Stanley Wawzonek and the Introduction of Polar Aprotic Solvents into Organic Electrochemistry

by Albert J. Fry

Interest in the electrochemical behavior of organic compounds arose in the late 19th century.[1,2] But early experiments in this area had been focused only on determination of the products of electrochemical transformation, not on how the observed products had been formed, *i.e.*, on what we now refer to as the mechanism of their formation. Suppose that an investigator wished to learn as much as possible about the inorganic substances: polarography had generally been carried out in water, but organic compounds tend not to be very soluble in water. Early polarographic studies on organic substances were therefore carried out in mixtures of water with an organic solvent such as dioxane[7,8] or 2-methoxyethanol.[9] This permitted obtaining useful information about the electrode behavior of organic substances, such as reduction potentials unsaturated hydrocarbon, *e.g.*, stilbene (**1**) (see Fig. 1). Earlier polarographic experiments had already established the fact that stilbene exhibits a two-electron polarographic wave in aqueous dioxane.[7] Preparative-scale electrolysis of **1** under such conditions affords dihydrostilbene, more commonly known as bibenzyl (**2**).[11] These data demonstrate that the overall reduction process necessarily involves two electrons and two protons.

Polarographic Studies in Acetonitrile and Dimethyl-formamide

II. Behavior of Aromatic Olefins and Hydrocarbons[1]

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ABSTRACT

Stilbene, anthracene, and 9-anisylidenefluorene are reduced stepwise polarographically in anhydrous acetonitrile and in dimethylformamide. Triphenylethylene, tetraphenylethylene, styrene, and 1,1-diphenylethylene give only one reduction wave. Large-scale electrolytic reductions in these solvents indicate that carbanion intermediates exist for a short period of time. 1,2,3,4-Tetraphenylbutane and *meso*-diphenyl succinic acid have been prepared electrolytically from stilbene in dimethylformamide.

mechanism of the electrochemical reduction of a typical unsaturated hydrocarbon even as recently as 1954. Even though linear sweep voltammetry (LSV)[3] had recently been introduced, its use had not yet become common. Cyclic voltammetry was still ten years in the future.[4] In 1954 polarography at the dropping mercury electrode, which had been invented many years before,[5,6] was the most widely used technique for studying organic substances.

When contemplating a study of this sort, one must confront the most obvious difference between organic and and the number of electrons transferred. For example, as early as 1954 Bergman reported the reduction potentials of a large number of polycyclic aromatic hydrocarbons, including anthracene,[9] and a series of studies of the polarographic behavior of a wide variety of substituted benzenes had been initiated by Zuman about the same time.[10]

Unfortunately, there are real problems associated with electrochemical experiments in protic media. To appreciate this, suppose that in 1954 one had wished to understand the electrochemical reduction of a typical Clearly a conversion involving addition of four elementary particles cannot occur in a single step. However, from this polarographic information one cannot determine anything more about the sequence of reactions involving the four particles, in the course of which **1** is converted into **2**.

In fact, until the publication of this paper, this was a general problem in organic electrochemistry. Stanley Wawzonek of Iowa State University had initiated a program in organic electrochemistry some time earlier and was obviously interested in such

problems when he wrote in 1952 in the *Journal of The Electrochemical Society* (abbreviated hereafter simply as JES) that "Media which do not have the hydroxyl grouping either have been used to a limited extent (formamide) or have too low a dielectric constant (benzene, toluene, and aniline."[12] Indeed, it is clear that he had already begun work in the area because his first paper on electrochemistry in aprotic media, titled "Polarographic Studies in Acetonitrile. I. Behavior of Inorganic Salts," appeared later that same year.[13]

That paper described relatively uninteresting electrochemical measurements, by contemporary standards, on the polarographic reduction of simple inorganic ions in acetonitrile. However, the second paper in the series, titled "Polarographic Studies in Acetonitrile and Dimethylformamide,"[14] had an immediate effect on the development of organic electrochemistry and is the topic of this article. It describes the polarographic and preparative scale reductions of stilbene, anthracene, 9-anisylidenefluorene, triphenylethylene, tetraphenylethlene, styrene, and 1,1-diphenylethylene in acetonitrile (AN) and/or dimethylformamide (DMF).[14] The key discovery described in the manuscript was the fact that several of the compounds (stilbene among them) exhibit two one-electron waves in AN or DMF instead of the two-electron waves previously observed for them in aqueous dioxane.[7] The positioning of the waves was intriguing: the two-electron wave in aqueous media[7] is at the same potential as the first wave in DMF or AN.[14]

The connection between the two kinds of behavior was shown by a series of experiments involving addition of increasing amounts of water to the polarographic medium. This resulted in the height of the first wave increasing, with a corresponding decrease in the height of the second, as the proportion of water was increased, such that the total height of the two waves remained constant. Addition of benzoic acid to the DMF solution had the same effect as added water: a single two-electron wave was observed at the potential of the original first wave and less benzoic acid was required to produce the transition from two waves to one. These observations led Wawzonek to suggestion that reduction at the first wave affords a reasonably stable stilbene anion radical (**3**). It was suggested that added water or other proton donor water to the medium results in protonation of **3** (see Fig. 2) to afford the neutral radical (**4**), which is then quickly reduced and protonated, resulting in overall addition of the elements of hydrogen to the double bond. These processes are exemplified for stilbene in Eqs. 1-4 (Fig. 2). The second polarographic wave was explained by
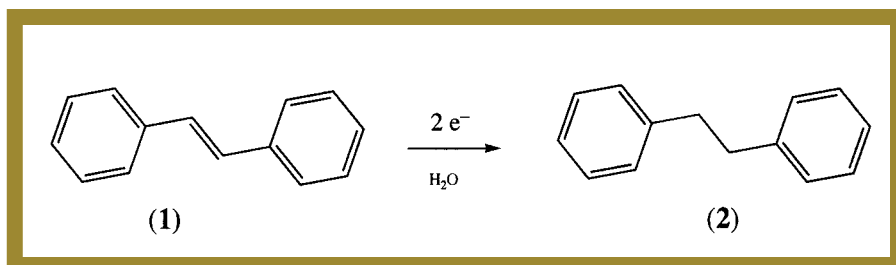

Fig. 1. *Reduction of stilbene in acetonitrile containing water.*
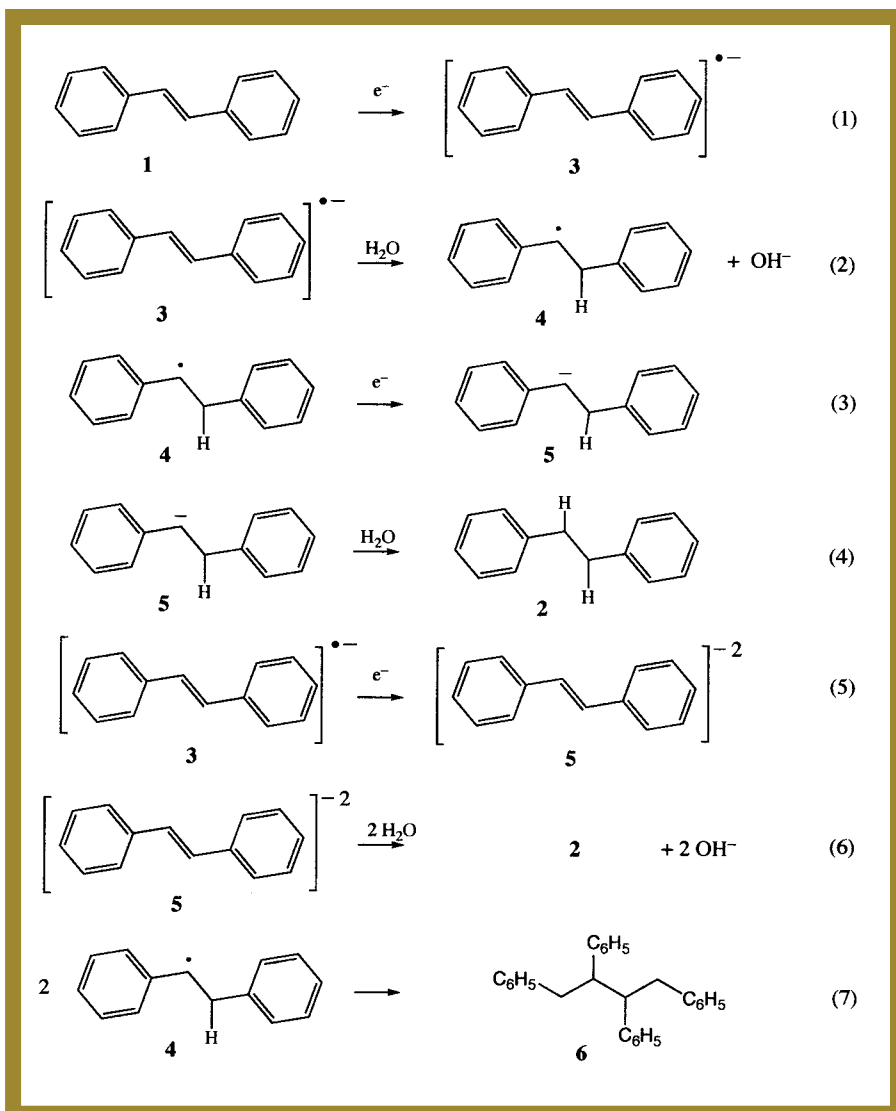

Fig. 2. *Mechanistic steps in the electrochemical reduction of unsaturated hydrocarbons in the presence of proton donors, as exemplified by the reduction of stilbene (**1**) in the presence of water.*

the fact that in the absence of water, **3** is reasonably stable and would be reduced to a dianion (**5**) at more negative potentials. Stepwise protonation of **5** would lead to **2** (Fig. 2, Eqs. 5-6).

Further evidence for intermediates **4** and **5** was obtained from bulk electrolysis experiments. Although bibenzyl (**2**) was the only produced upon electrochemical reduction of stilbene in acetonitrile, electrolysis in DMF also produced a small amount of 1,2,3,4-tetraphenyl butane (**6**) together with the major product

bibenzyl.[14] Formation of **6** apparently comes about by escape of radical **4** into solution, where it then dimerizes (Fig. 2, Eq. 7). Saturation of the solution with carbon dioxide resulted in formation of diphenylsuccinic acid (**7**) in excellent yield (92%) (Fig. 3, Eq. 8). In similar vein, electrolysis in the presence of ethyl iodide afforded 1,2-diphenylbutane (**8**) (Fig. 3, Eq. 9). Both reactions have well-known counterparts in the reaction of carbanionic organometallic species such as Grignard and alkyl lithium reagents.

The reactions of Fig. 3 present strong evidence for nucleophilic (carbanionic) attack by **4** on the added electrophile, either carbon dioxide or ethyl iodide.

Implications

The mechanistic framework outlined by Wawzonek in Scheme 1 has held up well with time. Much subsequent work by a variety of investigators, nicely summarized and interpreted in a review by Peover,[11] has fleshed out Wawzonek's mechanism in much fuller detail. The lasting value of the polarographic and electrosynthetic experiments described in this paper lies in the fact that they provided for the first time a reasonable and testable theoretical framework for understanding the mechanism of reduction of unsaturated hydrocarbons and, by extension, unsaturated organic substances in general. A number of questions still remained. For example, anthracene and stilbene, to cite just two examples, were found to exhibit two one-electron polarographic waves in DMF but the products of their preparative-scale reduction were found to be the corresponding two-electron dihydroproducts and the anion radicals, now known to be deeply colored, were apparently not observed even transiently.[14] The problem apparently lies in the difficulty in drying DMF to acceptable levels because it binds water very tenaciously.[16,17]

We now know that this is a matter of experimental time scales. The rate of reaction of the trace amounts of water in the solvent with the anion radicals is too low on the polarographic time scale of seconds to be an issue, but the synthetic electrolysis takes hours, providing adequate time for protonation by the pathway shown in Eqs. **1-6** to take place. Furthermore, to explain the two-electron wave in protic media, it was necessary to postulate that the intermediate radical **4** is easier to reduce than the initial hydrocarbon **1** and thus accepts an electron as quickly as it is formed. No explanation for why this should be so was offered. Coincidentally, the explanation for this had recently been published. G. J. Hoijtink and coworkers had been studying the polarographic reduction of unsaturated hydrocarbons in 96% dioxane simultaneously with Wawzonek (the Hoijtink papers were published in 1954 and Wawzonek's publication was submitted to JES in August 1954).[18,19] They found that many such substances behave in this medium similarly to their behavior in DMF and AN, *i.e.*, exhibiting two one-electron polarographic waves. Because of the lower concentration of water in 96% dioxane compared to 75% dioxane[7] protonation of **3** is sufficiently slow on the polarographic time scale to permit observation of the second wave for reduction of it to the diianion **5**. Also, Wawzonek postulated the formation of such dianions in those cases where two polarographic waves were observed, but no experimental evidence for them was found. It is now known that such species are highly basic[20] and hence readily scavenge even traces of moisture present in the medium. In carefully dried DMF, cyclic voltammetry shows that species **5** are stable, at least on the CV time scale.[21]

An Historical Puzzle

It is hard to underestimate the influence of this first study[14] and the simultaneous work of Hoijtink[18] of solvent effects on subsequent research in organic electrochemistry, not simply the electrochemistry of unsaturated hydrocarbons. Previously, a solvent would have been chosen simply on the basis of convenience, such as the solubility of the substrate to be studied in it and perhaps also ease of purification. This work brought home in unmistakable fashion the role of the solvent in directing the very course of the electrochemistry taking place in it. In particular, the Wawzonek paper demonstrated the existence of discrete short-lived intermediates that could be trapped by added reagents, as in the preparative electrolyses of stilbene in the presence of proton donors, carbon dioxide, and ethyl iodide. Much of modern organic electrochemistry is in fact based exactly on the search for reactive intermediates and applications that exploit them for synthetic purposes. Yet the Wawzonek paper does not appear on a list of the 100 most frequently cited publications in the JES.[22] In fact, a recent search of the literature indicates that the paper has been cited not more than 10 times.

How can this possibly be for such a significant paper? I suspect that it comes from the rapid, almost instant, acceptance by those interested in organic electrochemistry of the notion that by operating in aprotic media once can learn much more about the course of the reactions they are studying. This notion was apparently so self-evident that it required simply one or two papers pointing it out for the change to happen. (Such phenomena are not unknown, either in science or outside it; they have been referred to as "paradigm changes"[23] or "tipping points".[24]) The use of dipolar aprotic solvents (DMF, AN, and dimethylsulfoxide DMSO) as solvents for organic electrochemistry quickly became universal. (I can testify to this: when I first entered the field of organic electrochemistry in 1965, the use of DMF and acetonitrile had already become essentially a universal practice, even though the Wawzonek paper had been published only ten years before. Like probably most of the many others entering the field around that time,[25] I soon became aware of the Wawzonek paper and studied it very carefully for the concepts it introduced.) In effect, the paper was a victim of its own success. ◼

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 chemistry 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. His early research interests were in the electrochemical reduction of alkyl halides, during which benzyl and geminal halides, 1,3-dibromides, and dihalcyclopropanes were some of the systems investigated. More recently the Fry group has studied the anodic oxidation of silanes, alkenes, and cyclooctatetraene. Another area of research over the last eight years has been computational organic electrochemistry. Topics under investigation include ion-pairing and solvation effects in organic media, substitutent effects on oxidation and reduction of organic systems, and the cathodic behavior of polynitrocalixarenes. Prof. Fry is Chair of the ECS Organic and Biological Electrochemistry Division. He may be reached at afry@wesleyan.edu.
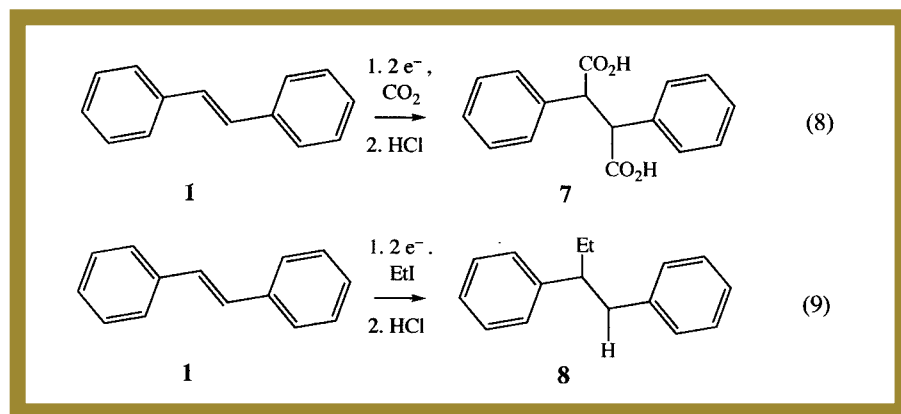
FIG. 3. *Results of trapping anionic intermediates in the electrochemical reduction of stilbene by organic electrophiles.*

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