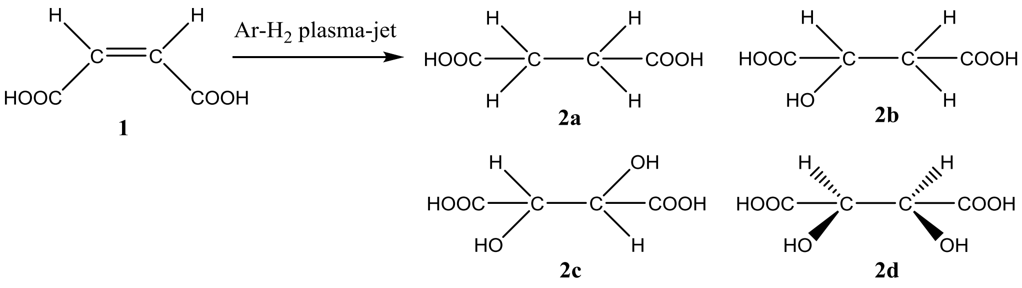
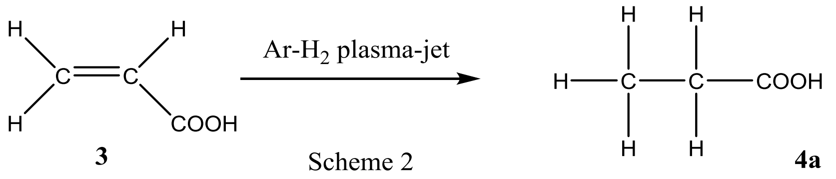
INTRODUCTION

Plasma-induced reactions have been investigated for several decades from the viewpoints of fundamental research and industrial applications [1-4]. The types of plasma-induced reactions can take place in gasses, solutions, solid phases, and their phase boundaries. The gaseous, solution, and phase boundary reactions are relevant to organic syntheses [1-2, 4] and simulation of prebiotic reactions. Harada and coworkers [5-19] have investigated the reactions in solution phase and the phase boundary between gas and solution using glow discharge [5-8, 11-12, 14-17], flame [11], and plasma jet [9-11, 13, 18-19], for both purposes. Plasma jet is an application of the arc plasma phenomenon to produce a jet flow from a torch. This type of reaction can accelerate oxidation, reduction, amination, carboxylation, and other reactions [9-11, 13, 18-19]. It is thought that these reactions commence with the dissociation of water molecules to form hydroxyl and hydrogen radicals [18]. These radical species withdraw hydrogen from carbon-hydrogen bonds to form carbon radicals that undergo hydroxylation, hydrogenation, carboxylation, and other reactions [11]. Oxidation and reduction of the carbon-carbon double bond in maleic acid (**1**) have been also carried out using a glow discharge [8] and an argon- hydrogen plasma jet [19] to afford succinic acid (**2a**), malic acid (**2b**), DL-tartaric acid (**2c**), and meso-tartaric acid (**2d**) (Scheme 1).

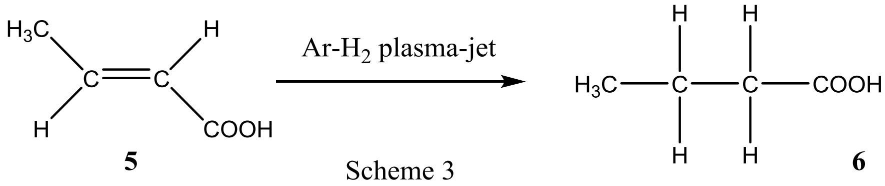


Scheme 1

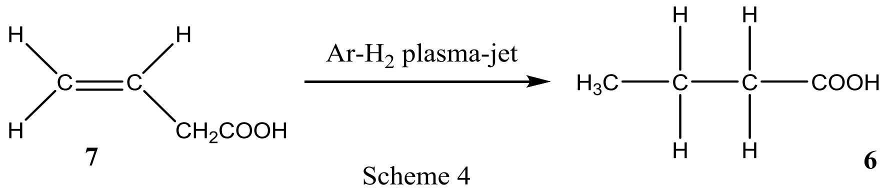
This research addresses the reduction of mono-alkene-bearing monocarboxyl (**3, 5, 7**) and monoamino groups (**8**) by argon-hydrogen plasma jet blowing into aqueous solutions to demonstrate the effectiveness of reduction by an argon-hydrogen plasma jet (see Schemes 2 to 5).



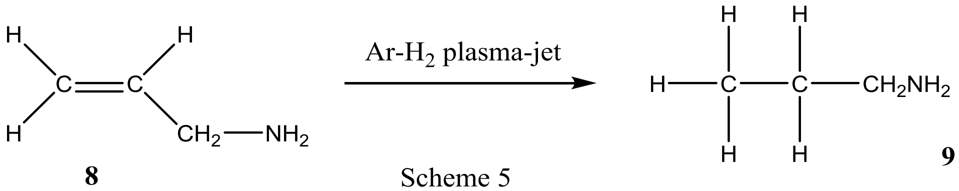
Scheme 2



Scheme 3



Scheme 4



Scheme 5

Experimental

Substrates (acrylic acid (**3**), crotonic acid (**5**), vinylacetic acid (**7**), and allylamine (**8**)) and the standard compounds (**4, 6, 9**) of reaction products were purchased from Tokyo Chemical Industry Co., Ltd.

The apparatus used for the reactions induced by an argon-hydrogen plasma jet is shown in Fig. 1. A plasma jet generator Well Pen NP-7 (Nippon Welding Co.), through a stream of an argon-hydrogen gas mixture, was used as the energy and hydrogen source for the reactions. A plasma torch incorporating a tungsten rod cathode (100 mm × 2.5 mm I.D.) and a copper nozzle anode (1.8 mm I.D.) was immersed from the central vent into a reaction solution (300 mL) containing a substrate compound in a cylindrical reaction vessel. The reaction vessel was a double-walled structure in which the inner chamber contained the reaction solution and the outer chamber contained circulating water to cool the reaction solution. The reaction temperature was maintained at 30 °C by this cooling system. The reaction vessel had another vent to which a Liebig condenser was connected. The argon-hydrogen flow rate was controlled at 2.0 mL/min.

After bubbling argon gas into the reaction solution to remove dissolving oxygen, the plasma jet at the torch was introduced into the reaction solution. A small amount of the reaction solution was removed every ten minutes for analysis.

The removed reaction solution was acidified with 1M-HCl and the resulted solution was extracted with ether. To the ether extract was added a diazomethane solution in ether for methyl esterification. Methyl esters of carboxylic acids in the ether solution were analyzed by means of a Hitachi-163 gas chromatograph equipped with an OV-1 glass packed column (1.5 m × 3 mm I.D.) using nitrogen as the carrier gas. Detection was performed with a flame ionization detector. Allylamine and propylamine were analyzed with a Hitachi 835 amino acid analyzer.

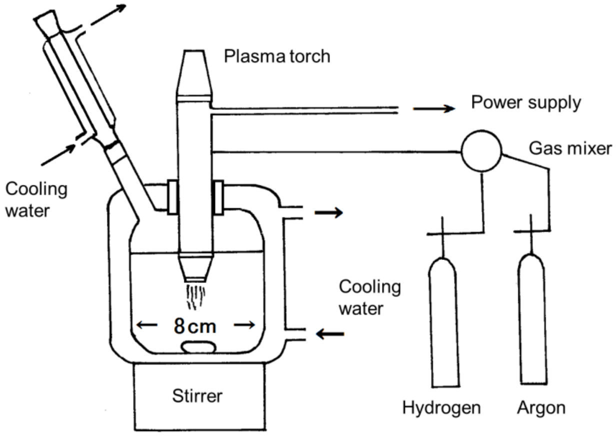


Fig 1: Apparatus for argon–hydrogen plasma jet blowing.
A plasma jet generator Well Pen NP-7 (Nippon Welding Co. Ltd.), through a stream of an argon–hydrogen gas mixture (argon–hydrogen: 2.0–0.0, 1.9–1.0, 1.7–0.3, and 1.5–0.5 L/min), was used as the energy and hydrogen source for the reactions.

RESULTS AND DISCUSSION

A plasma jet was blown into an aqueous solution containing 0.1 M acrylic acid at a controlled flow rate: argon 1.5 L/min and hydrogen 0.5 L/min. The power supply was maintained at 30 A and 15 V during plasma jet blowing. The remaining acrylic acid and the yield of propionic acid are shown in Figure 2. Acrylic acid (**3**) rapidly decreased with time until depletion of the substrate at 90 min. Propionic acid (**4a**) formed over time with a maximum yield of 33% at 60 min, and gradually decreased afterwards.

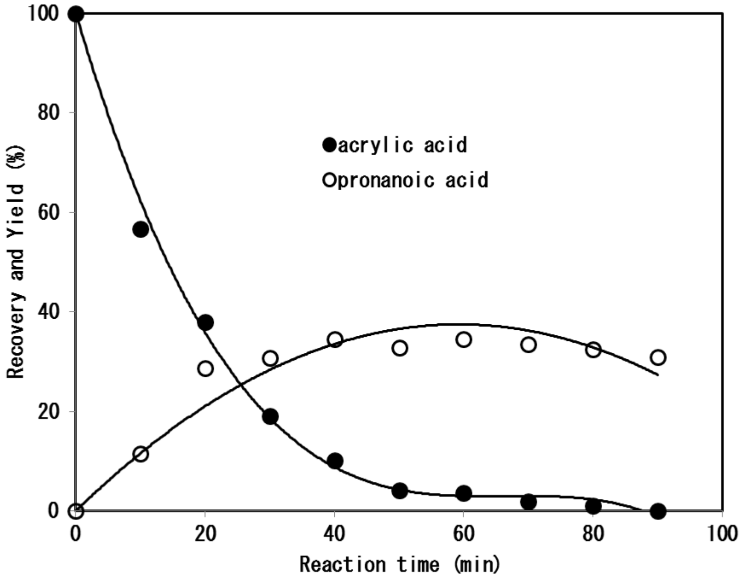


Fig 2: Formation of propanoic acid from an aqueous solution of acrylic acid (100mM) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 1.5 L/min and hydrogen 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: acrylic acid, ○: propanoic acid.

Figure 3 shows the correlation between the maximum yield of propionic acid (**4a**) and the flow ratio of argon and hydrogen. The total flow was set at 2 L/min. A flow rate of 1.5-0.5 L/min argon-hydrogen, which contains the highest hydrogen flow rate to generate a plasma jet stably using the generator (Wen Pen NP-7), gave the maximum yield (33%) at 60 min. The maximum yield decreased at lower hydrogen ratios, as follows: 30% at 50 min when the flow rate was 1.7-0.3; 25% at 40 min when the flow rate was 1.9-0.1; and 5% at 10 min when the flow rate was 2.0-0.0 L/min. However, even when the hydrogen flow rate was 0.0 L/min, the yield of obtained propionic acid (**4a**) was 5%. Argon plasma jet, even without hydrogen, can reduce the carbon-carbon double bond of acrylic acid (**3**) due to the formation of hydrogen radicals by the disproportionation of water molecules.

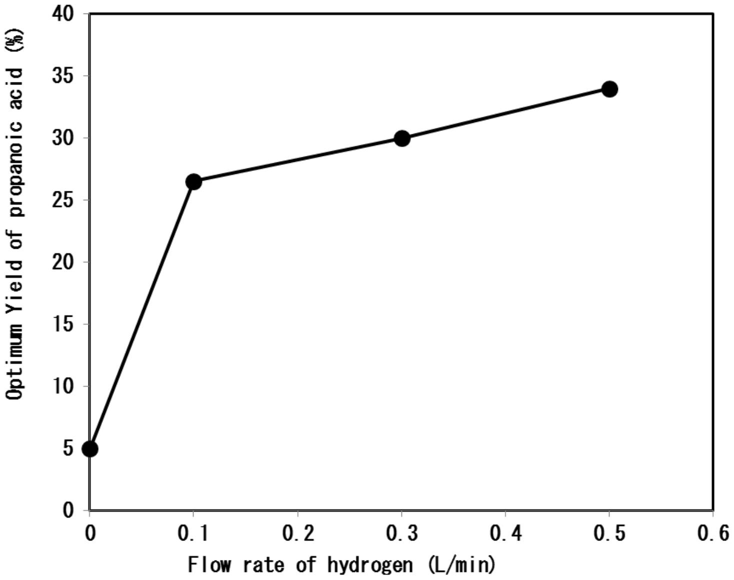


Fig. 3: Correlation between the flow rate of hydrogen and the optimum yield of propanoic acid from an aqueous solution of acrylic acid (0.1 M) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 1.5 L/min and hydrogen 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V.

Figure 4 shows the correlation between the maximum yield of propionic acid and the initial concentrations of acrylic acid (**3**). The maximum yield of propanoic acid (**4a**) achieved by plasma jet blowing at these different concentrations was plotted against the initial concentrations, set at 1, 5, 10, 50, and 100 mM. The highest maximum yield (48%) was obtained in the case of 10 mM at 60 min. The results in Figures 3 and 4 show the optimum conditions for the formation of acrylic acid (**3**) were the following: flow rate of argon-hydrogen 1.5-0.5 L/min and concentration of acrylic acid (**3**) 10 mM.

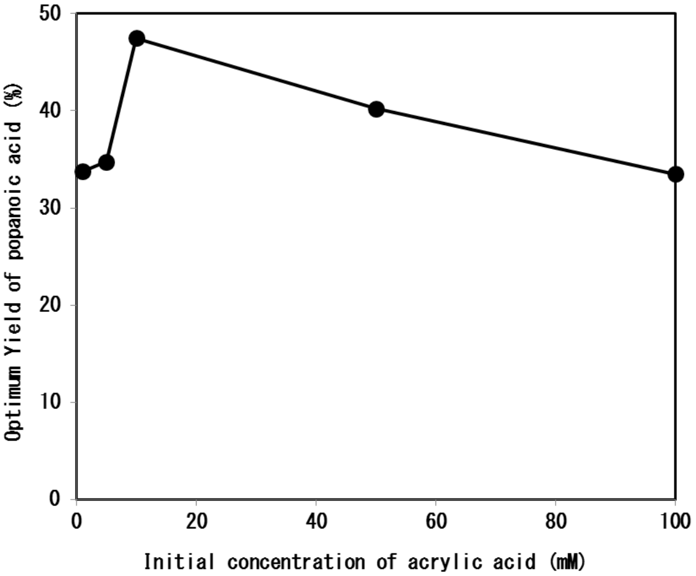


Fig. 4: Correlation between the initial concentration of acrylic acid and the optimum yield of propanoic acid at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 1.5 L/min and hydrogen 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively.

Figure 5 shows the time course of propionic acid (**4a**) formation and the decrease in acrylic acid under the optimum reaction conditions (argon-hydrogen 1.5-0.5 L/min, acrylic acid (**3**) 10 mM).

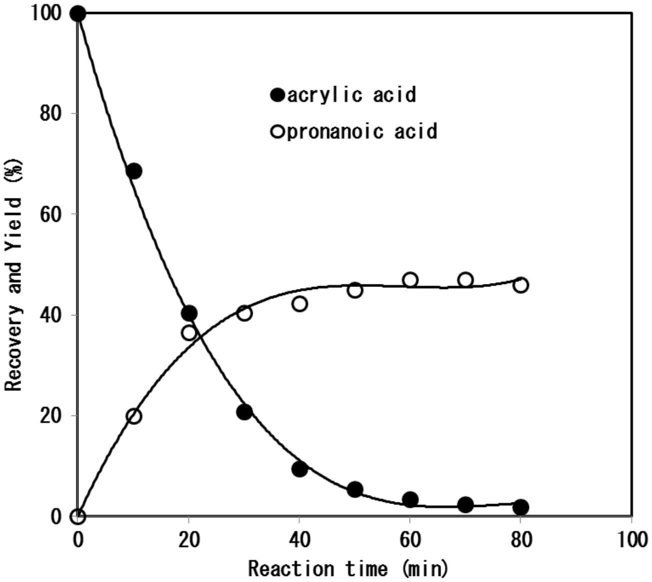


Fig. 5: Formation of propanoic acid from an aqueous solution of acrylic acid (10mM) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 1.5 L/min and hydrogen 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: acrylic acid, ○:propanoic acid.

Figure 6 shows the time course of the reaction of argon plasma jet blowing into 10 mM acrylic acid. Although the reaction conditions were not suitable for the hydrogenation of the carbon-carbon double bond due to no hydrogen, oxidation proceeded due to the hydroxyl radicals, formed by the disproportionation of water molecules. Results in Figure 6 show a low yield of propionic acid (**4a**) (5.5%) at 10 min and the formation of acetic acid (**4h**) (1.5%). The low yield of propionic acid (**4a**) could be explained by the oxidation mechanism shown in Scheme 6.

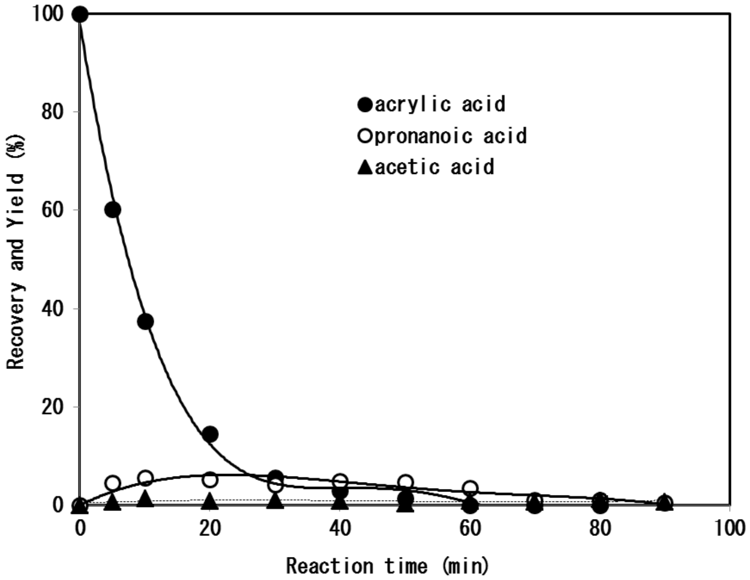
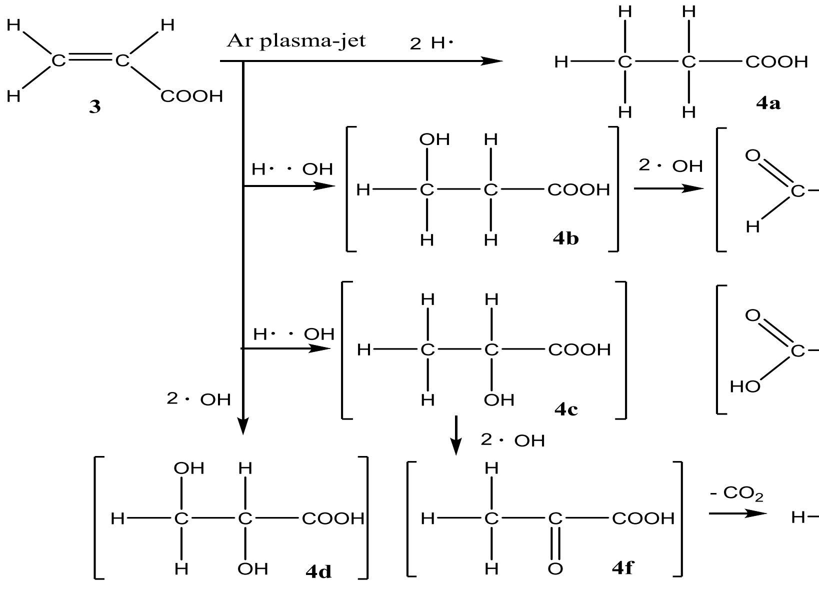


Fig. 6: Formation of propanoic acid from an aqueous solution of acrylic acid (10mM) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 2.0 L/min and hydrogen 0.0 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: acrylic acid, ○: propanoic acid, ▲: acetic acid.



Scheme 6

Acrylic acid (**3**) seems to undergo hydrogenation, hydration, and hydroxylation to form compounds **4a-d**.The dissociation of water molecules to hydrogen and hydroxyl radicals by contact glow discharge [17] and argon plasma jet [18] is reported in the literature [17, 18]. The formation of compounds **4a-d**, induced by argon-hydrogen plasma jet, is supported by the results of the reactions of maleic acid using the same energy source [19]. The hydrogenated product **4a** was obtained in a yield of up to 48%. Although compounds **4b-d** were not analyzed by gas chromatography, the formation of acetic acid (Figure 6) suggests that its precursors (**4f** and **4g**) formed during the reaction. Compound **4b** would afford malonic acid **4g**, via aldehyde **4e**, by oxidation. This reaction pathway is an alcohol oxidation, proved by the results of the argon plasma jet blowing into an aqueous solution of propylamine [9]. 3-Hydroxyl-propanoic acid (**4c**) and malonic acid (**4g**) were detected as intermediates, leading to acetic acid (**4f**) [9]. Results of argon-hydrogen plasma jet blowing into maleic acid also support the pathway, because malonic acid (**4g**) and acetic acid (**4h**) were detected in the reaction mixture [19]. Similarly, the pathway from lactic acid (**4c**) to acetic acid (**4h**) can be explained by the stepwise oxidation in the presence of hydroxyl radicals. Compound (**4d**) may be rapidly oxidized to a carbonate as there are many carbon-oxygen bonds present.

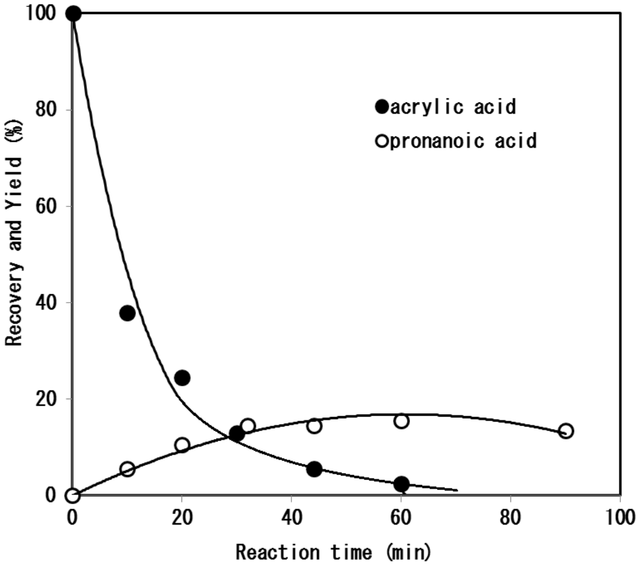


Fig. 7: Formation of propanoic acid from acrylic acid (10 mM) in 10% formic acid at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 2.0 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: acrylic acid, ○ propanoic acid.

Such oxidation reactions (Scheme 6) can be suppressed in the presence of formic acid. The higher yield (18%) of propionic acid (**4a**) at 60 min in 10% formic acid as a scavenger indicates the existence of an oxidizing agent induced by an argon plasma jet (Figure 7); the oxidized compounds shown in Scheme 6 were not detected.

Figure 8 shows the time course of the formation of 1-butanoic acid (**6**) from crotonic acid. Crotonic acid (**5**) rapidly decreased with time and had almost disappeared by 90 min, while 1-butanoic acid (**6**) gradually formed up to 51% yield at 60 min.

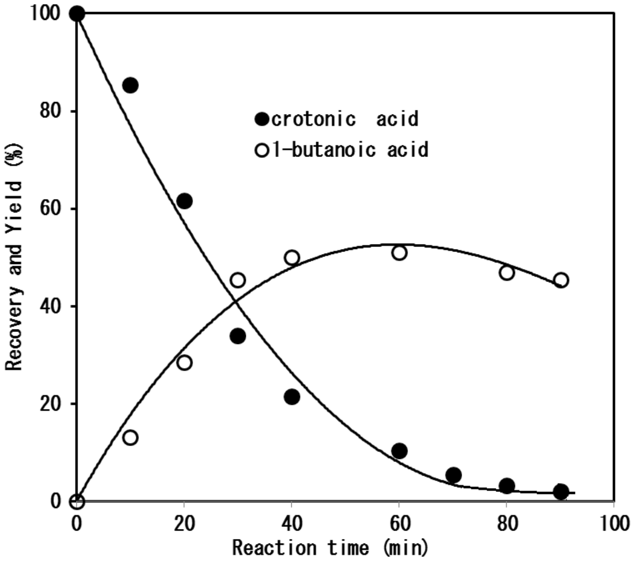


Fig. 8: Formation of 1-butanoic acid from an aqueous solution of crotonic acid (10 mM) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 1.5 L/min and hydrogen 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: crotonic acid, ○: 1-butanoic acid.

Figure 9 shows the time course of the hydrogenation of vinylacetic acid by argon-hydrogen plasma jet blowing. Vinylacetic acid (**7**) rapidly decreased and almost disappeared by 90 min. The product 1-butanoic acid (**6**) gradually formed up to 47% yield at 50 min.

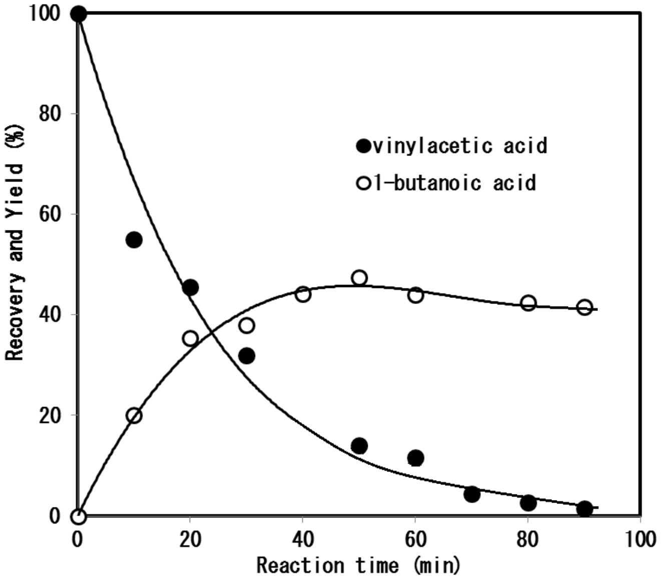


Fig. 9: Formation of 1-butanoic acid from an aqueous solution of vinylacetic acid (10 mM) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon 1.5 L/min and hydrogen 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: vinylacetic acid, ○: 1-butanoic acid.

Figure 10 shows the time course of the reduction of allylamine (**8**) by argon-hydrogen plasma jet blowing. Allylamine (**8**) rapidly decreased to almost 10% by 90 min. The product propylamine (**9**) gradually formed up to 31% yield at 60 min. The yield of propylamine (**9**) was lower than that of the carboxylic acids after the reduction of mono-alkene substrates induced by argon-hydrogen plasma jet. Oxidation of the product may take place during reaction. The oxidation of propylamine was reported in the literature [9].

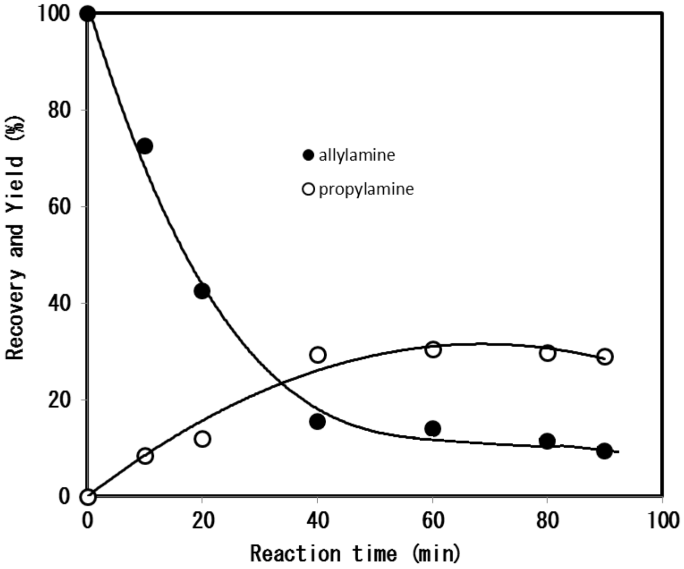


Fig. 10: Formation of propylamine from an aqueous solution of allylamine (10 mM) at 30 °C induced by argon–hydrogen plasma jet blowing at the gas flow rates: argon, 1.5 L/min and hydrogen, 0.5 L/min. Electric current and voltage were maintained at 30 A and 15 V, respectively. ●: allylamine, ○: propylamine.

Table 1 summarizes the results of the reduction of substrates 3, 5, 7, and 8 induced by argon-hydrogen plasma jet blowing into the aqueous solutions.

Table 1: Summary of the results of the reduction of substrates 3, 5, 7, and 8

Substrate	**Product**	**Optimum Yield (%)**
acrylic acid (**3**)	propanoic acid (**4a**)	48
crotonic acid (**4**)	1-butanoic acid (**6**)	51
Vinylacetic acid (**7**)	1-butanoic acid (**6**)	47
allylamine (**8**)	propylamine (**9**)	31

CONCLUSION

Mono-alkene monocarboxylic acids and amines were reduced to corresponding alkyl monocarboxylic acids and amines in yields of 31-51%. The higher yield of reduction products obtained using argon-hydrogen plasma jet compared with pure argon plasma jet demonstrates the effectiveness of the argon-hydrogen plasma jet in the reduction of the carbon-carbon double bond. This research shows a new kind of direct reduction of carbon-carbon double bond by plasma jet containing hydrogen.

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