

NEW PAIRED ELECTROSYNTHESIS ROUTE FOR GLYOXALIC ACID**Abraham F. Jalbout,* Suhong Zhang***Department of Physics, Dillard University, 2601 Gentilly Blvd., New Orleans, LA 70112;**Department of Chemistry, The University of New Orleans, New Orleans, LA 70148;**Ajalbout@ejmaps.org**Received 18-04-2002***Abstract**

Through paired electrosynthesis, oxalic acid and glyoxal were separately reduced and oxidized on cathode and anode to yield glyoxalic acid synchronously. Thus, both the space and the current in the anode and cathode were sufficiently used. Electrolytic conditions are discussed and all data are given in this paper.

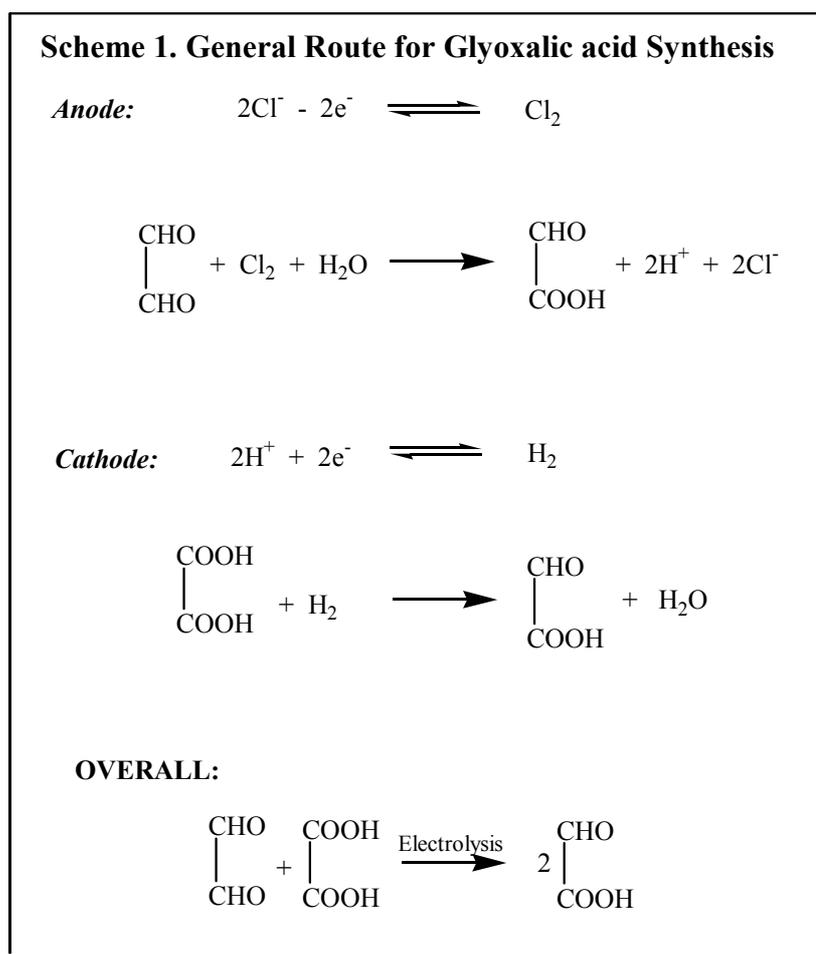
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Introduction

Reactions between strong nucleophiles and strong electrophiles, which are of interest to synthetic chemists, have been thoroughly investigated in the recent literature (Reference 1, and references therein). Charge transfer mechanisms allow for two very powerful reagents to come together, and are in fact routine in synthetic chemistry.^{2,3} Thus, it is possible (through electron transfer) in pulsing the potential of an electrode alternately to anodic and cathodic potentials to generate electrophiles and nucleophiles in solution.^{4,5} The use of electrodes for organic synthesis is well known documented methods for chemical reactivity involving charge transfer mechanisms.⁶

In the industrial production of glyoxalic acid through reduction of oxalic, with increase of the current density, the selectivity and the current proficiency decrease dramatically, and only low concentrations of glyoxalic acid can be obtained in cathode solution. In this work, we adopted the paired electrosynthesis techniques, in which the chlorine gas produced at the anode was used to oxidize glyoxal to glyoxalic acid. This procedure takes advantage of the high percentage of transformations as well as the high selectivity of the oxidation of glyoxal to glyoxalic acid by chlorine gas. In this case, both the anode and the cathode currents were fully used. Compared to the production of glyoxalic acid only by cathode, it saves energy and decreases production cost significantly.

In our synthesis route, paired electrosynthesis was adopted to produce glyoxalic acid as was shown in scheme 1. Glyoxal is soluble in water but without any form of conductivity, in order to get a high enough current, certain kinds of supporting electrolytes must be added to the solution. Due to the high percentage of transformation and the high selectivity in the oxidation of glyoxal by chlorine gas, chloride ion containing electrolytes were our first choice for this reaction.



In the oxidation process, both the chlorine gas and the oxygen gas could be used as an oxidizing agent for the glyoxal. The percentage of transformation and selectivity are higher by chlorine gas than those by oxygen gas, which allows us to focus on the chlorine gas products. Also, under the reaction conditions hypochlorite cannot be excluded as an active reagent.

Experimental Section

All reagents used in this work were analytically pure except solid oxalic acid (this was obtained at the industrially pure level of quality) and were obtained from the Aldrich chemical corporation. The electrochemical equipment used was of an entirely conventional nature. In our paired electrosynthesis routes, we chose graphite (which was soaked in sodium silicate for two hours according to previously reported procedural notes⁷) as the anode, Pb plate (99.99%) as the cathode (both had areas and thickness of around 300 mm² and 3 mm), and the distance between the two electrodes was set to around 10 mm. The volume ratio of anode and cathode compartment is 1: 6 (100:600 ml) and the anode and cathode electrolyte solution is 80:480. Polycarbonyl styrene cationic exchanging membrane was used to separate anode cell and cathode cell. All analytical methods for the synthesis of glyoxalic acid are in reference 8. Rotary evaporation apparatus concentrated the ultimate electrolytic solutions.

Since the Pb cathode could also easily deactivate, we used the same methods as in the reductions of the oxalic acid, whereby we added 10-mmol/L tetraethyl ammonia bromide to the cathode solution in order to protect the cathode. Meanwhile, solid oxalic acid was constantly added to the cathode solution to make sure that the oxalic acid was saturated, and around 25% glyoxal to the anode solution. To separate the anode and the cathode cells from one another, a carbonyl polystyrene cationic exchange membrane was used.

Results and discussion

In the paired electrosynthesis of glyoxalic acid, there are some factors crucial to the final results; below we will discuss them. Temperature is one of the most important conditions, increasing the temperature allows for an increased solubility of oxalic acid, without actually increasing the concentration of the glyoxalic acid. The electroreduction of oxalic acid is a two-step process,⁹ in which absorbance is crucial in the first step, while temperature is the most decisive factor in the second step. From our observations, 25 °C was best for the reduction of oxalic acid in cathode (25 °C, the highest concentration of glyoxalic acid in cathode was 4.45%, while, 20 °C: 3.62%, 30 °C: 3.01%, at 4.5 V, hydrochloric acid as electrolyte), and the temperature in the anode

agreed with that in the cathode. The working potential has to be set carefully, since high voltage leads to the occurrence of many by-reactions, while low voltage leads to low current density, which decreases the temporal and spatial proficiency of the apparatus, the best results were obtained at 4.5 V.

Meanwhile, for all the experiments, solid oxalic acid was constantly added to the cathode solution to make sure that the oxalic acid was saturated, and around 25% glyoxal to the anode solution.

In the following experiment, we will discuss another two important factors in our process leading to the paired electrosynthesis of glyoxalic acid.

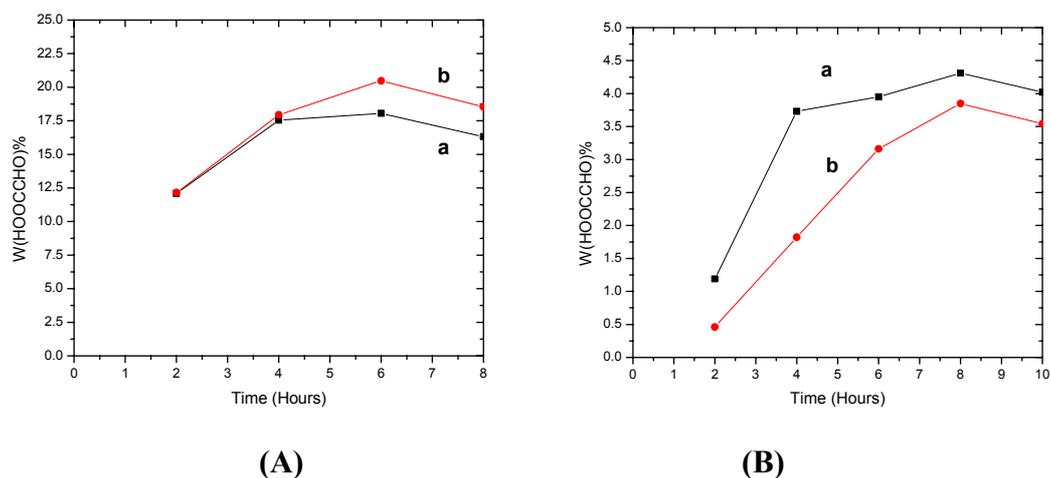


Figure 1. (A). The dependence of the concentration of glyoxalic acid in the anode on time, where (a) shows the addition of hydrochloric acid in one batch and (b) shows the addition of hydrochloric acid in several batches. (B). The dependence of the concentration of glyoxalic acid in cathode on time, where (a) and (b) are the same as for the anode.

(a). HCl Additions

When we added the 6% hydrochloric acid (the concentration after adding) in one batch, the current decreased from 1.8 A to 1.0 A after keeping it at 1.8 A for four hours, large amounts of chlorine gas were released from the anode solution (within the first four hours) which indicated to us that too much chlorine gas was produced being produced. Thus, we added the 6% hydrochloric acid in several batches, in which 4% was added in the first batch, and the rest was added in several batches as soon as the current had decreased. In this case, the current was kept constant and higher

concentrations of glyoxalic acid were acquired in both the anode and the cathode solutions. This is partly due to the constant current that can keep prolong a steady formation of chlorine gas and reductive hydrogen, which were just enough for our synthesis requirements. Another advantage for this process is that no absorbance apparatus for the chlorine was needed. Figures 1A-B, represent the comparisons of our results for the two ways of adding hydrochloric acid.

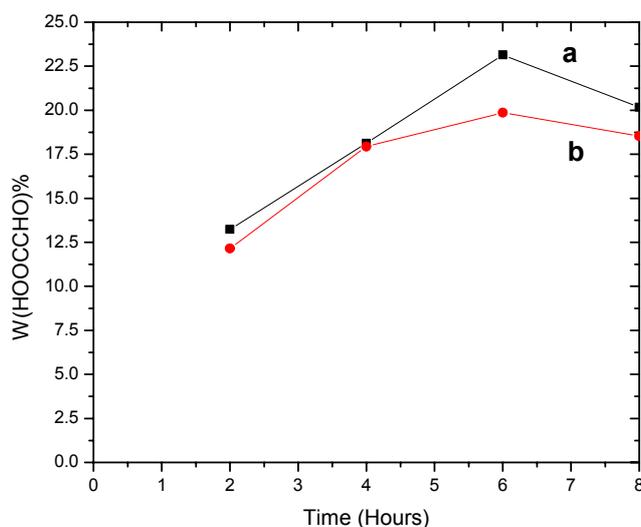


Figure 2. The dependence of the concentration of glyoxalic acid on time, where in (a). the pH was less than 7, and in (b). a pH of 7 were used.

(b). pH Effects

Previously¹ it has been reported that in an acidic environment, the oxidation selectivity of glyoxal to glyoxalic is around 70%, while in a neutral environment this selectivity increases to almost 99%. From figure 2 we show our results when 6% hydrochloric acid (the concentration after adding) is added in several batches in both the cathode solution and the anode solution (b), and only the cathode solutions (a). In acidic environments, the oxidative ability of chlorine gas is much higher than that in the neutral one, poor results were obtained, partly because the glyoxalic acid was oxidized to oxalic acid or perhaps even to carbon dioxide.

Conclusions

In the paired electrosynthesis of glyoxalic acid, the electrolytic conditions are: Anode: graphite, cathode: Pb (99.99); The ratio of cathode and anode volume is 1:6; Electrolytic temperature: 25 °C; Electrolytic voltage: 4.5 V; pH=7 in anode; Anode solution: 25% glyoxal solution; Cathode: saturated oxalic acid and 6% hydrochloric acid (the concentration after adding, which was added in several batches).

The glyoxalic acid concentration obtained in the cathode solution was around 4.5% (after being distilled at low pressures) and 21.7% in the anode were obtained. The methods that we used were for glyoxalic acid from the anode solutions. Glyoxal was not completely transformed into glyoxalic acid, since part of this was oxidized to oxalic acid. It has been reported^{11–15} that the existence of glyoxal will disturb the reaction between glyoxalic acid and urea, thus leading us to find a different method for this process (and the resultant importance of this reaction may become obsolete since the products can be used for further reactions). There are many ways to separate glyoxalic acid, but most have high complications associated with them, yield products of low purity, are high in cost and are potential factors for pollution. To minimize these effects we used NaOH and CaCl₂ to precipitate the oxalic acid and the glyoxalic acid separately by controlling the range of the pH. Through a rotary evaporation process, both cells can get a yield of around 40% glyoxalic acid (the rest being impurities of untreated materials including oxalic acid). The advantage of using these paired electrosynthesis methods in the formation of glyoxalic acid are their increased efficiency and purity by which it can be produced. Our experimental procedures are based on older methods but the route is novel and timely.

Our techniques have the advantage of high percentage for the yield, high selectivity and low pollution. The synthesis that we have presented are very difficult to perform by normal conventional chemical methods, and almost impossible at our level of purity, and yield. Thus, The importance of temperature, pH, and other factors influencing the formation of the target molecule were of severe importance, since a powerful equilibrium to the formation of other products was substantial.

A main focus of this work was to use materials that could be of potential use in an industrial process, which is a main goal in our selection of these materials, in the study.

The actual industrial implementation of these materials is currently being investigated by advanced Bayesian methods in our groups¹⁰ and the prospects are very promising.

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Povzetek

Z elektrosinteznim pristopom lahko oksalno kislino istočasno reduciramo na katodi in glioksal oksidiramo na anodi in dobimo glioksalno kislino. V prispevku opisujemo elektrolizne pogoje in podatke o reakciji.