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Synthesis of Carboxylic Acids from Alcohols by Contact Glow Discharge with Recycling System

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ABSTRACT

The topic of this research is oxidation of alcohols and trapping of the carboxylic acid oxidation products, because the oxidation products degrade during the contact glow discharge electrolysis. The trapping was carried out by recycling from the reaction solution through an anion exchanger column to the reaction solution. The yield of formic acid and acetic acid using this trapping system improved to 43% and 7.9% compared with the yield of these carboxylic acids (6.2% and 5.6%) without the recycling system.

Keywords: Glow discharge, alcohol, carboxylic acid, recycling

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INTRODUCTION

Glow discharge electrolysis (GDE) is classified as a low-temperature plasma and an equilibrium plasma [1–4]. GDE in the gas phase containing alcohol and water vapor was carried out by Klemenc [5]. The application has been developed by Hickling and co-workers [6–8]. Their works were mainly relevant to the reactions of inorganic compounds such as hydrogen peroxide, ferrous sulfate and so on [8]. Brown and co-workers synthesized an organic compound, oxamide [9]. Although at that time the action of free hydroxyl radicals in the synthesis was suggested, this has now been proved by Hase and Harada [10]. Harada called GDE at the gas–solution interface contact glow discharge electrolysis (CGDE) by “contact of the anode with an aqueous solution mixture” [11]. CGDE has been applied to simulation reactions (Harada discharge) of prebiotic chemistry [12] and organic syntheses [13]. The process of CGDE is characterized by a two-step mechanism [8]. The first step is dissociation of a water molecule to hydrogen and hydroxyl radicals between the gas and aqueous phase or at the boundary between those. The second step is the reactions induced by these radical species. Many organic syntheses using CGDE are summarized in the review articles [12, 13]. However, it seems that oxidation reactions proceed [13, 14] rather than reductions in many cases [13]. In particular, the lower molecular weight compounds containing C–O or C=O bonds, such as alcohols [14] and carboxylic acids, were decomposed by the action of hydroxyl radicals.

This research demonstrates a trapping process that prevents decomposition of the oxidized compounds. The research uses methanol and ethanol as substrates, which can be oxidized to the corresponding carboxylic acids: formic acid and acetic acid. The oxidized products from ethanol were also analyzed.

Experimental

Chemicals

Methanol, purchased from Kanto Chemical Co., Inc., was used after distillation. Ethanol, purchased from Nippon Alcohol Corporation, was used after distillation over calcium oxide. Formic acid and acetic acid were purchased from Kanto Chemical Co., Inc. Glycolic acid and glyoxylic acid monohydrate were purchased from Aldrich Chemical Company Inc.

Apparatus for the reaction and methods of contact glow discharge reactions

The apparatus involving a product-trapping system is shown in Figure 1. The apparatus has two modules. One is a reaction cylinder for CGDE and the other is a system for trapping the carboxylic acids produced and recycling alcohol.

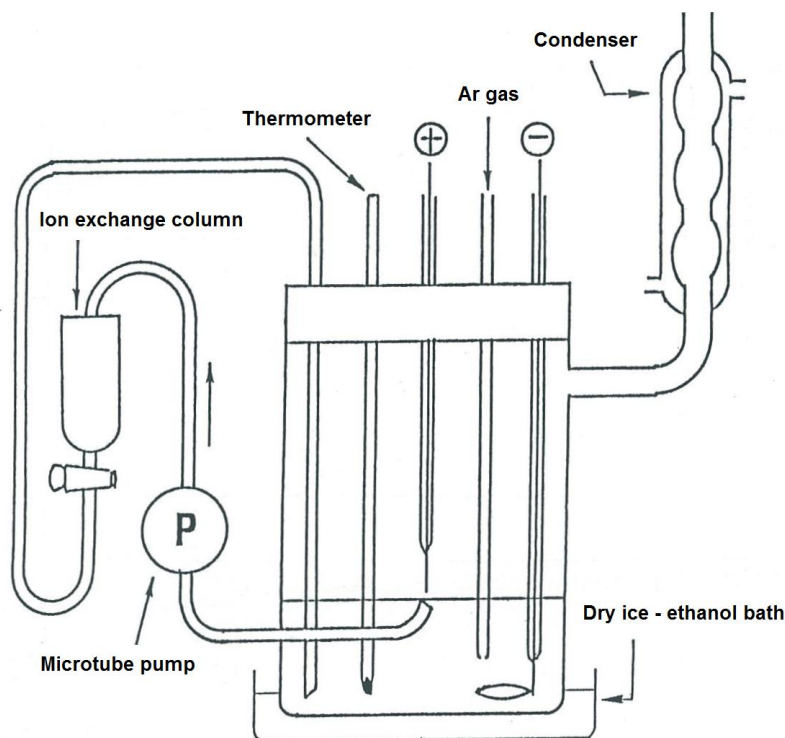


Figure 1: Apparatus for contact glow discharge with recycling system.

The reaction cylinder (7.8 cm depth and 5.6 cm I.D.) contains 49 mL sodium hydroxide aqueous solution (1 mM) and substrates (methanol or ethanol). After 30 min argon bubbling, contact glow discharge using a Model PS-1515 power supply (Toyo Solid State, 600–700 V, 20–30 mA) was carried out between the platinum anode above the solution and the cathode in the solution over argon bubbling. The reaction cylinder was cooled by a dry ice–ethanol bath during the reactions to maintain the temperature of the reaction solutions at 0 to 30 °C. When the trapping module was not used, the reaction solution (0.2 to 0.3 mL) was removed every 30 min for the reaction of methanol and 60 min for the reaction of ethanol for analysis.

The trapping module is connected through a glass pipe set in the reaction solution just under the anode. When the trapping module was used, the reaction solution was sucked out at a constant flow rate (6.0, 11.0 or 22.0 mL/min) from just under the discharge point by a microtube pump (EYELA MP-3) to be loaded onto a glass column filled with the anion exchanger DOWEX1 (1.45 mequiv/mL hydroxyl-form and 12 mL wet volume). After the reaction had proceeded until the remaining alcohol decreased below 5%, the anion exchanger column was washed with 50 mL of 1 M sodium hydroxide three times. The obtained wash solution was analyzed.

Analysis of the reaction solutions

(1) Gas chromatographic analysis

A Hitachi 163 gas chromatograph equipped with a packed column, Gaskuropak 54 (2 m × 3 mm I.D.) was used for the analysis of methanol and ethanol. The column temperature was programmed at 180 °C (constant). The carrier gas was nitrogen. Detection was carried out with a flame ionization detector.

(2) Isotachophoresis analysis

A Shimadzu capillary tube isotachophoresis IP-2A was used for the analysis of the oxidation products: formic acid, acetic acid, glycolic acid and oxalic acid.

(a) Analysis for the recycling reactions: The conditions for analysis of the reactions using methanol and ethanol were as follows. The leading electrolyte solution (pH 3.5) was an aqueous solution containing 0.01 M hydrogen chloride, 0.02 M 4-aminobutanoic acid and 0.5% triton X-100. The terminal electrolyte solution was an aqueous solution of 0.5% hexanoic acid. The electric current was set at 0.200 mA for the first 21 min and 0.100 mA for the later analytical time. The sizes of the pre-column and the analytical column were 40 mm × 1.0 mm I.D. and 100 mm × 0.5 mm I.D., respectively. The detection was carried out using an electric potential gradient detector at 20 °C.

(b) Analysis for the reactions without a recycling system: The analytical conditions for the reactions without a recycling system were as follows. The pH of the leading electrolyte solution was 3.8 for the analysis of the reactions using ethanol. The electric current was set at 0.200 mA for the first 10 min and 0.100 mA for later times in the case of analysis of the reaction solution with methanol, 0.150 mA for the first 10 min and 0.050 mA for later times with ethanol.

(3) High performance liquid chromatography

Acetic acid formed in the reaction without a recycling system was analyzed by means of a Jasco high performance liquid chromatography system composed of a Trirotar-V flow pump, Uvidec-100-IV UV spectrophotometer and a TSKgel ODS-80TM (250 mm × 4.6 mm I.D.) column. UV absorption at 210 nm was detected. An ammonium phosphate buffer (pH 2.4, 20 mM) was used for the analysis at a flow rate of 0.5 mL/min.

RESULTS AND DISCUSSION

Figure 2 shows the time course of oxidation of methanol (0.1 M) induced by glow discharge in the aqueous solution. Methanol gradually decreased with time up to 300 min. Formic acid increased very slowly compared with the decrease of methanol. The optimum yield was only 6.7%. Figure 3 shows a plausible mechanism. A hydroxyl radical withdraws a hydrogen radical and then the resulted carbon radical couples with a hydroxyl radical to give a di-hydroxyl-methane [12, 13]. Similar oxidation proceeds to afford formic acid.

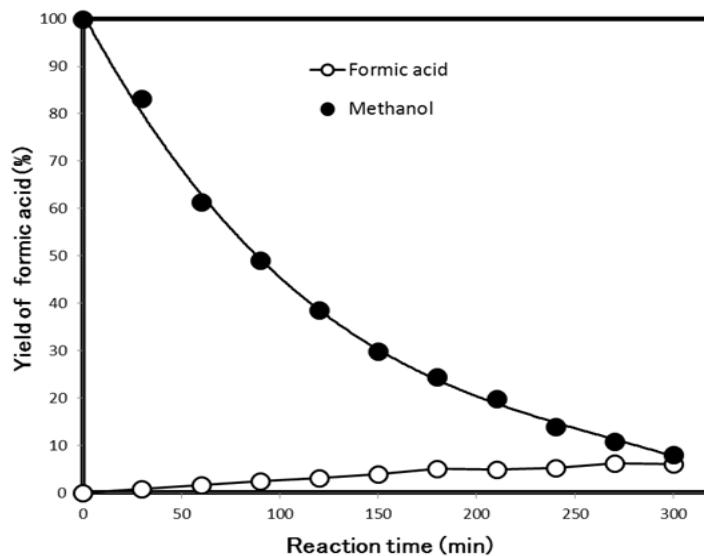


Figure 2: Oxidation of methanol in aqueous solution (0.1 M) induced by GDE (500–900 V, 19–37 mA). ○: Formic acid; ●: Methanol.

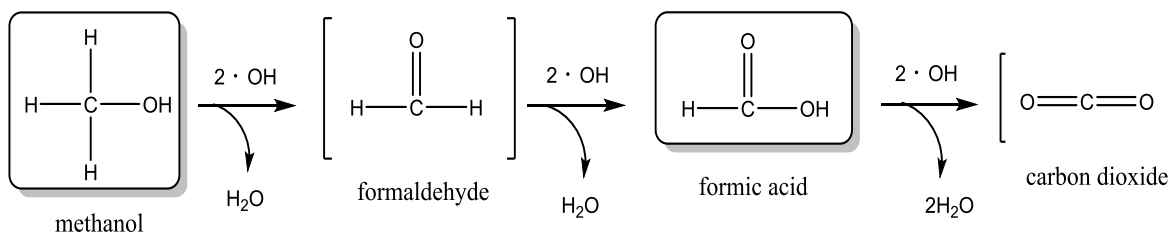


Figure 3: Oxidation of methanol to formic acid and carbon dioxide in CGDE reaction.

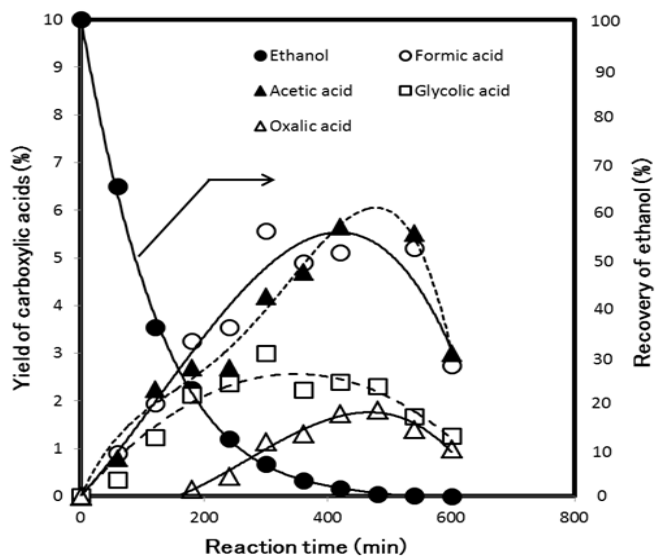


Figure 4: Oxidation of ethanol in aqueous solution induced by GDE (500–1000 V, 21–27 mA). ●: Ethanol; ○: Formic acid; ▲: Acetic acid; □: Glycolic acid; △: Oxalic acid.

Figure 4 shows the time course of oxidation of ethanol (0.1 M) induced by glow discharge in aqueous solution up to 600 min. First, formic and glycolic acids increased up to 5.7% and 3.0% at 300 min, respectively; second, acetic acid increased up to 5.6% at 420 min; and third, oxalic acid formed up to 1.9% at 480 min. The formation order suggests the relation between precursors and products. Scheme 2 shows a plausible reaction pathway for the reaction. A plausible mechanism for the oxidation is shown in Figure 5. The formation of glycolic and glyoxylic acids is supported by several references [12, 13], but glyoxylic acid could not be detected in this reaction because of its instability.

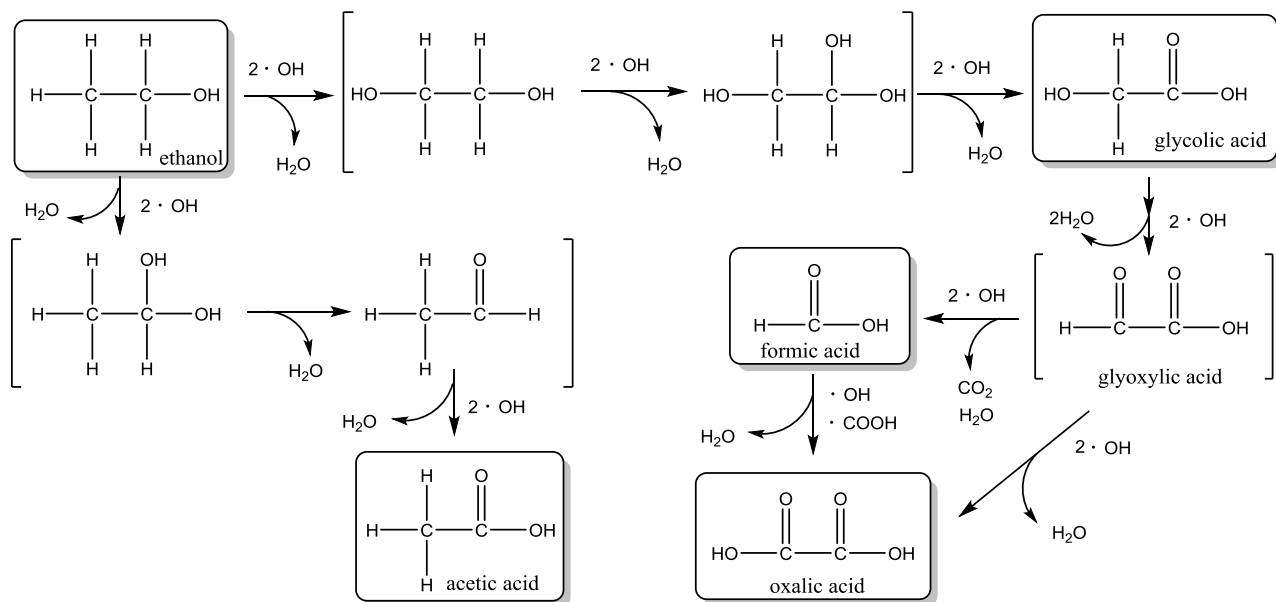


Figure 5: A plausible mechanism to form carboxylic acids from ethanol induced by contact glow discharge.

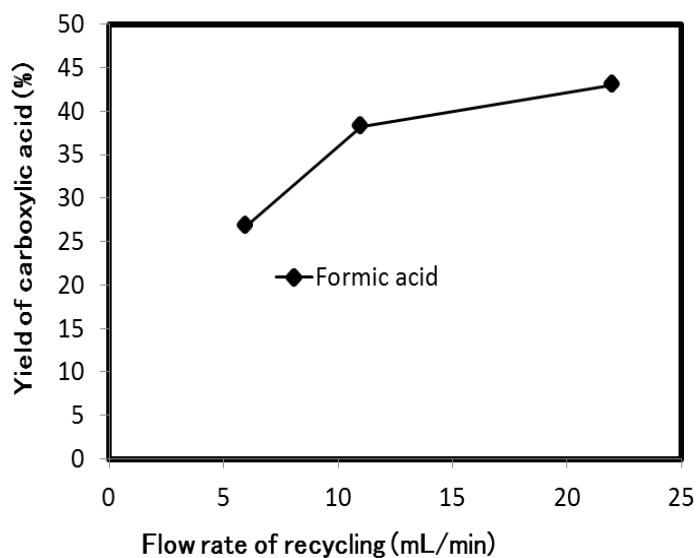


Figure 6: Effect of flow rate on the yield of formic acid obtained in aqueous solution of methanol (0.05 M) by glow discharge.

Figure 6 shows the effect of the flow rate of recycling through the ion exchange column.

Different recycling flow rates were used as follows: 6, 11 and 22 mL/min. The optimum yield reached 44% at the flow rate of 22 mL/min. Although a faster flow rate was used for the reaction, the yield of formic acid was almost the same as the yield at the flow rate of 22 mL/min.

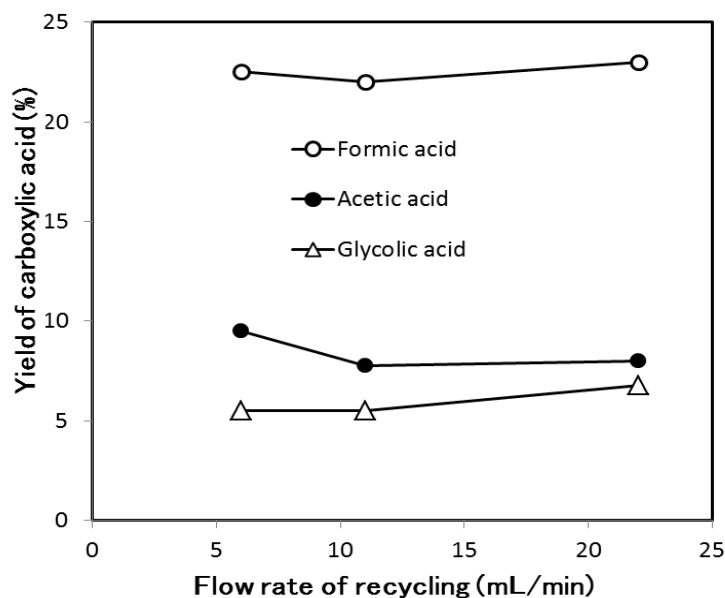


Figure 7: Effect of flow rate on the yield of carboxylic acids obtained in aqueous solution of ethanol (0.05 M) by glow discharge.

Figure 7 shows the effect of flow rate on the yields of formic acid, acetic acid and glycolic acid obtained in the aqueous solution of ethanol (0.05 M) by glow discharge. The yield of formic acid was higher (22–23%) than those of acetic acid (7–10%) and glycolic acid (5–7%) at all flow rates used. The results show the advantage of the recycling system to protect the products. It is clear that the yields of carboxylic acids were higher with the recycling system than those without the recycling system as follows: formic acid, 5.7%; acetic acid, 5.6%; and glycolic acid, 3%. However, the yields of these carboxylic acids did not depend on the flow rate.

Table 1: Formation of carboxylic acids in aqueous solutions of alcohols induced by glow discharge

Substrate alcohols (mM)	Yield of carboxylic acid (%)			
	Formic acid	Acetic acid	Glycolic acid	Oxalic acid
Methanol (10)	41	–	–	–
Methanol (5)	43	–	–	–
Methanol (100)	33	–	–	–
Methanol (100)*	6.2	–	–	–
Ethanol (50)	23	7.9	6.7	–
Ethanol (100)	15	6.9	5.2	–
Ethanol (100)*	5.7	5.6	3.0	1.9

*without recycling system

The yields of carboxylic acids in the reactions of methanol and ethanol are summarized

in Table 1. The results demonstrate the effectiveness of the contact glow discharge with the trapping system. Recycling through the trapping module avoided the further oxidative degradation of the carboxylic acids.

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