

Organic Electrochemistry as a Community

by Albert J. Fry

I am deeply appreciative to ECS for the Manuel Baizer Award in Organic Electrochemistry and also for the opportunity and incentive this award address has offered me to look into and ponder some questions I have had for some time. First of all, let me explain the term "community" in the title of this manuscript. In this usage, I have been influenced by a small but insightful book *Little Science, Big Science*, published in 1963 by Derek De Solla Price.¹ To paraphrase Price, a scientific community is a group of individuals with common research interests and special expertise. For example, one can speak of the communities of laser spectroscopists or population biologists. Other characteristics define a community; most significant of these is the fact that recent findings are shared within the community by both research papers and regular conferences and symposia. These vehicles promote growth of both the subject and the community. As we shall see, organic electrochemists do now constitute a community. But when and how did it form? And what are its implications for the future?

To begin to answer these questions, I ask another, "How many organic electrochemical papers have ever been published?" A search of *Chemical Abstracts* was carried out for all papers containing any of the terms "organic electrochemistry," "organic electrochemical," "organic electrosynthesis," and "electroorganic." This search, though still unlikely to locate all relevant papers, leads to the result shown in Fig. 1. Clearly something began to happen around 1960. What was the situation in the years before 1960? Individual research groups were publishing throughout the 20th century, e.g., those under Sherlock Swann (1900-1983) at the University of Illinois and Friedrich Fichter of the University of Basel (1869-1952), but there seems to have been little synergy among them. Activity waxed and waned; there were more publications (six) in 1898 than in 1956 (four)! However, the threshold had arrived: 1957 was the first year with more than 15 papers (18) published in organic electrochemistry, and the numbers continued to increase steadily

thereafter, until the 662 papers in 2007 represent a vastly different research landscape from 1957. Who began this growth spiral? Petr Zuman, then at the Heyrovsky Institute in Prague, published his first organic electrochemical paper in 1950,² beginning a prolific research career that continues to the present. Henning Lund, an earlier Baizer Award winner, published his first organic electrochemical paper in 1957.³ Manuel Baizer's first electrochemical paper was published in 1963, summarizing his groundbreaking studies of the electrochemical hydrodimerization of activated alkenes.⁴

The ingredients for formation of a true scientific community were now at hand, but they had not yet coalesced since, above all, people define a community. Many individuals who were eventually to become prolific contributors to the area now began to explore problems in organic electrochemistry. The first organic electrochemical papers by Ebersson, Evans, Matsumura, Nishiguchi, Osa, Peters, Shono, Schäfer, Simonet, Steckhan, Tanaka, Torii, Tokuda, Utley, and Fry all appeared in the years 1964 to 1968. The consequences of these

and many other new investigators were quickly felt: 21 organic electrochemical papers appeared in 1962, 106 in 1972, and 194 in 1982, until now, as we have already seen, the numbers are approaching 700 per year. This growth has implications, to which we will return. The final component of a scientific community came with the first large symposium on organic electrochemistry, held in 1968 under the auspices of the U.S. Army Research Office in Durham, North Carolina. But more was needed. Much of the contemporary electrochemical technology we now take for granted was either primitive or non-existent as late as 1960. The hanging mercury drop electrode was described by Kemula in 1958,⁵ and Adams and his coworkers began intensive studies on solid electrode voltammetry around the same time.⁶ Potentiostats for preparative electrolysis in organic solvents, *i.e.*, with compliance voltages of 100 V or more and currents in the 1 A range, appeared only in the mid 1960s. The use of polar aprotic solvents in electrochemistry was pioneered by Wawzonek in the late 1950s; this was to be of enormous importance to later studies of reaction

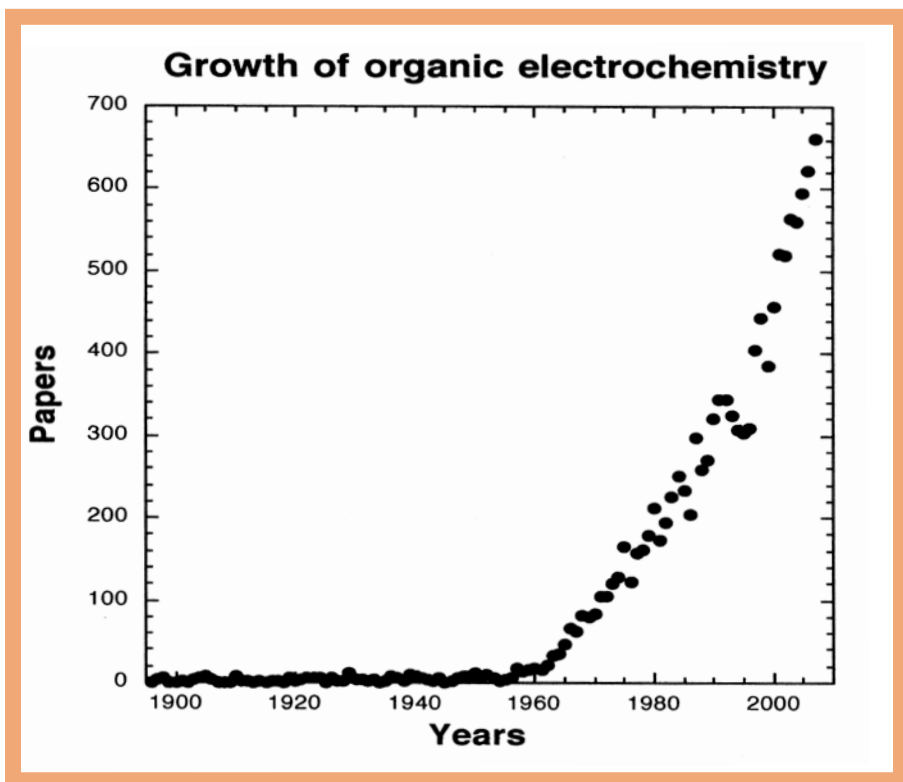


Fig. 1. Growth in annual numbers of organic electrochemistry publications from 1896 through 2007.

Ed. Note: This article was condensed from the Award Address presented at the Organic & Biological Electrochemistry Division's Manuel Baizer Symposium at the ECS meeting in Phoenix, Arizona, in May 2008.

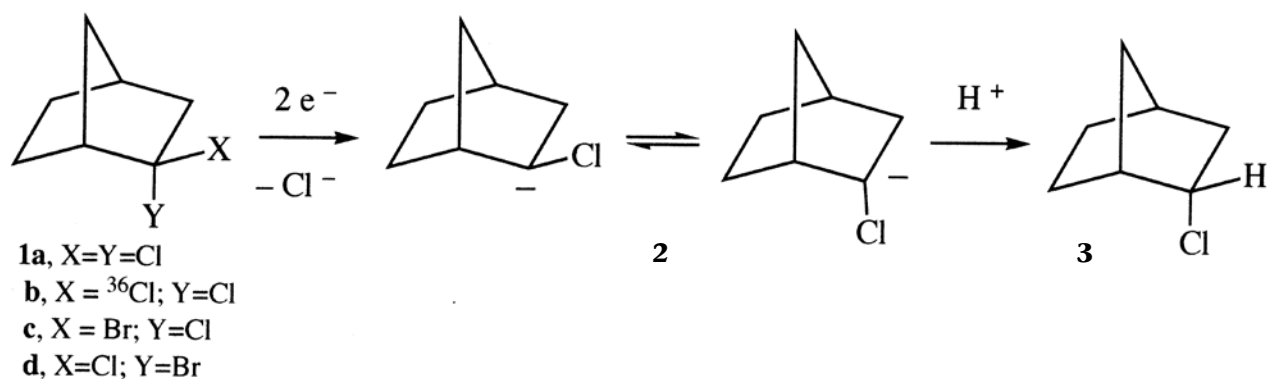


Fig. 2. Cathodic reduction of 2,2-dihalonorbornanes.

mechanisms involving reactive anionic intermediates.⁷ Polarography at the dropping mercury electrode had been a well-established technique for many years, but the theory of voltammetry at stationary electrodes in unstirred solution did not exist until the elegant theoretical analyses by both Savéant and his coworkers and Shain and Nicholson, beginning in the early 1960s.⁸ The first methods for the digital simulation of voltammograms, now a major tool in determination of mechanisms of electrode reactions, were described by Feldberg in 1964.⁹ Thus the techniques of modern organic electrochemistry were appearing at precisely the same time that new investigators were turning to the field in substantial numbers. The community of organic electrochemists was forming, and its members were coming from diverse backgrounds. The new techniques had been developed primarily by analytical chemists, who increasingly applied the new techniques to organic problems. Many others entering the field were organic chemists who were beginning to appreciate the power of electrochemical techniques to solve purely organic chemical problems or to carry out transformations previously impossible by traditional organic methods. Investigators trained in one of these two areas have now met at conferences for more than forty years, read each other's publications, and adopted methods and approaches from each other. As a result, cross-fertilization has taken place such that it is common to see research projects employing a wide range of synthetic and electroanalytical techniques to understand a problem more deeply than would have been possible by organic or electroanalytical methods alone.

Two studies will serve as illustrations. In 1968 Buchta and Evans described the electrochemical behavior of dibenzoylmethane in dimethylsulfoxide.¹⁰ I was greatly influenced by this publication, not so much by the complex chemistry that Buchta and Evans uncovered in the

course of their study, but by the large number of instrumental and computational approaches they brought to bear on the problem. In addition to techniques such as polarography applied both to the starting materials and products and the solution during electrolysis, controlled potential electrolysis, and coulometry, they examined ESR spectra of the electrolysis mixture and of suspected products, and then solved the set of differential equations describing an autocatalytic process (in which the decomposition of an initial electrolysis product is catalyzed and thus accelerated by the product of the decomposition). This permitted them to simulate the current-time behavior of the electrolysis for different rate constants and thus obtain kinetic information on the decomposition. This elegant study demonstrated how much better a battery of techniques is for understanding any given electrode reaction than just one or two, and I resolved to expand the range of techniques used in my own research. The opportunity soon arose. At that time I had begun a study of the electrochemical reduction of organic halides. In Fig. 2, the reduction of dichloride (1a) in protic media involves a rapidly interconverting intermediate chlorocarbanion (2) and protonation of 2 affords *endo*-chloronorbornane (3).¹¹ A question of particular interest was whether the electrode is capable of distinguishing between the two stereochemically nonequivalent chlorine atoms of 1a in the first step. This question was answered in two ways. The specifically ^{36}Cl radiolabelled substance (1b) and the two isomeric bromochlorides 1c and 1d were synthesized. Reduction of 1b was shown to afford 3 containing only 7% of the radiolabel, demonstrating a 13:1 preference for removal of the *exo*-chlorine. DC polarographic theory for totally irreversible processes was then applied to show that heterogeneous electron transfer to 1c is three times faster than to 1d.¹¹ The conjecture that an electrode can discriminate

between two chemically identical but stereochemically different sites in a molecule was therefore demonstrated unequivocally by both synthetic experiments and electrochemical theory, illustrating the value of using both approaches to gain the maximum of information.

A Further Look at Growth

We saw earlier that the literature of organic electrochemistry began to increase sharply in the 1960s. It is time now to examine that growth more closely and to inquire into its implications. First, the data of Fig. 1 fit very well to an exponential function ($R^2 = 0.971$), demonstrating that organic electrochemistry has actually been growing at an exponential rate ever since its beginnings more than a century ago. These observations are not surprising. DeSolla Price showed that by many measures science as a whole grew at an exponential rate over a much longer time scale than this.¹ To choose just two examples from many quoted by Price, the number of scientists in the United States grew smoothly and exponentially ($R^2 = 0.999$) from 1,000 in 1800 to one million in 1950 and the number of world journals of science increased at exactly the same rate ($R^2 = 0.999$) from 1750 to 1950. But that is not to say that such growth is still taking place. Exponential growth cannot continue forever. Living organisms do grow at something like an exponential rate in their youth, but they ultimately attain a constant size. This has been termed "logistic" growth (Fig. 3). The field of organic electrochemistry might at some point in the future take this path, by which a stable population of organic electrochemists is eventually reached, publishing a roughly constant number of papers per year. But human activities are not living organisms. Other factors often govern their growth. Price discerned several patterns that might develop at the end of the rapid growth stage of logistics growth (Fig. 4).¹ We should look hard at these

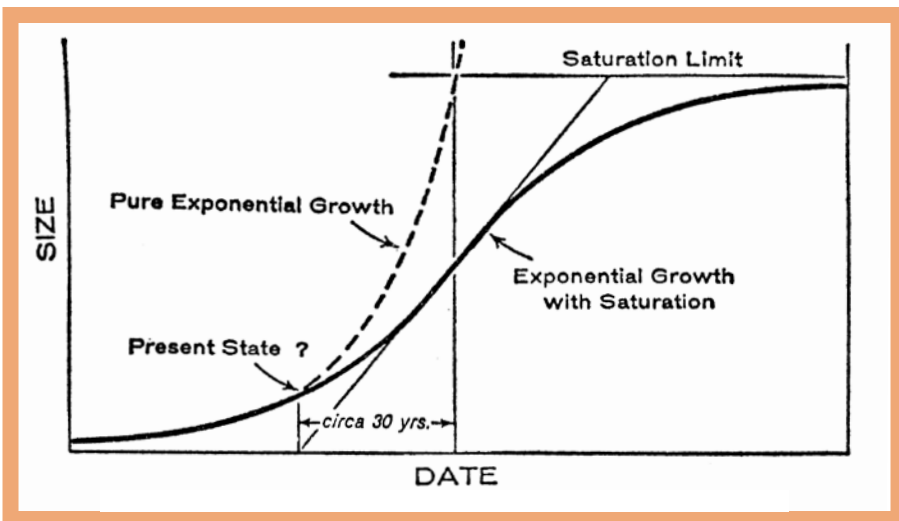


Fig. 3. Logistic growth behavior.¹ Copyright © 1963 Columbia University Press. Reprinted with permission of the publisher.

patterns because they may tell us something about the future of our own discipline, organic electrochemistry. Price describes pattern b (“loss of definition”) as a situation where “it becomes impossible to continue to measure the variable in the same way in the same units.” This is unlikely in our case since the annual number of papers in organic electrochemistry will always be readily countable. Publication rates in organic electrochemistry could eventually decrease, though, because the possibilities of the field are exhausted or it falls out of fashion. Price described curves c and d, (“Divergent” and “Convergent” oscillation, respectively), as representing cybernetic responses to impending loss of growth:

restorative processes set in but then overcompensate, causing overshoot in the opposite sense, until the system either goes out of control (divergence) or settles down to the logistic plateau (convergence). However, though such oscillations often take place in electrical circuits, it’s hard to imagine mechanisms by which this might happen in organic electrochemistry. So a reasonable conclusion at this point might be that the alternatives facing our community would appear to be to either stabilize at some size level or decline for one reason or another. However, consider the first of Price’s scenarios. He defined “escalation” as follows: “Changes in the measured quantity allow a new phenomenon to be counted together

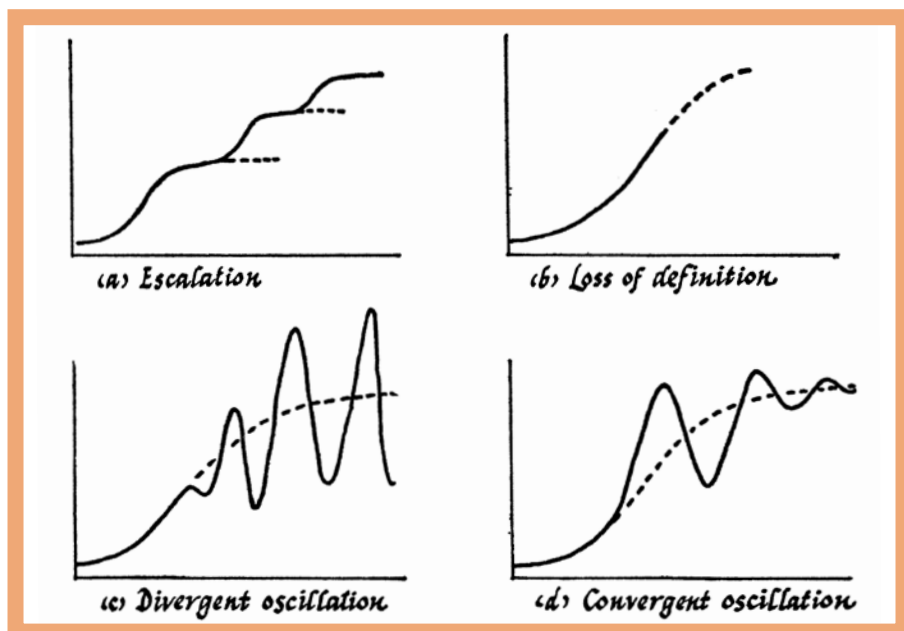


Fig. 4. Alternatives to logistic growth.¹ Copyright © 1963 Columbia University Press. Reprinted with permission of the publisher.

with the old.” In other words, the quantity being measured is redefined. In Price’s words,¹ “the curve rises Phoenix-like from the ashes of the old” (an appropriate option considering the venue of this symposium). Does it make sense to say that the fate of a research field can change simply by redefining the yardstick by which it is measured? Is there any precedent in chemistry for the escalation phenomenon? Price described a very good example that is based on the very nature of chemistry. He constructed a plot of the number of chemical elements known as a function of time (Fig. 5).¹

This illustration clearly shows a series of steps. Ten elements, *e.g.*, gold, silver, and iron, were known to the ancients, but during the interval from 1700 to 1850 another fifty or so elements were discovered by the traditional methods of “wet” chemistry: extraction, precipitation, crystallization, etc. By 1850 such methods had mostly exhausted their usefulness and the rate of new discoveries was leveling off. But a new phenomenon then entered the picture: the next half-century was characterized by introduction of a variety of physical techniques for the discovery of new elements: observation of new spectroscopic lines, electrolytic separation, analyses of the composition of air, and radioactivity measurements. These innovations, then, account for the series of steps over this time interval. In effect, the definition of an element was being expanded from “a substance that can be identified by wet chemistry methods” to “a substance that can be identified by either wet chemistry methods or by use of one or more purely physical methods.” A final surge, continuing to the present, began in the mid-20th century with the production of new elements in high energy accelerators. It is clear that escalation can be a real phenomenon in chemistry. Each age thought it had come to a reasonable definition of what a chemical element is, only to be overtaken by the development of new kinds of experiments. It is my thesis that we have entered a new age of escalation in organic electrochemistry. Some genuinely new techniques have been developed recently which promise to expand the ways that electrochemistry can be done or the information we can obtain about electrochemical processes. The examples I will cite include the introduction of microreactors for electrosynthesis, microelectrode arrays, scanning tunneling microscopy, and application of quantum chemical computations to the understanding of electrochemical processes.

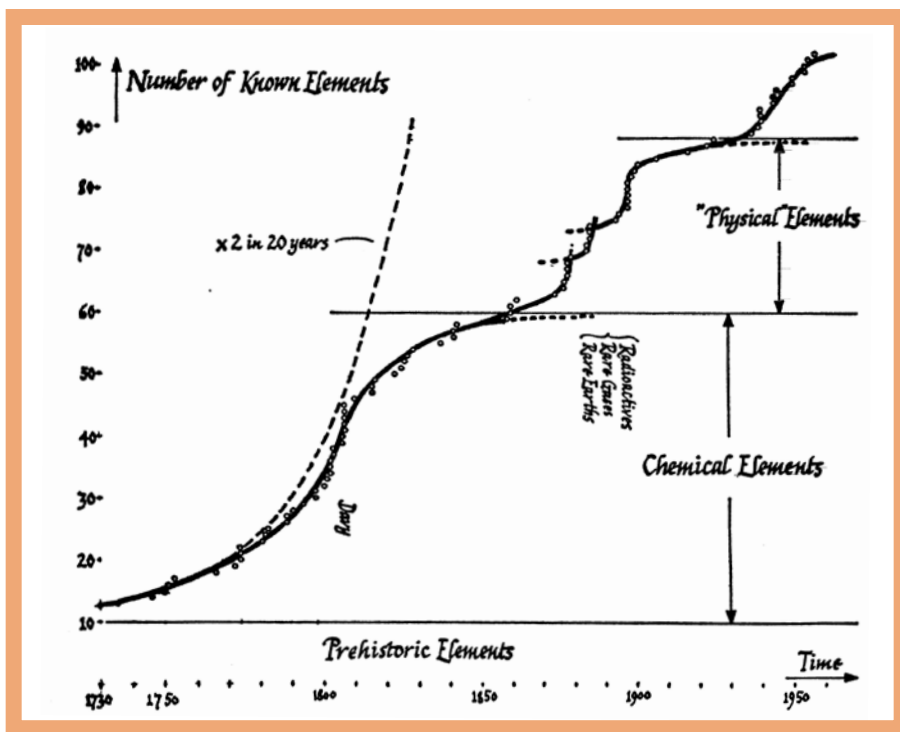


Fig. 5. Discovery of the chemical elements as a function of time. Reprinted from Derek J. de Solla Price, *Science Since Babylon*, Yale University Press, New Haven (1961). Copyright © 1961 Columbia University Press. Reprinted with permission of the publisher.

Electrochemical Microreactors

A microreactor is a small scale continuous flow reaction chamber into which reagents may be introduced by pumping; it can be as simple as a length of tubing (of inner diameter in the millimeter range) into which two components are pumped from separate sources and in which mixing and reaction take place as the components pass through the reactor. Microreactors offer many advantages over conventional processes because they permit precise control over reaction parameters including speed, temperature, and yield. Yoshida and his coworkers have recently described a wide variety of applications of microreactors in electrochemistry. For example,^{12a} a cation unstable at room temperature can be generated at -78°C by continuous electrolysis of a precursor and then pumped to a narrow-bore tubular microreactor into which an allyl silane or other electrophile is simultaneously pumped. The pumping speeds and length of the tubing reactor can then be optimized to achieve complete conversion to the desired product. The work has been extended to a variety of non-electrochemical applications.^{12b}

Microelectrode Arrays and Electrode Surface Modification

Microelectrodes, *i.e.*, those with dimensions in the micrometer range, have been used for many years. Similarly, many investigators have modified the

surface of electrodes to achieve improved efficiency and/or selectivity. However, a highly creative new development in the laboratory of Moeller involves the combination of these two technologies by the use of chips containing up to 12,540 individually addressable microelectrodes and the associated technology to permit both (a) selective attachment of chemical entities to one or more electrodes in the array^{13a} and (not a trivial task) (b) analysis of the chemical structures of components bound to each electrode in the array by a site-selective mass spectrometric method.^{13b} Figure 6 represents a portion of a 1 cm^2 chip containing 1,024 electrodes; the bright spots are electrodes to which a fluorescent tag has been selectively

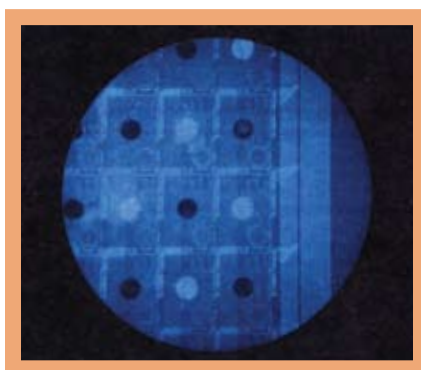


Fig. 6. Close-up view of a 1024-electrode array to which a fluorescent probe has been electrochemically attached to alternate electrodes in a checkerboard pattern. Picture supplied by Prof. K. Moeller of Washington University at St Louis.

attached without any effect on the neighboring electrodes (dark spots). The work is intended ultimately to permit recognition of specific structural motifs in biomolecules. Methods being developed in other laboratories involve attachment of enzymes¹⁴ and DNA components¹⁵ to electrode surfaces to take advantage of the very high selectivity inherent in biomolecules.

Computational Electrochemistry

Advances in hardware and software in the last decade or so have made it possible to compute the geometries and energies of typical (MW 100 or more) organic substances, intermediates, and transition states to chemical accuracy by quantum chemical methods. This now permits obtaining information about chemical processes that in most cases cannot have been obtained in any other fashion. An excellent example was contributed recently by Little, *et al.* (Fig. 7).¹⁶ Anodic oxidation of compound 4 was found to afford alkene 6, which appears to be produced by electron removal from 4 to form cation radical 5; this is followed by a 1,2-shift involving migration of the bridge methylene group labelled with the asterisk (path A). There is no immediately obvious reason why the methylene group of 5 should not migrate equally well by path B, but quantum chemical computations clearly showed that the migration of the labeled carbon atom has the lower activation energy.¹⁶ This is information that is invaluable in any proposed synthetic application. My group has also contributed a variety of computational electrochemistry applications, including studies of ion-pairing and solvation effects on voltammetry,^{17a} substituent effects on redox potentials,^{17b} and the solvent dependence of anodic oxidation of cyclooctatetraene.^{17c}

Scanning Tunneling Microscopy

The invention of the scanning tunneling microscope (STM) by Binnig and Rohrer¹⁸ permitted for the first time the visualization of atoms and molecules on surfaces. This has revolutionized the field of surface chemistry. Processes occurring at surfaces and interfaces can now be directly probed. Recent advances in technique and data analysis are providing increasing degree of detail in the structures being visualized. In an exciting recent development, Yau *et al.* reported visualization of the electropolymerization of aniline, using STM on a gold surface (Fig. 8).¹⁹ Image enhancement techniques show that panel a consists of a highly ordered array of individual aniline molecules before commencement of electrolysis. Panels b and c show the progressive appearance of long chains of polyaniline when

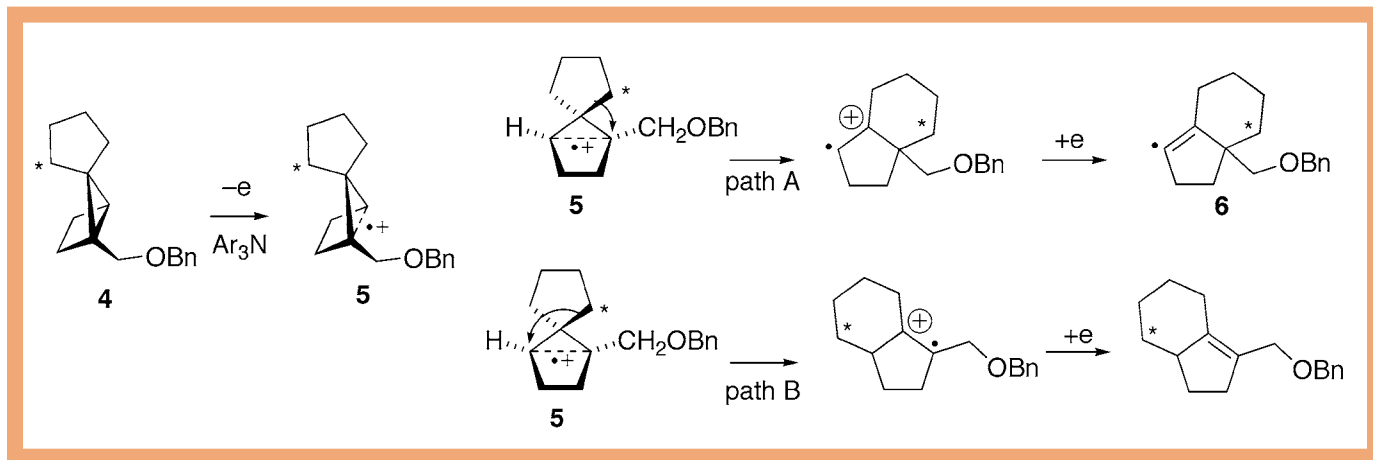


Fig. 7. Mechanism of anodic oxidation of a bicyclic ether, illustrating selective migration of a bridge methylene group.

the potential is increased to a value at which aniline is oxidized. Under higher resolution (panel d), one such chain is seen to be a series of individual spots. Each spot is exactly the size expected for a benzene ring, as can be seen from the structure of the polyaniline fragment superimposed on the STM image. It is not unreasonable to postulate that further advances in technology will someday permit even better resolution, possibly enough to identify intermediates in electrosynthetic transformations.

Conclusion

The message is clear: organic electrochemistry is in a state of escalation. In fact, the escalation is multi-dimensional: unlike Fig. 1, expansion is actually taking place in many different directions at once, such that our definitions of what constitutes a paper in organic electrochemistry and what information can be gained in an organic electrochemical study are being transformed rapidly. At one time the

goal was to study the electrochemical behavior of a given system, including products, mechanisms, rates, and analytical applications. Now the availability of STM, computational resources, microelectrodes, microreactors, and more has given us the ability not only to address such goals better and faster, but also to ask new questions, gain deeper insights, and carry out important new tasks. The prospects for organic electrochemistry are better than any previous time in its history.

Acknowledgments

The author has learned from the work, help, and advice of many friends and colleagues over the years, only a few of whom could be listed in the References because of space considerations. ■

About the Author

ALBERT FRY earned a BS in chemistry from the University of Michigan in 1958 and a PhD in organic chemistry from the University of Wisconsin in 1963. After a postdoctoral year at Caltech with George S. Hammond, he joined the faculty of Wesleyan University in Middletown, Connecticut, where he is now the E. B. Nye Professor of Chemistry. Professor Fry received the 2008 ECS Manuel Baizer Award in Organic Electrochemistry.

Fry became fascinated by organic electrochemistry shortly after joining the Wesleyan faculty. Early research was on the mechanism of electrochemical reduction of alkyl halides, benzyl and benzal halides, and dihalocyclopropanes. The discovery that reduction of dibromoketones could be induced by metallic mercury under ultrasonic irradiation (the first reported organic chemical reaction to be effected by ultrasound) led to a series of papers

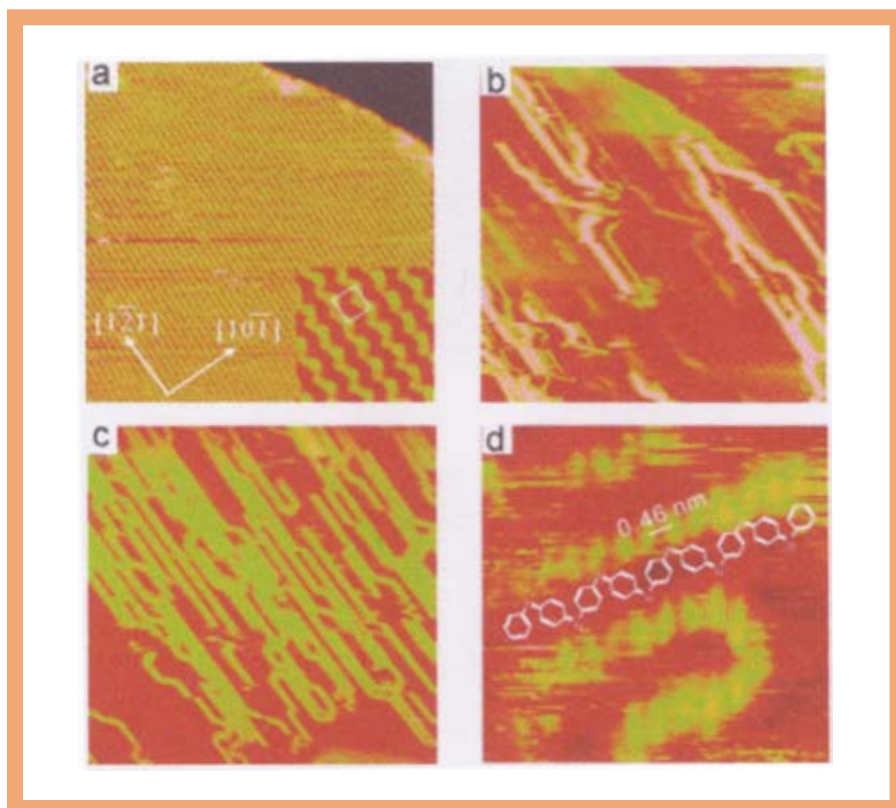


Fig. 8. Scanning tunneling microscopic study of the anodic oxidation of aniline at a gold electrode. Reprinted with permission from L. Y. O. Yang, C. Z. Chang, S. H. Liu, G. Chyn, and S. I. Yau, *J. Amer. Chem. Soc.*, **129**, 8076 (2007). Copyright © 2007 American Chemical Society.

comparing electrochemical reduction with that by ultrasonically dispersed mercury. More recently, the Fry group has been studying the electrocatalytic oxidation of silanes, arylsubstituted alkenes, and cyclooctatetraenes, and developing new high oxidation potential electrocatalysts to effect such oxidations. Another area of research over the last seven years has been computational organic electrochemistry, *i.e.*, application of quantum chemical methods to understand problems in organic electrochemistry, including the nature of ion-pairing and solvation effects in organic media, the anodic and cathodes behavior of cyclooctatetraene, and substituent effects on the electrochemical oxidation and reduction of organic substrates. The research has been described in *ca.* 150 research papers and three books.

Prof. Fry is Chair of the ECS Organic & Biological Electrochemistry Division and a (very) amateur musician. He may be reached at afry@wesleyan.edu.

References

1. D. DeSolla Price, *Little Science, Big Science*, Columbia Univ. Press, New York (1963).
2. P. Zuman, *Coll. Czech. Chem. Commun.*, **15**, 839 (1950).
3. H. Lund, *Acta Chem. Scand.*, **11**, 283 (1957).
4. M. M. Baizer, *Tetrahedron Lett.*, **4**, 973 (1963).
5. W. Kemula and Z. Kublik, *Anal. Chim. Acta*, **18**, 104 (1958).
6. R. N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York (1969).
7. S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).
8. (a) J. M. Saveant and E. Vianello, *Electrochim. Acta*, **8**, 905 (1963); (b) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
9. S. W. Feldberg and C. Auerbach, *Anal. Chem.*, **36**, 505 (1964).
10. R. C. Buchta and D. H. Evans, *Anal. Chem.*, **40**, 2181 (1968).
11. A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **94**, 8475 (1972).
12. (a) J.-I. Yoshida and D. Suga, *Chemistry – A European Journal*, **8**, 2650 (2002); (b) H. Usutani, Y. Tomida, A. Nagaki, H. Okamoto, T. Nokami, and J.-I. Yoshida, *J. Amer. Chem. Soc.*, **129**, 3046 (2007).
13. (a) E. Tesfu, K. Roth, K. Maurer, and K. D. Moeller, *Org. Lett.*, **8**, 709 (2006); (b) C. Chen, P. Lu, A. Walker, K. Maurer, and K. D. Moeller, *Electrochem. Commun.*, **10**, 973 (2008).
14. P. M. Guto, C. V. Kumar, and J. M. Rusling, *J. Phys. Chem. B*, **111**, 9125 (2007).
15. F. Jelen, A. B. Olejniczak, A. Kourilova, Z. J. Lesnikowski, and E. Palecek, Emil, *Anal. Chem.*, **81**, 840.
16. Y. S. Park, S. C. Wang, D. J. Tantillo, and R. D. Little, *J. Org. Chem.*, **72**, 4351 (2007).
17. (a) A. J. Fry, *Tetrahedron*, **62**, 6558 (2006); (b) L. D. Hicks, A. J. Fry, and V. C. Kurzweil, *Electrochim. Acta*, **50** (2004); (c) G. Connors, X. Wu, and A. J. Fry, *Org. Lett.*, **9**, 1671 (2007).
18. G. Binnig and H. Rohrer, *Helv. Phys. Acta*, **5.5**, 726 (1982).
19. L. Y. O. Yang, C. Z. Chang, S. H. Liu, G. Chyn, and S. I. Yau, *J. Amer. Chem. Soc.*, **129**, 8076 (2007).



General Topics

Please Note the Earlier Abstract Deadline: November 16, 2009

- › Batteries, Fuel Cells, and Energy Conversion
- › Biomedical Applications and Organic Electrochemistry
- › Corrosion, Passivation, and Anodic Films
- › Dielectric and Semiconductor Materials, Devices, and Processing
- › Electrochemical / Chemical Deposition and Etching
- › Electrochemical Synthesis and Engineering
- › Fullerenes, Nanotubes, and Carbon Nanostructures
- › Physical and Analytical Electrochemistry
- › Sensors and Displays: Principles, Materials, and Processing