

Electroorganic processes practiced in the world

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Abstract - The upsurge in world-wide activity in organic electrochemical synthesis that followed upon the 1965 commercialization of Monsanto's Adiponitrile and Nalco's Tetraalkylead processes has resulted in the development beyond the small glass cell scale of more than one-hundred processes. These will be shown in a Table. Special emphasis will be placed on the diversity of reactions and of countries involved.

Present research which ensures that this pace will continue or accelerate will be discussed under the categories: cells, electrodes, electrolytes, and hybrid technologies. One particular development, the increasing use of undivided cells, will be examined in more detail since it is one of the means for promoting greater economy in processing. Three examples will be used to illustrate how one obstacle after another can be removed with dedicated effort: the reduction of benzene to 1,4-cyclohexadiene, and the paired syntheses leading to 2-butane from 2,3-butane-diol and sorbitol plus gluconic acid from glucose.

INTRODUCTION

The time is out of joint: - O cursed spite
That ever I was born to set it right!
Hamlet I,5.

Has there ever been a time when any thinking person could not have said that? Have there ever been periods when, except in historians' retrospective view, life's patterns hardly changed and homo sapiens led a tranquil contented life? Above all, has any citizen of the State of Israel failed to think Hamlet's thought without necessarily expressing it? We are here now, so that in every generation there must have been visionaries who transformed "O cursed spite" into "O what an opportunity to make things better." Israel is a country of visionaries: without them the State would not have been created; without them it would be devoured.

Fanatical though I be about the subject, I cannot say that organic electrochemical synthesis will set the world right, not even that miniscule part called the chemical world. But it will help at least a smidgin. That is as much as most of us can do who haven't the genius of Newtons and Einsteins to find a place for Archimedes' fulcrum and move the world.

In the last fifty years and particularly in the last twenty-six, organic electrochemical synthesis has ceased to be a laboratory curiosity, a methodology to be tried when all else fails, a procedure that involves mysterious black boxes and dials and wires. This science and technology are now well developed although not mature. The Monsanto adiponitrile and the Nalco tetraalkylead commercial processes in 1965 broke the barriers erected by mistaken pre-conceptions. The former involves very large-scale manufacture of a relatively low-cost product; the latter involves a practical synthesis using a non-aqueous system.

The surge of activity which followed these successes has now led to over one-hundred processes which looked promising enough in the laboratory to be carried forward to large bench-scale or pilot plant or commercial development. Note that a considerable variety of reactions is represented. Those of us who are active in the field and are keeping abreast of current developments are convinced that "what's past is prologue." Perhaps economic conditions will not permit electrochemical production of commodity chemicals but the synthesis of drugs, pharmaceuticals, fine and specialty chemicals is still very attractive. Those of us with a strong bias would venture to say that unless an oxidation can be done with air and a reduction with hydrogen the electrochemical approach can be made the superior one. (In some cases even *in situ* electrogenerated hydrogen may be preferable to tank hydrogen.) And this does not even take into account the "second order" synthetically useful results that come from gain or loss of an electron.

It is impossible in such a brief period even to summarize all the ongoing research on the various components of organic electrochemical synthesis which may have important impacts on the future practical applications of this methodology (ref. 1). Instead I will mention some of this work, which is discussed more extensively in the references cited, and will comment somewhat more extensively on recent personal experiences with a promising technological approach, namely, the use of paired syntheses.

The overall obvious practical objectives are to use: (1) reactors (cells) made of low-cost materials and so designed as to allow maximum space-time yields in, preferably, continuous processes, (2) low-cost durable electrodes (unless they are purposely "sacrificial" as in the tetraalkylead process) giving the highest specificity and the lowest overvoltage for the desired reaction, (3) "inert" supporting electrolytes - unless they are meant to be reactants - with an electrochemical domain wide enough to allow the desired oxidation or reduction of the substrate to occur without destruction of the re-usable electrolyte, (4) sturdy membranes, preferably ion-selective, if needed, offering minimum electrical resistance in order to reduce overall power requirements, (5) economical separations schemes particularly if partial conversion of the starting material is to be used as an intrinsic potentiostatic control.

All of these objectives have obviously been achieved at least to a satisfactory, if not optimal degree, in the processes cited. It cannot be emphasized too strongly that after a process is installed a continuous program of improvements must be maintained. The Monsanto adiponitrile process originally practiced successfully in divided cells with cation exchange membranes now uses undivided cells of greatly simplified design at a fraction of the original cost. It should also be pointed out that if the raw material is of relatively low cost some sacrifice in yield will be more than offset by the economies of simplified operation. The costs of the total of the procedures involved, not just the electrochemical step (which may be only a small part of what is required to convert starting material to saleable product), must be considered in analyzing the economics of a process. This is often not appreciated by the bench chemist. A good discussion is given in a recent paper (ref. 9).

CELLS

Very useful discussions of cell design, optimization, and economics in general are given by Alkire (ref. 2), Jansson (ref. 3b), Beck (ref. 4) and Landaez-Machado et al. (ref. 5). Of more restricted scope are the papers by White et al. (ref. 6) on the parallel plate model, by Robertson et al. (ref. 7) on the "Swiss roll" cell in Vitamin C production, by Bellamy and Simpson (ref. 8) on electrooxidations in a tubular flow cell.

ELECTRODES

In addition to the ideal specifications mentioned before it is desirable to have high surface-area and/or porous electrodes to maximize space-time yields and to permit convenient continuous operations. These goals are achieved in some of the newer electrode materials/forms mentioned below.

Various carbons have been the subject of considerable recent study: reticulated vitreous carbon, RVC (refs. 10-12), vitreous carbon (refs. 13-17), graphite felt (ref. 18) and carbon cloth (ref. 19) and activated carbon and carbon black (ref. 20).

Many other electrode materials, some new some old, have been recently evaluated for their particular advantages: titanium/titanium dioxide (ref. 21), poly-sulfur nitride (ref. 22), lead dioxide (ref. 23), boron nitride and graphite layered compounds (ref. 24), titanium nitride (ref. 25) and metal oxides (ref. 26). Four categories merit special comment: chemically modified electrodes (CME's), dimensionally stable anodes (DSA's), conducting polymers, and catalytic cathodes, especially of Raney nickel.

The study of CME's (ref. 27-31) has expanded enormously since their disclosure twelve years ago. Despite the fascinating and novel results that have been obtained with them, no practical applications are in sight and will not be until their durability extends beyond the time necessary for writing another research grant application.

DSA's have revolutionized the chlorine-caustic industry but to the best of my knowledge they have not been used successfully in organic electrochemical synthesis (ref. 32).

Despite spectacular successes in the battery field it is still early days for conducting polymers (ref. 33-37) and pre-dawn for their use in synthesis.

The situation is very different, however, with respect to the development of catalytic electrodes, particularly Raney nickel cathodes. While the use of the latter for electrocatalytic hydrogenations was mentioned several years ago, the last three or four years have seen an increasing number of papers on this subject (refs. 38-45). A dramatic demonstration of the efficacy of this type of cathode was found in a study of the paired oxidation (to gluconic acid) and reduction (to sorbitol) of glucose in undivided cells (ref. 40). A variety of cathodes including amalgams, had given a maximum of ca. 60% cathodic current

efficiencies; Raney nickel gave 90-100%. There are physical problems in handling this sort of material on a large scale and questions of poisoning and re-activation but these are all solvable.

The time is now right for expanding the scope of utility of catalytic electrodes in synthesis.

ELECTROLYTES

There have been advances in the study of molten salts ("ionic liquids"), currently of limited value in organic synthesis (refs. 46-48), of systems using microelectrodes and no supporting electrolytes (refs. 49-50) but perhaps most importantly (from the point of view of applied organic electrochemical synthesis), of solid polymer electrolytes (SPE's) (refs. 51-56). Use of the latter permits one simply to remove the SPE by filtration and proceed with the isolation of the products by appropriate conventional means; it eliminates the need for separating a soluble supporting electrolyte from the system, purifying it when necessary before recycling it, and inevitably incurring finite losses of material.

HYBRID TECHNOLOGIES

It is almost certain that important advances in synthesis will be made by electrochemistry-catalysis and electrochemistry-photochemistry. The use of catalytic electrodes has already been mentioned; much still remains to be done. An intriguing example of photoelectrochemical dimerization of toluenes to bibenzyls has been reported (ref. 57) but the implications have not been pursued.

TOWARD GREATER ECONOMIES IN ORGANIC ELECTROCHEMICAL PROCESSES

The ultimate criterion leading to the commercialization of an organic electrochemical process is that it provides the desired product at a lower overall cost (including costs of disposing properly of environmental pollutants) than any competitive process. It's that crass. Novelty, elegance, publishability and patentability are irrelevant factors. Who wants an air-tight patent on a too expensive process? When electrochemistry can use a much cheaper raw material than does an alternative process or can achieve a given transformation uniquely or even only especially well, then it has a good chance of being used even in "conventional" cells and systems that have been developed over the years. There are more than one-hundred pieces of evidence that the problems have been solved at least satisfactorily if not optimally. But innovative changes in cells and systems can make electrochemical methodology much more broadly competitive than it is now. Perhaps the SPE's mentioned above are in this category. I will cite two examples with which I am personally well acquainted: the use of undivided cells and the design of paired syntheses.

Undivided cells

The economics that can be realized by using undivided cells rather than two- or three-chamber cells involving membranes or diaphragms are too obvious to warrant discussion. And yet it has become established practice, almost dogma, to do oxidations frequently in undivided cells and reductions usually in divided cells. There is the obvious desire to avoid re-oxidation of the reduced intermediate or the starting material of the product at the counter-electrode, the interaction of anodically generated intermediates or products with the corresponding entities produced at the cathode, etc. But there are means other than simply introducing a divider for avoiding these undesired reactions: choice of electrode material, design of a proper system for continuous operation in a flow system, etc. Three of the several existing examples are provided here; many more will surely be forthcoming. The first involves the reduction of benzene to 1,4-cyclohexadiene with oxygen evolution as a sacrificial anodic reaction; the second and third involve paired syntheses.

Reduction of benzene to 1,4-cyclohexadiene It has been calculated that the direct cathodic reduction of benzene would require a cathodic voltage beyond the electrochemical domain of the best solvent/supporting electrolyte systems available. Benzene has however been reduced indirectly via solvated electrons (electrochemical Birch Reaction). The products may be cyclohexadienes or cyclohexene or even cyclohexane depending upon conditions (ref. 58).

The reduction of benzene emulsions in aqueous tetraalkylammonium hydroxides gave surprisingly good yields of 1,4-cyclohexadiene in divided cells (ref. 59). As might have been expected, this reduction in an undivided cell with platinum or carbon anodes led to oxidation and rearomatization of the diene. However, use of the oxygen-evolving DSA anode (TIR-2000) allowed high yields of the diene to be obtained with good current efficiency (ref. 58). It was not clear whether a quaternary ammonium amalgam - since mercury was the only satisfactory cathode - or solvated electrons were the electron-transfer agents. Subsequent work (ref. 60) seemed to favor the former explanation.

Paired reactions in undivided cells "Paired reactions" have previously (ref. 61) been defined to encompass (necessarily) simultaneous cathodic and anodic reactions which both contribute essentially to the formation of the final product(s). There may be one or more starting materials and one or more products. The main objective is to get twice the normal productivity from a given cell. There are no or minimal "sacrificial" products.

It is a sine qua non in devising suitable systems that the starting material from which the desired intermediate or product is made by oxidation (or reduction) be more easily oxidized (or reduced) than any derived still electroactive entity. This condition permits the attainment of very high selectivity even under constant current rather than constant potential control, so long as a significant excess of starting material is present. It is also very desirable but not essential that the same number of electrons be supplied and removed at the cathode and anode respectively. If this condition does not prevail then there will surely be some "sacrificial" reactions.

The conditions, particularly pH, for achieving optimal results for the anodic reaction are often somewhat different from those required for optimal cathodic results but satisfactory compromises can be found. The potential savings by operating in this mode more than offset departures from the individual optima.

One must also anticipate and plan to circumvent all deleterious chemical reactions which the products may undergo with all species in the medium.

A persistent caveat about paired reactions in undivided cells has emphasized the difficulties in separations that may be involved. True enough. One must early in the study choose an appropriate candidate pair, reflect on the degree of conversion (usually less than 100%) of raw material(s) to product(s), and assess the utility of differences in physical properties (volatility, solubilities, etc.) in affecting these separations. This is not beyond the wit of man (used generically not sexistly).

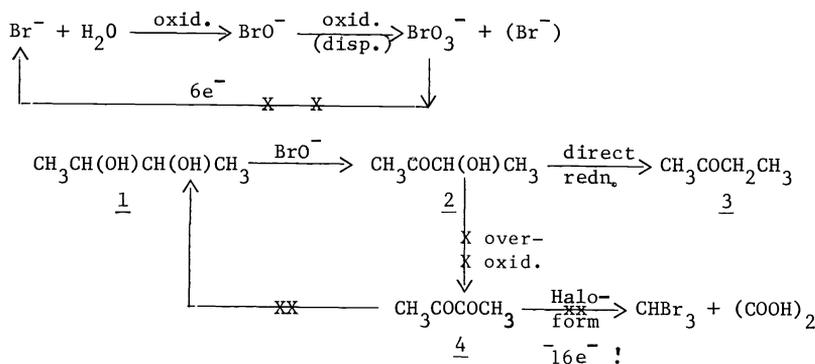
Conversion of 2,3-butanediol to 2-butanone

The diol is a biomass-derived, very water-soluble, high boiling liquid available in 10% aqueous solution; it has very little intrinsic utility. A useful objective is to convert it electrochemically by simple means to more useful volatile or less soluble product(s).

Of several possible alternatives, e.g., converting it to acetaldehyde in an oxidative decoupling reaction (ref.62) or to hydrocarbons by reduction of suitable derivatives (ref. 63) we chose initially to involve it in a paired syntheses leading to 2-butanone (ref. 64).

The functional group transformations involved in converting the diol 1 to the ketone 3 via 2 are plainly the replacement of one of the hydroxyl groups by hydrogen (a reduction) and the oxidation of the other to carbonyl. Since reduction of an alcohol to its parent hydrocarbon is very difficult unless the alcohol is first derivatized (ref. 65) but is facile if it is adjacent to an electron-withdrawing group, the sequence for the "paired" syntheses demands that the oxidation be done first. To support a desired necessary cathodic reaction simultaneously, a small amount of the product to be formed in the oxidation is charged initially.

It soon became evident that an indirect oxidation of 1, preferably with anodically generated bromonium species, was superior to a direct oxidation and that initially at least direct reduction of 2 with amalgamated lead or zinc cathodes would be satisfactory. The traps into which the electrochemical/chemical system involved might lure us are indicated in the scheme below. (~~→~~ and ~~←~~ indicate undesired reactions.)



Some of these side-reactions would simply lead to a loss of current efficiency, which could be tolerated if necessary; others would lead to chemical by-products which were intolerable.

Preliminary experiments in H-cells showed that under the proper conditions it would be possible to obtain 3 exclusively. Two types of flow systems in undivided cells were then evaluated. Satisfactory results could be obtained under the following conditions: electrolyte, 0.8-1.0 M sodium bromide; substrate, 10% 1 (77% meso- and 23% DL-); electrodes, packed bed, amalgamated lead or zinc cathodes, graphite chip anodes; parallel current and electrolyte flow; pH ca. 7; ambient temperature; current density 2 mA cm⁻²; five-minute residence time outside the cell. The not fully optimized conditions gave 75% yields and 60% current efficiency. Means for improving these results are under investigation.

Conversion of glucose to sorbitol and gluconic acid

Both sorbitol and calcium gluconate are commercial products. Each separately has been made electrochemically from glucose. The sorbitol process was an important successful moderately large-scale electro-organic process from 1937-1948 (ref. 66) when it was replaced by a catalytic process. The indirect oxidation by hypobromite of glucose to gluconic acid (or calcium salt) is still practiced (ref. 67). We did not have the fortitude our predecessors had to resist the temptation to conduct the oxidation and the reduction simultaneously in one undivided cell. The fact that in each case a two-electron step was involved was alluring. Even more sweet was the prospect that if we were successful in developing a viable process we would see sorbitol, originally made electrochemically, then by a more economic catalytic route, again made even more economically electrochemically because it was only half of a saleable pair of products.

Preliminary experiments indicated that: (1) the well-known indirect oxidation of glucose by hypobromite was superior to any other indirect or to a direct oxidation, (2) gluconic acid was not reduced at the cathode, (3) in a glucose-sorbitol mixture the former was by far preferentially oxidized, (4) sorbitol was not reduced at the cathode, (5) hydrobromite \rightarrow bromite \rightarrow bromide cycling could be a source of loss of current efficiency, (6) calcium bromide would be the preferred electrolyte since calcium gluconate was the desired end-product but calcium ions enhanced (useless) hydrogen evolution at the cathode, (7) the calcium ions depleted by forming the product salt could be replenished by calcium carbonate or lime, (8) all ingredients of the system except calcium gluconate are extremely water soluble and therefore separations would be a problem, (9) specifications for both commercial end-products indicated that only a low percentage of glucose could be tolerated but consuming all the glucose electrochemically would risk losing selectivity in the oxidation step, (10) pH control is very important in avoiding isomerization of glucose to fructose which is more easily reducible and leads to undesired by-products as well as degradation products.

Another problem unanticipated early in the work but then identified and solved presented itself. The first oxidation product of glucose is not gluconic acid but gluconolactone which is reducible (to glucose) thereby wasting current. Since the hydrolysis/saponification of the lactone is not instantaneous, enough time, at an appropriate temperature and pH, would have to be allowed in a holding tank for this to occur before the solution was recycled to the cell.

Our first report (ref. 68) indicated that the oxidation and reduction could indeed be paired, no by-products were formed, but the yields and current efficiencies were far from satisfactory under "optimum" conditions: amalgamated zinc cathode, graphite anode, 0.8 mol dm⁻³ sodium bromide as electrolyte, initial glucose concentration of 0.8 mol dm⁻³, pH of 7, and an electrolyte flow rate of 0.8 L min⁻¹. The oxidation went very well but the reduction was plagued by hydrogen evolution and recycling of gluconolactone. The latter problem was solved by the means mentioned above but the former was not, even by using other amalgamated cathodes and electrolytes with quaternary ammonium cations. It was clear that a drastic change in the nature of the cathodic reduction had to be undertaken.

While Raney nickel and similar catalytic cathodes had been used sporadically previously, their use was now beginning to attract more attention. Chiba et al. (ref. 44) had used Raney nickel successfully for the cathodic reduction of a variety of aromatic carbonyl compounds but reported that they were unsuccessful with the corresponding aliphatic compounds. We reflected that our conditions, particularly of pH, were very different from Chiba's and in addition we had faith that no dicta since the Ten Commandments are carved in stone.

Success quickly followed. Since the desired cathodic reaction was now discharge of protons there was no undesirable effect from the presence of calcium ions and we could use calcium bromide as the electrolyte. The pH range 5-7 was high enough to prevent dissolution of nickel and low enough to prevent glucose from undergoing its several base-catalyzed divergences. The other parameters were: 1.6 M glucose solution, 0.4 M calcium bromide, 60°, 250-500 mA per 10g of Raney nickel cathode, volumetric flow rate 100 ml min⁻¹. Yields and current efficiencies for the cathodic and anodic reactions approached 100% (ref. 40).

There are a number of secondary problems to be solved before this process is ready for scale-up. The powder electrode is pressed against a support, e.g., a glass disc, and therefore the circulation pattern must be such as to ensure contact. Other more rigid catalysts with a Raney nickel-like surface are available. The Raney nickel tends to become inactivated upon repeated use. Means for regeneration without interrupting the process in a bank of cells have been worked out and will be reported in due course. Above all, separation of products and starting materials in order to yield goods meeting specifications must be completed. Progress toward this end is not being impeded by lack of ideas.

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