Organic Electrode Processes: Kinetics, Mechanisms, and Prospects for Commercial Development

E. J. RUDD and B. E. CONWAY

1. Historical Aspects

Organic electrochemistry has its origins in the last century when quite a number of now well-known electrochemical oxidations and reductions had been achieved at electrodes and Kolbe's unique oxidative dimerization of aliphatic carboxylates had been described. (1-7) Developments in the dye industry in the early 1900s stimulated many studies on electro-organic procedures, e.g., reduction of nitro compounds to amines. In 1926, Brockman(7) gave an excellent account in his book of the many types of electrochemical routes for functionalizing organic compounds and for modifying existing functionalities by oxidation or reduction.

Unfortunately, mechanisms of elementary steps, e.g., electron transfer, in electrode processes were not at all well understood during the period of early development of electro-organic chemistry, and the significance of the fundamental relation between overpotential ("polarization") and current density was not appreciated until the work of Volmer, Gurney, Bowden,
Rideal, and Butler in the early 1930s.\(^{(8,9)}\) Similarly, the role of adsorption in electrode interface processes,\(^{(10)}\) which is of great importance in many, if not all, electrode reactions involving organics, was hardly appreciated until Frumkin's pioneering work, which formed a cornerstone of the research of the Russian school of electrochemistry.

To those who have been involved with electrochemical technology, it has often seemed somewhat illogical that there are so few established industrial processes based on organic electrochemistry. Indeed, the number of processes "on stream" at any time could probably be counted on the fingers of one hand. Yet, electrochemical processes are firmly established in the manufacture of some inorganic chemicals and extraction and purification of metals.\(^{(11,12)}\) For example, the production of chlorine and sodium hydroxide alone accounts for approximately 2% of the total consumption of electricity in the United States and, together with that for Al, much more. This apparent lack of acceptance of organic electrode processes as viable means for (certain types) of syntheses (see later) is perhaps all the more surprising when it is noted that electrolytic reactions are simply very direct oxidation and reduction processes which do not produce in the solution other conjugate reduced or oxidized species, respectively, such as would occur with homogeneous redox reagents.

The development of organic electrochemistry can be conveniently illustrated by the scheme shown as Figure 1. Early in the nineteenth century, the oxidation of acetic acid by Faraday\(^{(13)}\) demonstrated the ability of an electric current to decompose organic substances, and by the end of that century, Gatterman, Kolbe, Haber, and others\(^{(7,14)}\) had extended the field of electro-organic chemistry substantially. However, after this initial activity, the scientific community paid only minimum attention to organic electrode processes for some time until the resurgence of interest in the field took place in the 1960s.

Limitations to the acceptance of organic electrochemistry, particularly as a synthetic technique, may have been connected with the fact that electrode reactions are normally "two-dimensional," i.e., they are restricted to a surface and therefore require mass transport (see elsewhere in this chapter) and also because many reactions yield a complex mixture of products\(^{(15)}\) when the electrolyses are carried out using a constant current. However, as early as 1898, Haber\(^{(14)}\) had pointed out the importance of control of the electrode potential for the overall process, in his work where nitrosobenzene, phenylhydroxylamine and aniline were isolated selectively from the reduction of nitrobenzene. However, design of suitable controlled-potential equipment proved to be a practical barrier, even in laboratory studies, until 1942, when the potentiostat—an instrument capable of automatically controlling the electrode potential—was introduced.\(^{(16)}\) Without question, this instrument has facilitated electro-organic syntheses, mechanistic studies, and specific electro-oxidation and electroreduction processes. More modern and electronically