The Use of Platinum Anodes in Organic Anodic Processes

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Platinum, the most plentiful of the platinum group metals, has many uses due to its resistance to corrosion. In addition, it is extremely useful as a catalyst for oxidations, such as for the production of sulphuric and nitric acids, and for hydrogenation as in the production of many pharmaceuticals and chemicals. In inorganic chemical industry platinum is widely used as the anode in a number of electrochemical processes, but perhaps least known is its usefulness as an anode in the electrolytic oxidation of organic compounds.

This metal, unlike the others which have been used as electrodes in anodic processes, has the advantage of being essentially passive in most electrolytes. As a result it is possible to obtain graded potentials with platinum. With the non-platinum group metals, it is generally difficult to obtain such a stable anode potential, as the potential generally rises rapidly from the low value, at which the anode dissolves, to the high value for passivity and oxygen evolution. In those circumstances in which platinum is less passive, that is, in the presence of halogen acids, it is possible to counteract the action of these acids merely by incorporating 5 to 10 per cent of iridium into the electrode.

The Mechanism of Anodic Oxidation

One of the most widely used anodic organic reactions is the Kolbe reaction. Although Faraday, as early as 1834, demonstrated that upon electrolysis of an acetate solution he obtained some hydrocarbon (1), detailed data did not become available until Kolbe came
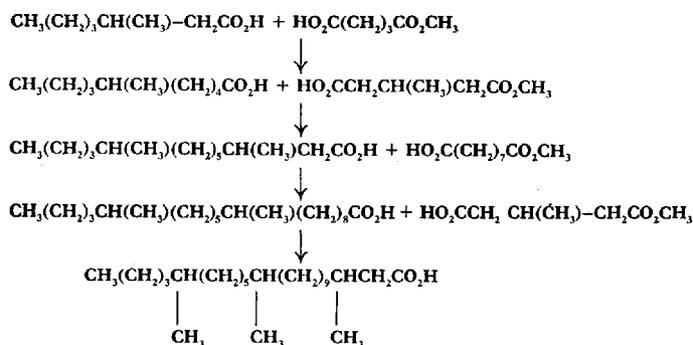
Electrochemical methods of preparing inorganic chemical products are well known, and the reactions taking place at anode and cathode are well understood. In the organic sphere an increasing interest is developing in electrolytic methods of preparation, but the processes are neither so widely used as yet, nor are the principles so well clarified. Dr. Allen, who is Director of the Physical Research Laboratories of CIBA, has devoted much energy and enthusiasm to studies in organic electrochemistry and he and his colleagues have devised a number of preparative methods for pharmaceutical products or intermediates based upon anodic oxidation and allied electrolytic processes. In this article he reviews the mechanism of these reactions and outlines some of the important syntheses capable of being effected with the aid of platinum anodes.

on the scene. He showed that electrolysis of an acetate salt yielded ethane and carbon dioxide (2):

$$2 \ CH_3COO^- \longrightarrow 2 \ CO_2 + C_2H_6 + 2e$$
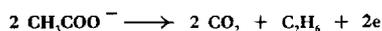
This process was considered by its discoverer to involve the oxidation of the carbonyl group by oxygen obtained from the electrolysis of water.

An interesting fact about this reaction is that in an aqueous medium, the hydrocarbon is formed in appreciable quantities only at a smooth platinum or iridium anode. If a

$$CH_3(CH_2)_3CH(CH_3)-CH_2CO_2H + HO_2C(CH_2)_3CO_2CH_3$$

$$\downarrow$$

$$CH_3(CH_2)_3CH(CH_3)(CH_2)_4CO_2H + HO_2CCH_2CH(CH_3)CH_2CO_2CH_3$$

$$\downarrow$$

$$CH_3(CH_2)_3CH(CH_3)(CH_2)_5CH(CH_3)CH_2CO_2H + HO_2C(CH_2)_7CO_2CH_3$$

$$\downarrow$$

$$CH_3(CH_2)_3CH(CH_3)(CH_2)_5CH(CH_3)(CH_2)_8CO_2H + HO_2CCH_2 CH(CH_3)-CH_2CO_2CH_3$$

$$\downarrow$$

$$CH_3(CH_2)_3CH(CH_2)_5CH(CH_2)_9CHCH_2CO_2H$$
$$\qquad\quad | \qquad\quad | \qquad\quad |$$
$$\qquad\quad CH_3 \quad\ CH_3 \quad\ CH_3$$

Synthesis of ($\pm$)-3,13,19-trimethyltricosanoic acid from 3-methylheptanoic acid in a series of four electrolyses

platinised platinum, gold, palladium, nickel or iron anode is used, the efficiency for hydrocarbon formation is considerably reduced and methanol is the predominant product from the electrolysis of acetates. Although the type of electrode material is not of as great importance when the Kolbe reaction is performed in non-aqueous media, from a practical point of view these types of media are not too desirable because of their greater resistance to the passage of current.
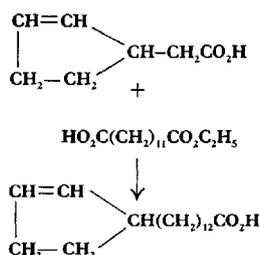
Much has been written concerning the mechanism of this reaction. Although numerous mechanisms have been proposed, they all have essentially one feature in common: the reaction that occurs via a free radical mechanism. Therefore it would be preferable to utilise a high over-potential state such as is found with platinum.

Synthesis of Fatty Acids

The applications of the Kolbe electrosynthesis are numerous, and have been described by the present author elsewhere (3). Only a few will be given here by way of illustration. For example, this electrochemical method has been found extremely satisfactory for preparation of many biologically active branched-chain fatty acids as found in nature (4). One such acid, ($\pm$)—3,13, 19-trimethyltricosanoic acid, has been synthesised from 3-methylheptanoic acid (5) in a series of four electrolyses.
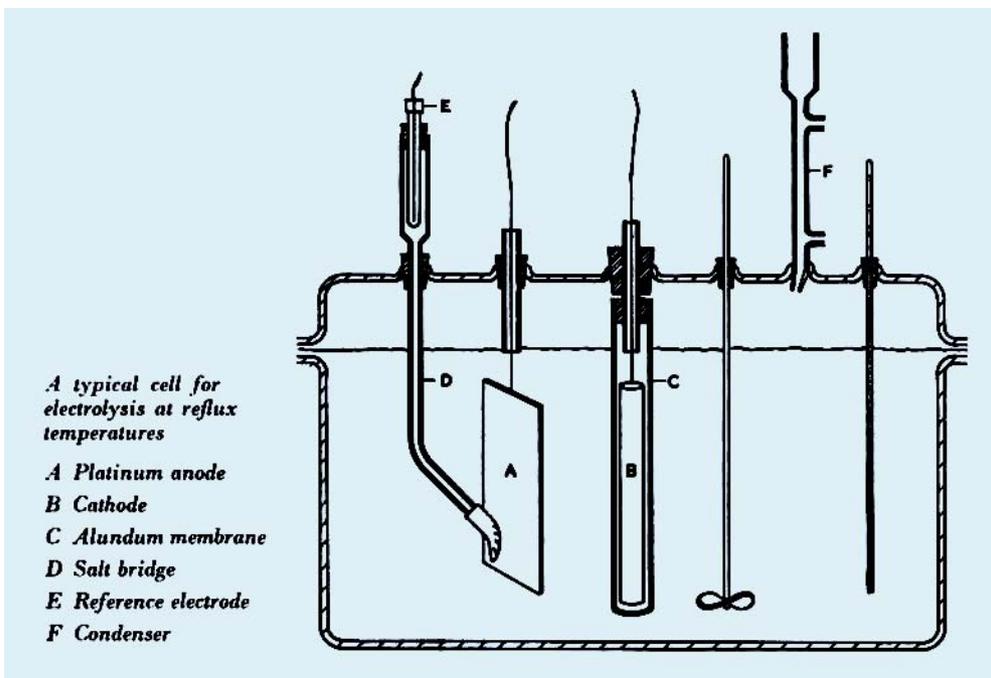
Of interest is the efficient method developed by Mislow and Steinberg (6) for the synthesis of chaulmoogric acid. Electrolysis of a mixture of (+)-cyclopentenyl acetic acid and ethyl brassylate, followed by saponification of the product mixture, yielded chaulmoogric acid identical with the natural product.

$$CH=CH$$
$$| \qquad\qquad\qquad CH-CH_2CO_2H$$
$$CH_2-CH_2$$
$$\qquad\qquad +$$

$$HO_2C(CH_2)_{11}CO_2C_2H_5$$

$$CH=CH \qquad\qquad \downarrow$$
$$| \qquad\qquad\qquad CH(CH_2)_{12}CO_2H$$
$$CH_2-CH_2$$

Synthesis of chaulmoogric acid from (+)-cyclo-pentenylacetic acid

Syntheses by Anodic Alkoxylation

Anodic alkoxylation reactions performed with a platinum anode have become an increasingly important tool in the synthesis of many intermediates that could not previously be prepared efficiently by the usual chemical methods. In this connection we may cite the methoxylation of furan. The reaction of furan with a methanolic solution of chlorine or bromine yields 2,5-dimethoxy-2,5-dihydrofuran (7). As the product obtained by the chemical method is often contaminated with a small quantity of halogen-containing impurity, the stability of the acid-sensitive di-

A typical cell for electrolysis at reflux temperatures

A Platinum anode
B Cathode
C Alundum membrane
D Salt bridge
E Reference electrode
F Condenser

methoxydihydrofuran is not too great. With the electrochemical method, a halogen-free product is obtained (8). In the reaction, a methanolic solution of ammonium bromide is mixed with the furan and subjected to electrolysis at a platinum anode at a temperature of −14°C. During electrolysis ammonia and hydrogen are liberated at the cathode; the bromine which forms at the anode reacts with the methanol and the furan to give the desired compound:

$$\text{furan} + 2\ CH_3OH + 2\ Br^- \longrightarrow CH_3O\text{-dihydrofuran-}OCH_3 + 2\ HBr$$
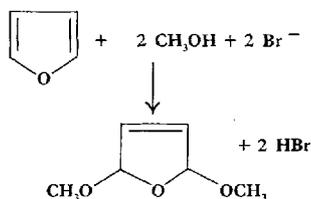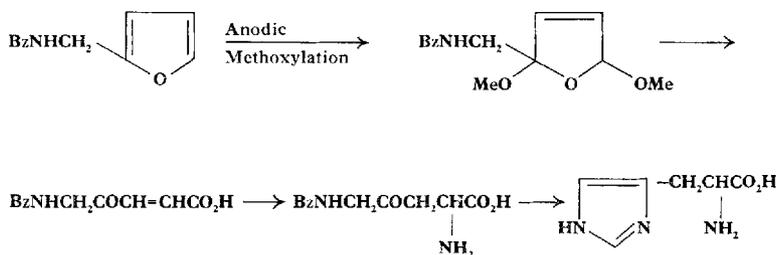
Anodic methoxylation of furan

The ammonia liberated at the cathode reacts with the hydrogen bromide to regenerate the ammonium bromide required in the process. This highly efficient process has been applied to the methoxylation of such furans as 2-methylfuran, furfuryl alcohol, and furfuryl acetate, with the final products being the corresponding 2,5-dihydro-2,5-dimethoxyfuran in each case (9). Ethoxylation of the furans has also been accomplished by using ethanol instead of methanol in the process. With furan under these conditions the 2,5-diethoxy-2,5-dihydroxyfuran is obtained (10).

More recently it has been demonstrated that the methoxylation of furan can be accomplished by utilising the medium of sodium hydroxide and methanol (11). Thus all possibilities of destruction of 2,5-dihydro-2,5-dimethoxyfuran by halogen are eliminated.

This method has been applied to a large number of furans with considerable success. In addition, it has opened the way to a number of interesting new syntheses.

A useful route to the synthesis of pyrroles has been developed by utilising the dialkoxy-dihydrofuran obtained by anodic substitution, reducing this to the tetrahydrofuran and then reacting it with a primary amine or ammonia. Application of anodic methoxylation to furfurylamine and its derivatives has resulted in a route to the synthesis of pyridols, which has

Anodic methoxylation applied to the synthesis of histidine

been extended to give a novel synthesis of the vitamin pyridoxine (12).

Another interesting application of this method is in the synthesis of histidine (13).

A modification of this reaction has made it possible to chloromethoxylate a number of steroids utilising a platinum anode and a medium of lithium chloride in methanol (14):
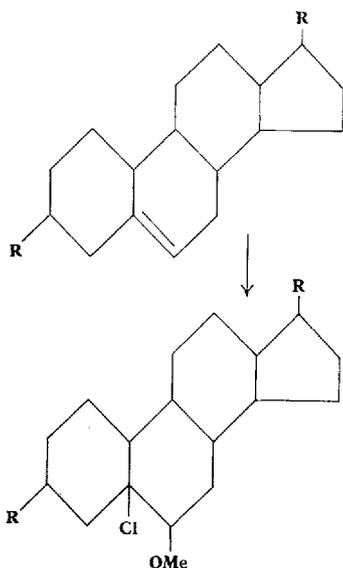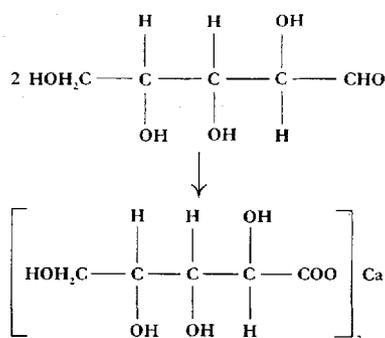

Anodic chloromethoxylation of steroids

## Some Anodic Oxidation Processes

Anodic oxidation has been used with great success in many organic processes. For example, calcium arabinate, a blood supplement given intravenously, is obtained by oxidation at a platinum anode in a medium containing calcium carbonate and a small quantity of calcium bromide (15):
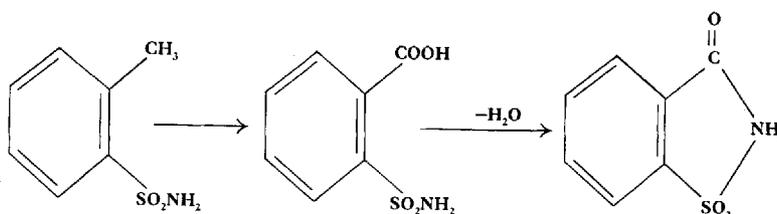

Anodic oxidation of arabinose, in a medium containing calcium carbonate and calcium bromide, yields calcium arabinate

Nicotinic acid is readily obtained by the oxidation of nicotine at a platinum electrode in an aqueous sulphuric acid medium (16):
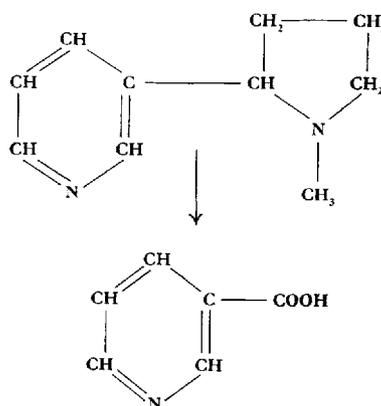
Anodic oxidation of nicotine to nicotinic acid

Synthesis of saccharin by anodic oxidation of o-toluene-sulphonamide

Alizarin, an important dyestuff, is prepared from anthraquinone. This intermediate is obtained by oxidation of a suspension of anthracene in an acetone-sulphuric acid medium at a platinum anode (17).

Of interest too, is the efficient synthesis of saccharin from o-toluene-sulphonamide using a platinum anode and a 2N sodium carbonate medium (18). In this process the sulphonamide is first oxidised to o-carboxyl-sulphonamide, which then loses a mole of water to form saccharin, as shown above. Earlier investigators had shown that oxidation of o-toluene-sulphonamide could readily be accomplished with a platinum anode in a 2N sodium carbonate solution at 600°C, a membrane not being required to separate anolyte from catholyte if a lead cathode were used. This procedure was reported to give a 40 per cent yield of saccharin. Addition of an oxygen carrier resulted in a yield of 75 per cent, the preparation of saccharin by an electrolytic process thus becoming a practical procedure.

Anodic Polarography

Any discussion of anodic oxidation processes, however brief, should make mention of the use of the rotating platinum electrode in anodic polarography. The introduction of a platinum electrode of such a design as to give reproducible results has created many possibilities for it in the study of anodic mechanisms and as an analytical tool (19). Its application to the study of the mechanism of oxidation of indole alkaloids and the quantitative determination of one in the presence of others indicates the potential usefulness of this technique (20).

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