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# Efficient Dimerization of Formic Acid in Aqueous Solution Induced by Ar-Arc Plasma

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Introduction of argon-arc plasma into an aqueous solution of formic acid resulted in the formation of oxalic acid. The reaction conditions for the dimerization were studied. The maximum yield of oxalic acid reached 47–50% when the reaction was carried out using sodium formate or calcium formate. Dimerization of acetic acid was also examined.

Various chemical reactions induced by plasma have been studied[1] in laboratory and also in industry. However, most of the reactions have been carried out in gaseous or solid phase, and few studies on plasma induced reactions in aqueous solution have been reported.[2] We have studied various types of plasma-induced chemical reactions[3–5] in aqueous solutions: these include various types of oxidation,[6–9] amination,[10–12] carboxylation,[13–15] hydrogenation,[16–17] and fixation of nitrogen.[18-22]

Formic acid has been used for carboxylation reactions in aqueous solution by the use of glow discharge,[13–15] argon-arc plasma,[23] or burning flame.[24] In these reactions, the primary products are hydroxyl and hydrogen radicals[25,26] which are formed by dissociation of water molecules. These hydroxyl and hydrogen radicals substract hydrogen from formic acid to form carboxyl radical (•COOH). The latter radical is relatively stable in aqueous solution compared with other radicals and can be used for various carboxylation reactions of organic compounds in aqueous solution. In this paper, studies on the coupling reactions of formic acid and acetic acid are presented as shown in Scheme 1.

$$H_2O \longrightarrow \cdot H + \cdot OH$$

$$HCOOH \longrightarrow \cdot H + \cdot COOH$$

$$HCOO^- \longrightarrow \cdot H + \cdot COO^-$$

$$2 \cdot COOH \longrightarrow HOOC\text{-}COOH$$

$$2 \cdot COO^- \longrightarrow {}^-OOC\text{-}COO^- \text{ (Na or Ca salt)}$$

$$CH_3COOH \longrightarrow \cdot H + \cdot CH_2COOH$$

$$2 \cdot CH_2COOH \longrightarrow HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$$

Scheme 1. Dimerization reactions of formic acid and acetic acid.

## Results and Discussion

When argon-arc plasma was introduced into an aqueous solution of formic acid, a small amount of oxalic acid was detected. Oxalic acid was formed by dimerization of formic acid radicals. The main factors influencing the formation of oxalic acid could be the stability of monomer radical and the stability of the dimerized product. Therefore, the stability of oxalic acid, sodium oxalate, calcium oxalate, and oxamide in aqueous solution was examined by the introduction of argon arc plasma. Figure 1 shows the time course of the degradation of oxalic acid and its derivatives. Free oxalic acid was found to be very unstable. Therefore, it could be expected that oxalic acid formed by the dimerization of formic acid radical was rapidly decomposed under the reaction conditions. By employing the new information on the instability of various forms of oxalic

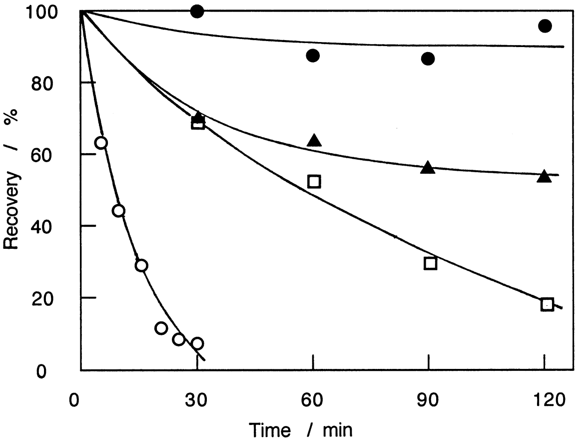

Fig. 1. Degradation of oxalic acid, oxamide, calcium oxalate, and sodium oxalate induced by Ar-arc plasma (10 V, 10 A).
●: Calcium oxalate (1.01 mmol/50 mL $H_2O$), ▲: Oxamide (1.18 mmol/50 mL $H_2O$), □: Sodium oxalate (1.09 mmol/50 mL $H_2O$), ○: Oxalic acid (1.06 mmol/50 mL $H_2O$).

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[#] Present address: Kobe Shoin Women's University, Nada-ku, Kobe, Hyogo 657-0015 acid shown in Fig. 1, the dimerization reaction was carried out by using sodium formate, calicium formate or formamide in aqueous solution by using Ar-arc plasma.

Figure 2 shows the time course of the dimerization reaction of 0.5 M sodium formate (1 M = 1 mol $dm^{-3}$). The maximum yield of oxalic acid reached 47%. In a similar way, Figs. 3 and 4 show the time course of the dimerization reaction of 0.05 and 0.25 M calcium formate. The maximum yield of oxalic acid reached 48% and 38%, respectively.

The great enhancement in the yield of oxalic acid from formic acid salts compared with the yield (1.3% and 0.44% shown in Table 1) of oxalic acid from formic acid could be due to the following two reasons. One is the enhancement of the stability of the resulting anion radical (•$COO^-$) compared with formic acid radicals (•COOH) under Ar-arc plasma blowing. The other reason is the stability of sodium and calcium salts of oxalic acid shown in Fig. 1. Under basic conditions, both the stability of the intermediate monomer radical and that of the resulting products contribute in the same direction to the increase in the yield of the dimerized products. In addition, in the case of the dimerization of calcium formate, the solubility of the resulting calcium oxalate is very low, and the product is precipitated out of the reaction mixture. This enables the product to further resist decomposition to carbon dioxide under the harsh high energy reaction conditions.

Figure 5 shows the time course of dimerization of a 0.5 M formamide solution. The maximum yield of oxamide was 14%. As shown in Fig. 1, the stability of oxamide under the conditions used is rather high. Therefore, the reason for the relatively low yield may be the instability of the carbamoyl radical (•$CONH_2$). However, the yield is much higher than that of the dimerization product of free formic acid. Thus, by the use of sodium or calcium formate and formamide, the dimerization reactions were carried out successfully. Summarized results of the dimerization reaction of formic acid and formamide are shown in Table 1.

Although the free formic acid gave much lower maximum

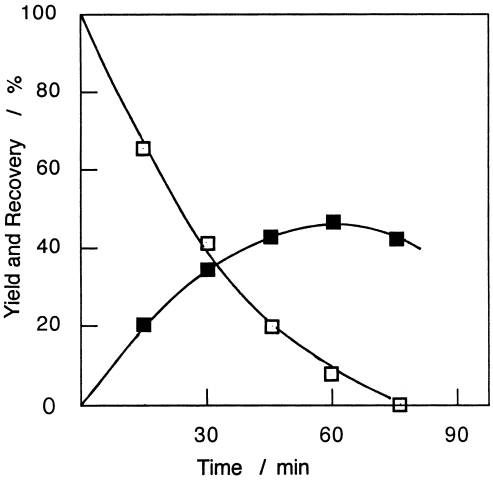

Fig. 2. Formation of sodium oxalate from 0.5M sodium formate solution induced by Ar-arc plasma (10 V, 10 A).
□: Sodium formate, ■: Sodium oxalate.

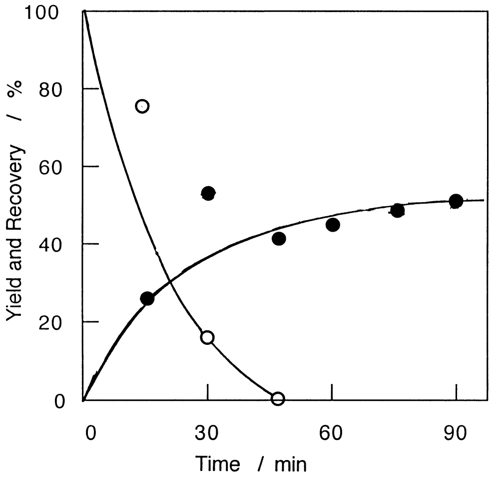

Fig. 3. Formation of calcium oxalate from 0.05 M calcium formate solution induced by Ar-arc plasma (10 V, 10 A).
○: Calcium formate, ●: Calcium oxalate.

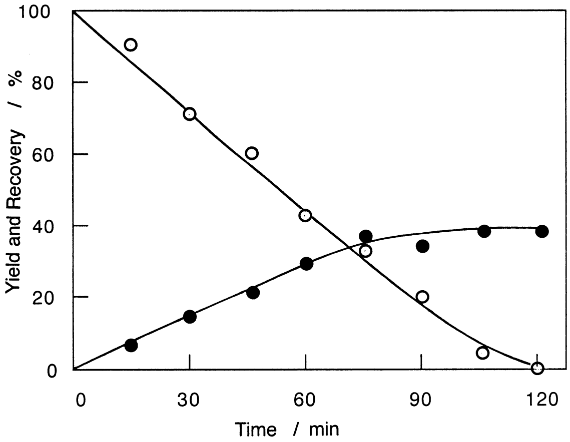

Fig. 4. Formation of calcium oxalate from 0.25 M calcium formate solution induced by Ar-arc plasma (10 V, 10 A).
○: Calcium formate, ●: Calcium oxalate.

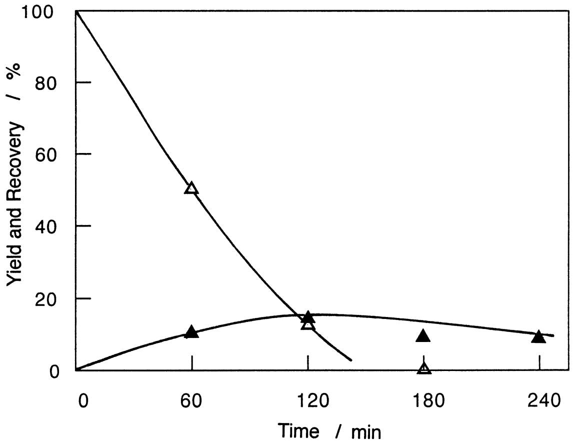

Fig. 5. Formation of oxamide from 0.5 M formamide solution induced by Ar-arc plasma (10 V, 10 A).
△: Formamide, ▲: Oxamide.

Table 1. Dimerization Reaction of Derivatives of Formic Acid Induced by Ar-Arc Plasma

| Substrate | Concentration | Product | Maximum yield | Reaction time |
|---|---|---|---|---|
| | M | | % | min |
| Formic acid | 0.1 | Oxalic acid | 1.3 | 10 |
| (HCOOH) | 0.5 | (HOOC-COOH) | 0.44 | 140 |
| Formamide | 0.005 | Oxamide | 4.3 | 10 |
| ($HCONH_2$) | 0.01 | ($H_2NOC-CONH_2$) | 9.8 | 20 |
| | 0.05 | | 10 | 30 |
| | 0.10 | | 14 | 45 |
| | 0.50 | | 14 | 120 |
| Sodium formate | 0.1 | Sodium oxalate | 33 | 15 |
| (HCOONa) | 0.5 | (NaOOC-COONa) | 47 | 60 |
| Calcium formate | 0.05 | Calcium oxalate | 50 | 90 |
| ($(HCOO)_2Ca$) | 0.25 | ($(COO)_2Ca$) | 38 | 105 |

yields (1.3%, 0.44%) of the dimerized product (oxalic acid), formamide and formic acid salts gave higher maximum yields of their dimerized products (oxamides: 4.3–14% and oxalic acid salts: 33–50%). The reasons were already described above. The maximum yields of oxamide were similar independently of the initial concentration of formamide. However, it took a longer time with the higher initial concentration of formamide until oxamide reached the maximum. Sodium formate and calcium formate gave almost the same yields of oxalic acid salts. The results showed clear effects of sodium and calcium salts of formate on the great enhancement of dimerization.

Similar reaction conditions were applied for the dimerization of acetic acid. However, the yields of the resulting succinic acid using free acetic acid, sodium acetate, calcium acetate, and acetamide at concentrations of 0.1–0.5 M were all in the range of 1–5%. In these reactions, the formation of malonic acid (2–6%) was observed. Malonic acid would be formed by the oxidative degradation of succinic acid, because the maximum yield of malonic acid was obtained after the decreasing of succinic acid. Figure 6 shows the time course of the dimerization of calcium acetate induced by Ar-arc plasma in aqueous solution. Degradation of succinic acid and malonic acid were studied under similar conditions, as shown in Figs. 7 and 8. The results indicate that succinic acid and malonic acid were unstable in the free and also in the salt form under the conditions used, compared with the salts of oxalic acid as shown in Fig. 1. The other reason for the low yield of succinic acid could be that the carboxymethyl radical ($\bullet CH_2COOH$) is unstable and is rapidly oxidized to glycolic acid, glyoxylic acid, and oxalic acid. These oxidized products were confirmed in the reaction mixture of aqueous acetic acid applied to electric discharge.[5] Thus, it was found that the effective dimerization of acetic acid by the use of Ar-arc plasma is difficult.

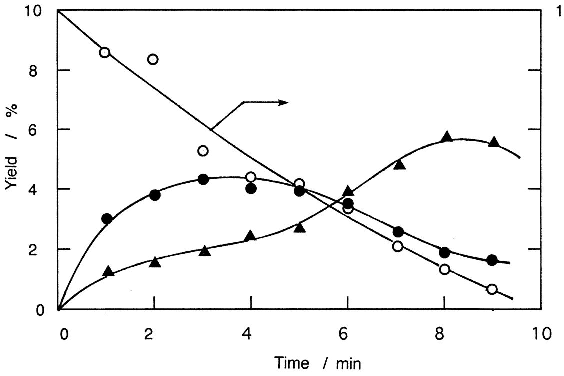

Fig. 6. Formation of calcium succinate and calcium malonate from 0.25 M calcium acetate solution induced by Ar-arc plasma (10 V, 10 A).
○: Calcium acetate, ●: Calcium succinate, ▲: Calcium malonate.

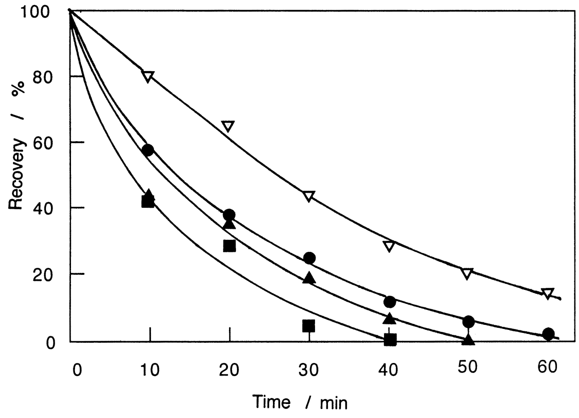

Fig. 7. Degradation of succinic acid, sodium succinate, calcium succinate and succinamide induced by Ar-arc plasma (10 V, 10 A).
▽: Succinamide (1.02 mmol/50 mL $H_2O$), ●: Succinic acid (1.04 mmol/50 mL $H_2O$), ▲: Sodium succinate (1.02 mmol/50 mL $H_2O$), ■: Calcium succinate (1.03 mmol/50 mL $H_2O$).

## Experimental

**Reagents:** Formic acid, sodium formate, calcium formate, oxalic acid, calcium oxalate, formamide, oxamide, acetic acid, malonic acid, acetamide, succinamide, sodium hydroxide, and calcium hydroxide used in this study were all special grade and were used without purification. Succinic acid was recrystallized from

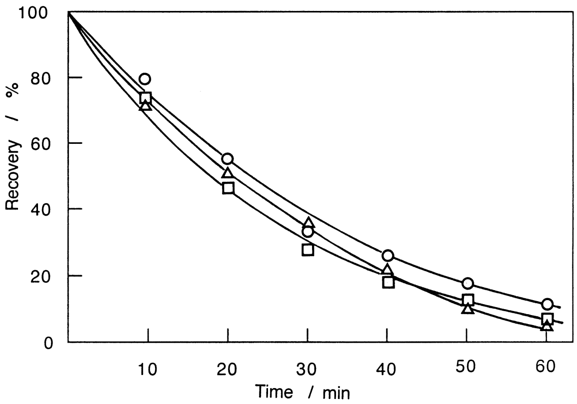

Fig. 8. Degradation of malonic acid, sodium malonate and calcium malonate induced by Ar-arc plasma (10 V, 10 A). ○: Malonic acid (1.03 mmol/50 mL $H_2O$), △: Sodium malonate (1.11 mmol/50mL $H_2O$), □: Calcium malonate (1.06 mmol/50 mL $H_2O$).

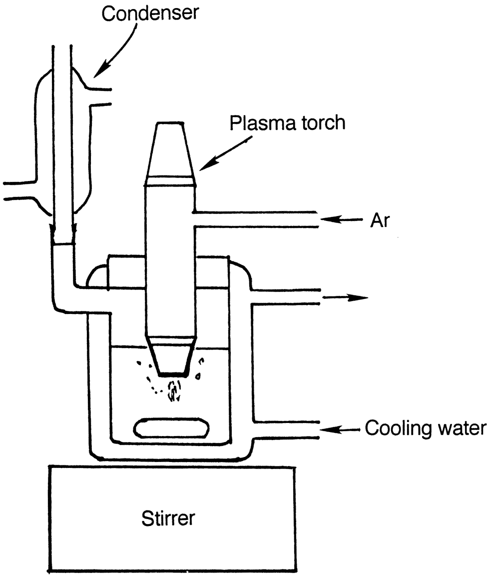

Fig. 9. Apparatus for Ar-arc plasma induced reaction in aqueous solution.

water, and calcium succinate was prepared by mixing sodium succinate and calcium chloride. Sodium oxalate, sodium acetate, calcium acetate, sodium succinate, sodium malonate, and calcium malonate solutions were prepared by neutralization of the corresponding aqueous solutions of the organic acids with sodium hydroxide or calcium hydroxide.

**Apparatus and Methods of Reactions :** The apparatus used for the dimerization reaction is shown in Fig. 9. The glass-made apparatus was equipped with a condenser; cold water (0–5 °C) was circulated at a flow rate of 19 L/min to prevent the rise of the aqueous reaction mixture (25–30 °C). The reaction mixture (50 mL) was stirred by a magnetic stirrer. The argon torch (Nippon Welding, WEL pen NP-7) was withdrawn at appropriate times, and the samples were subjected to a gas chromatograph (Hitachi 163), an isotachoelectrophoresis instrument (Shimadzu IP-2A), and an ion chromatograph (Dionex 2000i) to analyze the starting material, dimerized product, and other products. During the Ar-arc plasma reactions, the voltage and the current of the apparatus were maintained at 10 V and 10 A.

**Analytical Method:** In the analysis of the dimerization of formic acid, formic was analyzed by a Dionex 2000i ion chromatograph equipped with a Dionex HPICE-AS1 column (250 mm × 9 mm I.D.). Eluent: 0.125 mM octanesulfonic acid. Flow rate: 1.0 mL/min. Oxalic acid was analyzed using a capillary isotachoelectrophoresis apparatus (Shimadzu IP-2A). Leading electrolyte solution: 0.01 M hydrochloric acid containing 0.5% triton X-100 and $\beta$-alanine. Terminal electrolyte solution: 0.01 M hexanoic acid. Capillary column: 100 mm × 0.5 mm I.D. Detector: electropotential gradient detector at 20 °C.

The analyses of formic acid and oxalic acid formed in the dimerization of sodium formate were carried out on an ion chromatograph equipped with a Dionex HPICE-AS1 (250 mm × 9 mm I.D.) column and a TSK gel IC-Anion-PW column (50 mm × 4.6 mm I.D.), respectively. Eluent: 0.125 mM octanesulfonic acid (for formic acid) and boric acid buffer solution (pH 8.5) (for oxalic acid) which was composed of boric acid (360 mg), sodium tetraborate (500 mg), glycerol (5.0 g), potassium gluconate (300 mg), acetonitrile (120 mL), and 1-butanol (30 mL) in one liter of solution. Flow rate: 1.0 mL/min in both analysis.

Analyses of the reaction products obtained by dimerization of calcium formate were carried out using a capillary column isotachoelectrophoresis instrument. Leading electrolyte solution was similar to the one mentioned above, except that the pH was 3.7.

In the dimerization reaction of formamide, the resulting oxamide was analyzed by HPLC (JASCO Trirotar-V with a UV-Spectrophotometer UVIDEC-100-IV) at 215 nm, column ODS (250 mm × 4.6 mm I.D.), eluent liquid: $H_2O$, flow rate 0.5 mL/min. Formamide was analyzed by a gas chromatograph (Hitachi 163) under the following conditions: column, (UNISOLE F-200 (2 m × 3 mm I.D.) at 150°C; injection temp., 250°C; carrier gas, $N_2$; detector, FID (flame ionization detector).

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