

*Prospects for further industrial applications of organic electrosynthesis**

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Recent progress toward commercialization of organic electrochemical synthesis is reviewed and interpreted. The impact upon future prospects of the present-day need for industry to re-evaluate its technology because of costlier feedstocks and the need to minimize pollution and to conserve energy, are discussed. Steps to improve the future acceptability of organic electrochemical processes are suggested.

Following the announcement in 1965 of the commercialization by Monsanto of its electrohydrodimerization process for adiponitrile and by Nalco of its electrochemical route to tetralkyl leads there was a worldwide upsurge in activity, both industrial and academic, in organic electrochemical synthesis. By comparison with the relative lassitude in the field during the previous quarter-century, the infusion of new effort into the field could be called frenetic. Many new reactions were reported. Several new books appeared [1–7] which closed the gap between the classic Fichter and the present era. Interested organic chemists learned or could learn that organic electrochemistry embraced more than polarography, the Kolbe reaction and alternative means of oxidizing or reducing functional groups. The chemistry of electrogenerated ion radicals, radicals, and organic ions was greatly expanded. Forums for presenting and discussing new work became abundant. Some workshops and training courses became available, although more slowly in the US than elsewhere. Physical chemists, who could now rely on a wealth of data concerning products, by-products, and efficiencies of various syntheses, were spurred on to develop highly sophisticated means for elucidating mechanisms of organic electrode reactions.

Industrial firms which had previously ignored the relevance of organic electrochemistry to their own interests hastily activated or assembled

groups, sometimes of one member, to search for *their* magic switch. Alas, in their overeagerness they often overlooked the fact that many benign influences must be simultaneously at work before *any* innovative process is adopted; this point has been recently discussed in a narration of the adiponitrile case history [8]. As a result of the absence of at least one of the factors, the number of new processes (see below) commercialized in the period 1965–1980 is smaller than might have been expected.

The pace of industrial development would probably have been more rapid if organic electrochemical engineering had accelerated its growth earlier [9, 10]. However, we have now finally come a long way from having to choose only between plate-and-frame and stirred tank cells. Within a decade, if the present pace continues, electrochemical synthesis and electrochemical processing will be running side-by-side on parallel tracks. Even now, electrochemical syntheses of a number of major tonnage organic chemicals are judged to be competitive with ‘conventional’ syntheses [11].

A new era for the chemical industry can be said to have begun in 1973. Just as the ‘Youth Rebellion’ in the 1960s in the US drew into its vortex issues that were sometimes related only by being contemporaneous (protests against the Vietnam War, civil rights, women’s ‘liberation’, reforms of the university system), so the chemical

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industry has been faced simultaneously with serious increases in the price of petroleum feedstocks, more stringent demands for controlling effluent streams and the need for reducing energy consumption. One response of industry to this array of challenges has been to re-examine *all* its technology and to seek alternative processes which avoid as many of the difficulties mentioned above as feasible. Just as in an individual company replacement of an existing process by a new one is most likely to occur when old equipment is disintegrating or there is a foreseen demand for expansion of capacity, so the convergence of the problems mentioned above forces industry to examine previously uneconomic options it may have otherwise ignored or rejected.

It is a tribute to the dedicated efforts of many organic electrochemists and engineers who pursued their 'mission' through workshops, technical societies, journals, lecture tours and tutorial visits to industrial companies, that organic electrochemical technology is finally being assessed along with other technologies in industry's quest for solutions to its manifold manufacturing problems. *Fortunately* this scrutiny will continue for a considerable period; at the moment organic electrochemical technology, which is an adolescent, is being tried in the same court in which adult technologies are pleading their cases. *Unfortunately*, many industrial firms which dutifully chant the call for more innovation tend to be conservative, particularly in times of economic stress, and plead (from *The Soliloquy*) that the high cost of risks

'... makes us rather bear those ills we have
Than fly to others that we know not of'.
Of this, more anon.

That these reassessments are in individual cases national in scope is illustrated by the following three examples: (a) in the UK a survey under the leadership of Dr Derek Pletcher [12] has been conducted on the practices, prospects, and needs in industry for further utilization and development of electrochemistry; (b) in the US a study sponsored by the Department of Energy [13] has been made titled *A Survey of Organic Electrolytic Processes*; (c) in the Federal Republic of Germany, DECHEMA, at the behest of the Minister for Research and Technology, has produced a series of books on *Forschung und Ent-*

wicklung zur Sicherung der Rohstoffversorgung. Study (c) consists of three major parts. Part III has nine volumes of which Volume III (1976) is devoted to *Electrochemical Processes* (including organic). Each category is responsive to questions concerning (i) general aspects, (ii) current status of the technology and science, (iii) continuing developments and trends, (iv) desired developments, (v) proposals for research and development, (vi) *possible* developments (speculative).

Whilst the US study, by design, focused entirely on the question of energy savings *via* electrochemical processes, the DECHEMA inquiry was of greater scope, considering not only the question of raw materials (as indicated in the title) but also energy savings, pollution abatement, recycling, improvement of working conditions and the benefits to be gained from developing new technologies even though they are not yet economical.

It is plain that nowadays this entire complex of factors must enter into a broad evaluation of the prospects for industrial applications of organic electrosynthesis. Any specific application must in addition consider questions of:

1. *Scale*. Tonnage commodity chemicals? Medium volume products? Pharmaceuticals and fine chemicals?
 2. *Alternative technologies*. Existing and emerging.
 3. *Type of process*. Replacement of present oxidants and reductants used in stoichiometric quantities by electro-regenerated reagents? Replacement of multi-step by single-step processes? Uniquely electrochemical processes such as fluorination and paired syntheses (i.e. use of both anode and cathode reactions in a synthesis)?
 4. Likelihood of achieving *up-scaling* to the desired rate and volume?
 5. *Appropriateness* of an electrochemical process to a given domestic economy; advantageous siting of a plant?
- Some clues as to how industrial chemists and executives have analyzed for themselves these matrices of questions may be found in examining some of the processes which have recently been studied to at least the post-laboratory stage (Table 1). The author interprets these clues as follows:
- (a) The largest present electrochemical process

Table 1. Some reported practical electro-organic syntheses*

Product	Raw material	Company (Country)	Scale (Status)	Type of process
acetylenedicarboxylic acid	butynediol	BASF/FRG	(pilot plant)	oxidation of functional group
adiponitrile	acrylonitrile	Monsanto (US) Monsanto (UK) Asahi (Japan)	10 ⁸ kg/year (commercial) 10 ⁸ kg/year (commercial) 2 × 10 ⁷ kg/year (commercial)	reductive coupling
<i>o</i> -aminobenzyl alcohol	anthranilic acid	BASF (FRG)	(pilot plant)	reduction of functional group
1-amino-4-methoxynaphthalene	1-nitronaphthalene	BASF (FRG)	(pilot plant)	reductive rearrangement
<i>p</i> -aminophenol	nitrobenzene	(Japan) Holliday (UK)	(commercial) (commercial)	reductive rearrangement
aniline	nitrobenzene	(India)		indirect reduction [Ti(II)]
<i>p</i> -anisidine	nitrobenzene	BASF (FRG)	(pilot plant)	reductive rearrangement
anthraquinone	anthracene	Holliday (UK)	(commercial)	indirect oxidation
benzaldehyde	toluene	(India)	(past pilot plant)	indirect oxidation [Mn(II)]
<i>p</i> -carbomethoxybenzyl alcohol	dimethyl terephthalate	Hoechst (FRG)	(pilot plant)	reduction of functional group
1,4-dihydronaphthalene	naphthalene	Hoechst (FRG)	(pilot plant)	reduction
1,4-dihydronaphthyl ethers	naphthyl ethers	Hoechst (FRG)	(pilot plant)	reduction
dihydrophthalic acid	phthalic acid	BASF (FRG)	(commercial?)	reduction
2,5-dimethoxydihydrofuran	furan	(Japan) BASF (FRG)	(commercial) (commercial)	oxidative addition
fluorinated organics	hydrocarbons, aliphatic carboxylic acids	Dai Nippon (Japan)	(commercial)	anodic substitution
gluconic acid	glucose	(India)	3 × 10 ⁵ kg/year (commercial)	oxidation of functional group
glyoxylic acid	oxalic acid	(Japan)	(commercial)	reduction of functional group
hexahydrocarbazole	tetrahydrocarbazole	BASF (FRG)	(commercial)	reduction
hydroquinone or quinone	benzene	several (several)	(past pilot plant)	paired synthesis or anodic oxidation ± chemical reduction
maltol	furfuryl alcohol	Otsuka (Japan)	(past pilot plant)	oxidation
metanilic acid	<i>m</i> -nitrobenzenesulphonic acid	BASF (FRG)	(pilot plant)	reduction of functional group
2-methyl-1-naphthyl acetate	2-methylnaphthalene	BASF (FRG)	(pilot plant)	anodic substitution
pinacol	acetone	(Japan) BASF (FRG)	(past pilot plant)	reductive coupling

Table 1. (continued)

Product	Raw material	Company (Country)	Scale (Status)	Type of process
the pinacol	<i>p</i> -hydroxypropiofenone	Sorapec (France)	(pilot plant)	reductive coupling
piperidine	pyridine	Robinson Bros (UK)	1.2×10^5 kg/year (commercial)	reduction
propionic acid	propargyl alcohol	BASF (FRG)	(pilot plant)	oxidation of functional group
propylene oxide	propylene	BASF (FRG) others in UK and FRG	(past pilot plant) (past pilot plant)	paired synthesis
4,4'-bis-pyridinium salts	pyridinium salts	(Japan)	(past pilot plant)	paired synthesis
salicylaldehyde	salicylic acid	(India)	(past pilot plant)	reduction of functional group
sebacic acid diesters	adipic acid half esters	BASF (FRG) (Japan)	(past pilot plant) (past pilot plant)	Crum Brown-Walker
succinic acid	maleic acid	(USSR)	(commercial?)	
tetradecanedioic acid	monomethyl azelate	(India)	6×10^4 kg/year (commercial)	reduction
tetraethyl-lead	ethylmagnesium halide	Soda Aromatic Co. (Japan)	(commercial)	Crum Brown-Walker
		Nalco (US)	(commercial)	anodic

* A much more complete compilation is given in [13].

was carried through by a very large company (Monsanto). At stake was a specific and desired *chemical* transformation which could be realized by electrochemistry and could not be accomplished well by alternative technologies. The company was willing, in order to accomplish its objective, to train personnel internally, to devise suitable cells and systems and to maintain a continuous programme of improvement over many years.

(b) Probably the broadest range of electrochemical processes was again developed by a very large company (BASF) which produces a wide spectrum of products. Here the stress was on refining the *engineering* aspects of two types of cells (plate-and-frame and capillary gap) and, having acquired this expertise, to utilize the results in the synthesis of a variety of amenable products. Again the effort was sustained over years.

(c) The largest number of operating processes, albeit on a relatively small scale, exists in India and has at least hitherto focused on *families of products* which could be made by similar procedures. Local economic factors were of great importance: expense of catalysts, hydrogen, etc. Techniques developed to a high degree of sophistication involved the use of rotating working electrodes and metal ion-assisted electrochemical redox reactions.

(d) Several good processes have survived in the UK for many years despite the onslaught of competitive technologies.

All the above have come down to us from the pre-1973 era, before the newer exigencies of chemical manufacture became sharply evident.

There is no easy way to obtain information on what processes were taken to an early stage of development and then dropped and if so, whether the abandonment should now be reconsidered in view of the socio-economic developments of the last seven years. We are forced by the large number of patents that have issued but have not been consummated to face provocative questions: Were the inventions ultimately deemed to be uneconomical in the local context? Were they cost-estimated to death by hostile 'objective' cost estimators (not an uncommon phenomenon)? Or did conservative middle management inflict a lingering death on the new and retain the comfortable old by discussing and discussing and discussing (cf. government commissions)?

'And thus the native hue of resolution
Is sicklied o'er with the pale cast of thought
And enterprises of great pith and moment
With this regard, their currents turn awry
And lose the name of action . . .'

The face of applied organic electrochemistry, as it looks toward the future, will have a healthy hue if the following conditions prevail:

1. The capabilities of practical synthetic organic electrochemistry are more effectively conveyed to mission-oriented organic chemists and engineers. To all that has already been done must be added an attempt to introduce the discipline as part of undergraduate and graduate courses in organic chemistry and engineering.

2. The horrendous costs to industry of high-risk research and development are abated by academic-industrial co-operation and, if necessary, by initial government support. This type of activity has been of great benefit in the UK.

3. There are, as we expect there will be, continued advances in the much discussed obvious technical aspects of the field: cell designs of higher space-time yields, more desirable membranes (if needed) and electrodes, novel electrode materials (e.g., metal oxides) and forms (e.g., carbon fibres), more confident predicability of up-scaling, etc.

4. There is convincing demonstration that most, if not all, of the present processes which use stoichiometric quantities of reductants and oxidants (except air) can be replaced by electrochemical processes which use only catalytic amounts of these reagents.

5. There is greater emphasis on the type of synthesis which electrochemistry can accomplish uniquely or exceptionally well rather than in a 'me-too' fashion.

6. The manufacturers of medicinals, fine chemicals, and specialties, long considered obvious candidates for adoption of electrochemical processes, are targeted for special attention.

7. Research and development programmes in industry are much better thought out than in the past. A top echelon executive must agree that if a laboratory process is technically and economically sound, if the product involved is of enduring interest to the company, and if no completely unforeseen circumstances intervene, he will continue to provide economic and moral support until success is achieved.

8. As a corollary of some of the points above: chemists and engineers will work together on a given project from the time of the first successful laboratory demonstration of a synthesis.

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