

## Kinetics and Mechanisms of Electrochemical Dimerizations

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9-Cyanoanthracene is a particularly attractive model molecule for mechanistic studies on reductive electrochemical dimerization reactions in aprotic media. It does not give rise to side-reactions in very dry media and the dimerization reaction is reversible allowing the determination of the forward and backward rate constants as well as of the equilibrium constant. This was done as a function of temperature using double-potential step chronoamperometry. The effect of water was investigated using the same technique. The dimerization involves the radical-radical coupling of two anion radicals in dry media. Steric factors play an important role in the coupling reaction as revealed by temperature dependency investigations. These conclusions contrast those of recent studies implying that radical-radical dimerization of anion radicals, if even possible, is very uncommon. The causes of this misinterpretation of the experimental data are discussed. Addition of water accelerates the dimerization reaction. It is shown that this does not only occur through an "anion radical-proton donor complex mechanism" but also involves, at high water concentration, the coupling of two water-complexed anion radicals. Radical-radical coupling also occurs in the reductive dimerization of other molecules such as activated olefins although some evidence exists that a radical-substrate mechanism tends to prevail in very dry media. The role of water is again best rationalized in terms of specific solvation by water rather than in terms of an "anion radical-proton donor complex mechanism" which prevails only under particular conditions. The investigation of the mechanism of electrochemical dimerization reactions raises important methodological problems. It is shown that the use of "reaction order, without calculation" approaches in cases where the reaction is not controlled by a single rate determining step may lead to erroneous mechanistic conclusions. Besides the reduction of 9-substituted

anthracenes, the oxidative dimerization of 4-methoxybiphenyl is a typical illustration of the shortcomings of such oversimplified approaches. Important consequences regarding the chemistry of cation radicals ensue.

Being the base of a famous commercial electro-organic process, the reductive dimerization of activated olefins has been the object, among other organic molecules, of particularly active mechanistic investigation.<sup>1-5</sup> Most studies in this field have been carried out in solvents of low proton availability, such as acetonitrile, DMF and DMSO, in an effort to decrease the reactivity of the initially formed anion-radicals and hence to reach a better control of the kinetics of the follow-up reactions. It has thus been shown that: (i) for a number of activated olefins, the apparent number of electrons at the first wave, where dimerization occurs, is less than one per molecule on mercury, implying the occurrence of other reactions besides dimerization; enough water was then added to avoid these reactions with the aim of investigating the dimerization itself;<sup>2a</sup> (ii) *under these conditions*, the investigated compounds undergo a radical-radical dimerization accelerated by further addition of water;<sup>2a-2b</sup> (iii) the latter effect derives from *specific solvation of the anion radicals by water* and not from protonation in the investigated water concentration range;<sup>2b</sup> (iv) other activated olefins undergo an electrochemical dimerization reaction which appears as insensitive to the presence of water in a given water concentration range;<sup>2a-2b</sup> (v) for these two classes of activated olefins the electrochemical dimerization is of the radical-radical type.<sup>2a,2b</sup> The latter conclusion was thus regarded to hold in wet

medium as far as the first class of activated olefins is concerned. In other words, the mechanism was *not* considered as being the same in anhydrous and wet solutions as erroneously stated in recent literature.<sup>6a</sup> Where aprotic solvents containing low water concentrations are concerned, it was emphasized that the interference of radical-substrate coupling is likely with this type of activated olefins.<sup>2g</sup> Recent work<sup>6a-6b</sup> reached the same conclusion and appears therefore as bringing about a confirmation rather than a revelation. Note that although the interference of radical-substrate coupling under dry conditions can be viewed as likely,<sup>2g</sup> an unambiguous proof is still awaited since the experimental data do not exactly fit the predicted kinetics<sup>6a</sup> and the possible kinetic interference of the side-reactions has not been taken into account so far. Some more precision about how the specific solvation by water works has been recently brought up in the case of diethyl fumarate. The dimerization reaction appears as first order in water between 0.139 and 0.556 M,<sup>6c</sup> implying the coupling of two anion radicals one of which is complexed by one water molecule. This is still a mechanism involving the coupling of two anion radicals since the complex with water is regarded as not undergoing internal proton transfer and is therefore still an anion and still a radical. It should

however be emphasized that this particular nature of the rate-determining step may well not be general when passing to other substrates and/or higher water concentrations. As will be shown on the example of other molecules, specific solvation by water<sup>2b</sup> thus appears as a safer and more general description of the role of water.

#### ARE ANION RADICALS UNABLE TO UNDERGO RADICAL-RADICAL DIMERIZATION?

In connection with the case of activated olefins, the reduction of a structurally related molecule, 9-cyanoanthracene (ANCN) is of particular interest. There is no complication involving side-reactions by dry aprotic media. The dimerization reaction is reversible allowing the determination of the equilibrium constant and of both the forward and backward rate constants and of their dependence upon water and counter-cations. The kinetic and thermodynamic data obtained by double step chronoamperometry in dry DMSO containing  $\text{Bu}_4\text{N}^+$  as supporting cations will be described and discussed under their energetic and entropic aspects. In this connection, the conclusion of a recent investigation of the electro-dimerization of anthracenes

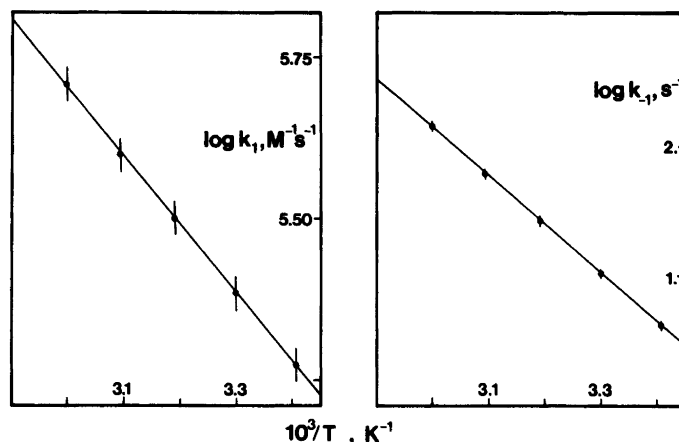


Fig. 1. Double potential step chronoamperometric analysis of the electro-dimerization of 9-cyanoanthracene in DMSO containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) in the presence of activated neutral alumina. —: working curve, ●: experimental data.  $C_{\text{ANCN}}=1$  mM. The value of the dimerization equilibrium constant,  $K$ , is indicated on each curve. On the horizontal axis:  $\theta$  is the potential inversion time and  $k_1$  the forward dimerization rate constant.  $R$  is the normalized ratio of the anodic current at  $2\theta$  over the cathodic current at  $\theta$ :  $R(\theta)=[i(2\theta)/i(\theta)]/[2^{-1/2}-1]$ . Temperature: (a): 20.5 °C, (b): 40 °C, (c): 50 °C.

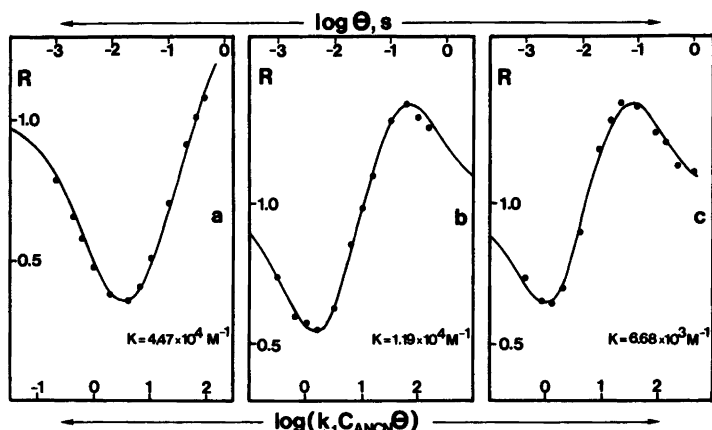


Fig. 2. Electrodimerization of 9-cyanoanthracene in DMSO containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) in the presence of activated neutral alumina. Arrhenius plots between 20.5 and 60 °C.  $k_1$ ,  $k_{-1}$ : forward and backward dimerization rate constants.

substituted with electron-withdrawing substituents, including ANCN, in DMF, according to which the simple radical-radical dimerization of the corresponding anion radicals surely does not take place,<sup>7</sup> will be discussed. This is indeed a rather striking statement which, if true, would cast doubts on the reality of radical-radical coupling for any kind of anion radicals, in particular for those deriving from activated olefins in wet medium since the mechanism is then still viewed as involving the coupling of two anion radicals.<sup>2b,6c</sup>

In dry DMSO containing 0.1 M  $\text{Bu}_4\text{BF}_4$ , we observed that the variations of the cyclic voltammetric cathodic peak potential of ANCN with the sweep rate and the substrate concentration are compatible with the occurrence of a radical-radical coupling and not with a radical-substrate coupling. The results obtained using double step chronoamperometry (typical examples of these are shown in Fig. 1) are also compatible with the radical-radical coupling pathway provided the reversibility of the dimerization is duly taken into account. The working curves were generated from the numerical resolution of the pertinent partial derivative equation systems as a function of two dimensionless parameters:  $\kappa = KC_{\text{ANCN}}$  and  $\lambda = k_1 C_{\text{ANCN}} \theta$  ( $K$ : dimerization equilibrium constant,  $k_1$ : forward dimerization rate constant,  $\theta$ : potential inversion time). Fitting of the experimental data with the working curves thus leads to the values of  $k_1$  and  $K$  and thus of  $k_{-1}$ ,

the backward dimerization rate constant. This was done at several temperatures ranging between 20 and 60 °C. The ensuing Arrhenius plots are linear (Fig. 2) leading to  $E_1^\ddagger = 4.6$ ,  $E_{-1}^\ddagger = 17.4$  K cal/mol for the forward and backward activation energies. Regarding the forward dimerization reaction, the Arrhenius pre-exponential factor is thus equal to  $7.910^8 \text{ M}^{-1} \text{ s}^{-1}$ , *i.e.*, much smaller than the collision frequency,  $\sim 2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ , that can be estimated for ANCN.<sup>8</sup> This is actually not very surprising for a molecule such as  $\text{ANCN}^-$  which is obviously sterically hindered toward dimerization. There is indeed ample theoretical background substantiating the role of steric factors for a number of reactions<sup>9a-9c</sup> particularly for dimerization reactions.<sup>9d</sup> A typical experimental example of the latter is the observation that the tri-*t*-butylcycloheptatrienyl radical has a dimerization activation energy of 1.7 K cal/mol while the corresponding rate constant is only  $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 22 °C.<sup>10</sup>

The electrochemical dimerization of ANCN thus appears to follow a simple radical-radical coupling mechanism contrary to the conclusion of recent work which excludes such a mechanism and invokes the intermediacy of a dimeric complex where the two anion radicals are not covalently bonded to each other.<sup>7</sup> Two reasons were given for substantiating the latter conclusion. One is the observation, as in our case, that the pre-exponential factor is much smaller than the standard collision frequency. As discussed

above this is actually perfectly compatible with a radical-radical coupling mechanism. The other reason is that derivative cyclic voltammetry (DCV) mechanism analysis produced slopes which are significantly different from that predicted by the rate law. The DCV analysis is very similar in its principles and capabilities to the double potential step method we used, as described above. The considered slopes are those of  $\ln R'_1$  vs.  $\ln(1/\nu)$  plots, where  $R'_1$  is the ratio of the peaks on the backward and forward DCV scans and  $\nu$  the sweep rate. These plots are approximately linear within a large portion of the pertinent sweep rate range.<sup>11a</sup> The slopes were found to be  $-0.268$ ,  $-0.264$  and  $-0.219$  for CHO, NO<sub>2</sub> and CN, respectively, instead of  $-0.307$  as predicted for an irreversible  $2\text{ANX}^- \rightarrow \text{XNA-ANX}^-$  dimerization. However, if we take the reversibility of the dimerization process into account, the data are perfectly compatible with the "simple" anion radical dimerization mechanism. This is shown in Fig. 3 in the case of ANCN. The experimental points (Tables 1 and 2 in Ref. 7) fall accurately on the working curve corresponding to a dimerization equilibrium constant  $K=1.4 \times 10^4 \text{ M}^{-1}$  and to a dimerization rate constant  $k=1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . It is clearly seen

why the slope obtained, even with the four highest sweep rates (80, 60, 40, 20  $\text{V s}^{-1}$ ), is different, smaller in absolute value, than that predicted for an irreversible dimerization. The working curves were generated from the numerical resolution of the pertinent partial derivative equation system, depending upon two dimensionless parameters,  $\kappa=KC_{\text{ANX}}$  and  $\lambda=(RT/F)(k_1C_{\text{ANX}}/\nu)$  along already known and repeatedly applied procedures devised for the situations where the kinetics involve more than a single rate-determining step (see e.g. Ref. 12). Using the same set of working curves, it was found that dimerization is less reversible for ANNO<sub>2</sub> and ANCHO which matches the observation that the experimental slopes are then closer to the value predicted for irreversible dimerization. The failure to recognize the existence of a "simple" radical-radical coupling mechanism thus merely derived from an artefact in the treatment of the kinetic data. This illustrates the limitations of the "reaction order", "without calculation", approaches insistently advocated in recent publications (Refs. 6, 7, 11 and references therein). These approaches, known for a long time (see, e.g., Ref. 13), should obviously be supplemented by further procedures involving some more

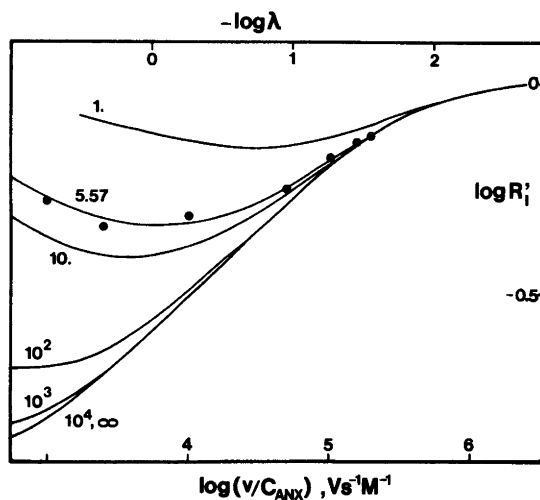


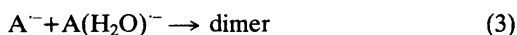
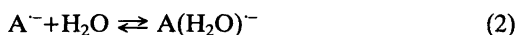
Fig. 3. Derivative cyclic voltammetric analysis of the electro-dimerization mechanism of 9-cyanoanthracene in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M). Comparison between experimental data (●)<sup>2b</sup> and predicted kinetics for a reversible radical-radical dimerization (—). The number of each curve is the value of  $\kappa=KC_{\text{ANX}}$ , the dimensionless dimerization equilibrium constant.  $\lambda=(RT/F)(k_1C_{\text{ANX}}/\nu)$  ( $k_1$ : dimerization rate constant,  $\nu$ : sweep rate).  $R'_1$ : ratio of the peaks on the backward and forward DCV scans.

algebra and computation when the kinetic scheme involves more than a single rate determining step.<sup>12</sup>

Our conclusion is thus that the answer to the question raised in the title of this section is *no*. 9-Cyanoanthracene anion radicals as well as other anthracene anion radicals substituted with electron withdrawing substituents are good candidates for "simple" radical-radical dimerization. The opposite conclusion recently drawn<sup>7</sup> arose from an artefact in the treatment of the kinetic data and from overlooking rather classical results of the chemical rate theory. The qualificative "simple" is, of course, rather subjective. More precisely, this reaction is to be viewed as an elementary step in the chemical sense. This, however, does not take place in vacuum and "complex" influences of the reaction medium (solvent, counter ions, water) on its thermodynamics and kinetics are anticipated.

#### THE ROLE OF WATER IN ORGANIC ELECTROREDUCTIVE DIMERIZATIONS IN APROTIC SOLVENTS. HOW GENERAL IS THE ANION RADICAL-WATER COMPLEX MECHANISM?

Addition of water often accelerates electroreductive dimerization of organic molecules in aprotic solvents. This has been observed with activated olefins<sup>1a,2a,2b</sup> as well as with carbonyl compounds.<sup>14</sup> This effect has been ascribed to specific solvation of the anion radicals by water molecules in the framework of a radical-radical coupling process.<sup>2b</sup> This interpretation was recently questioned and a more precisely specified reaction scheme accounting for the influence of water was proposed.<sup>6b</sup> It involves the coupling of an uncomplexed anion radical with an anion radical complexed by a single water molecule, resulting in an "anion radical-proton donor (water) complex mechanism"<sup>6b</sup> (eqns. (1)–(3)).



As a matter of fact, electrokinetic data (using derivative cyclic voltammetry) obtained with diethyl fumarate in DMF for water concentra-

tions ranging from 0.278 to 0.556 M do fit the kinetics predicted for such a reaction scheme.<sup>6b</sup>

We discuss in the following to what extent this "anion radical-water complex mechanism" is general and therefore should or should not replace the more general concept of specific solvation by water. The latter implies that two water complexed anion radicals may react together or that complexes involving more than a single water molecule may be involved.

As discussed above, 9-cyanoanthracene is a particularly attractive molecule for electro-dimerization studies due to the fact that the dimerization process is reversible which allows the equilibrium constant as well as the forward and backward rate constants to be determined. For the present purposes, attractive features are that both the anion radical and the dimer dianion are resistant to protonation by water in a very extended concentration range. Complexation by water is also weak allowing the effect of water on the dimerization process to be investigated progressively.

The investigation described below was carried out at 20 °C in DMSO in the presence of 0.1 M NBu<sub>4</sub>BF<sub>4</sub> as supporting electrolyte.

Linear sweep voltammetric peak shifts at low sweep rates (*i.e.*, under conditions where the reduction wave is chemically irreversible) with ANCN concentration and sweep rate (19 mV per log unit at 20 °C) indicate the occurrence of a radical-radical coupling dimerization process<sup>2a,15</sup> in the whole water concentration range (0–16 M). Chemical reversibility can be restored upon raising the sweep rate (this is obtained at 500 and 1000 V s<sup>-1</sup> for the highest water concentration which corresponds to the largest dimerization rate). It was noticed that the standard potential, as determined as the middle of the cathodic and anodic reversible peak potential, does not vary appreciably with the water concentration. This shows that complexation of the anion radicals by water is rather weak, the equilibrium constants being less than 5 × 10<sup>-3</sup> M<sup>-1</sup> which would correspond to a 5 mV positive shift.

The overall rate constants for the forward and backward dimerization reactions, *k<sub>f</sub>* and *k<sub>b</sub>*, were determined using double potential step chronoamperometry. Their variations with water concentration are shown in Figs. 4 and 5. Concerning *k<sub>f</sub>*, it is clearly seen that the *k<sub>f</sub>*[H<sub>2</sub>O]

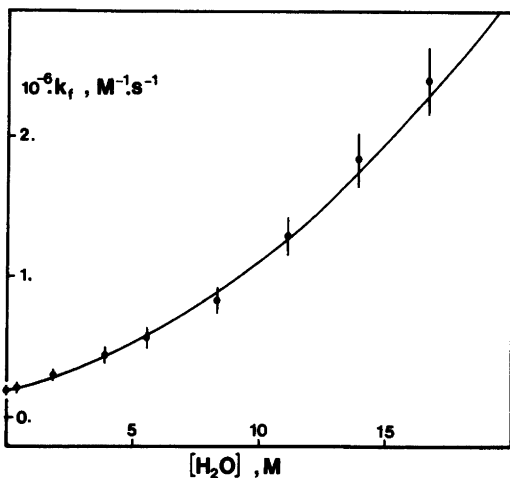


Fig. 4. Variations of the forward dimerization rate constant of 9-cyanoanthracene anion radical in DMSO (+0.1 M  $\text{NBu}_4\text{BF}_4$ ) with the water concentration ( $C^\circ = 10^{-3}$  M).

plot is not linear, ruling out the occurrence of the simple anion radical-water complex mechanism over the whole water concentration range. The data are compatible with the reaction scheme involving eqns. (4)–(10).

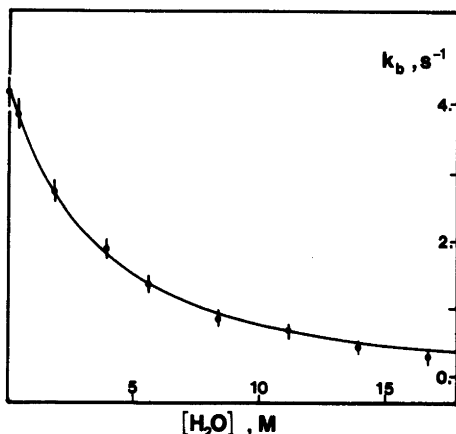
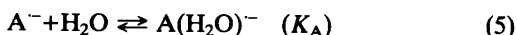
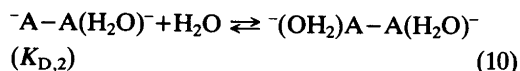
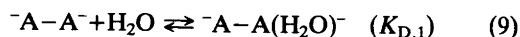
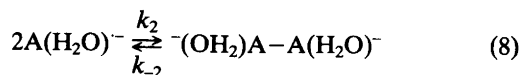
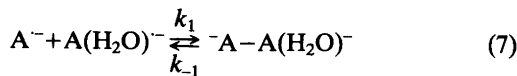


Fig. 5. Variations of the backward dimerization rate constant of 9-cyanoanthracene anion radical in DMSO (+0.1 M  $\text{NBu}_4\text{BF}_4$ ) with the water concentration ( $C^\circ = 10^{-3}$  M).



Assuming that the water complexation reactions are fast, thus remaining at equilibrium, as is very likely, the kinetics corresponding to the overall scheme amounts to a dimerization of  $\text{A}^-$  having a forward rate constant given by eqn. (11).

$$k_f = \frac{k_0 + k_1 K_A [\text{H}_2\text{O}] + k_2 (K_A [\text{H}_2\text{O}])^2}{(1 + K_A [\text{H}_2\text{O}])^2} \quad (11)$$

As the standard potential does not vary appreciably with water concentration it can be concluded that  $K_A [\text{H}_2\text{O}] \ll 1$  in the above expression which depends then only on the values of  $k_0$ ,  $k_1 K_A$  and  $k_2 K_A^2$ . Under these conditions, the best fit with the experimental data was obtained (see Fig. 4) for  $k_0 = 1.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_1 K_A = 4.5 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ ,  $k_2 K_A^2 = 4.9 \times 10^3 \text{ M}^{-3} \text{ s}^{-1}$ . As mentioned earlier,  $K_A$  is not known but may be regarded as smaller than  $5 \times 10^{-3} \text{ M}^{-1}$ . Taking this value one would obtain  $k_1 = 0.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_2 = 2 \times 10^8 \text{ m}^{-1} \text{ s}^{-1}$  which are minimal values of the two dimerization rate constants. It is seen that complexation by a water molecule greatly accelerates the dimerization process as compared to uncomplexed anion radicals.

The same scheme leads to the expression given by eqn. (12) for the backward rate constant:

$$k_b = \frac{k_{-0} + k_{-1} K_{D,1} [\text{H}_2\text{O}] + k_{-2} K_{D,1} K_{D,2} [\text{H}_2\text{O}]^2}{1 + K_{D,1} [\text{H}_2\text{O}] + K_{D,1} K_{D,2} [\text{H}_2\text{O}]^2} \quad (12)$$

As shown by the experimental results in Fig. 5,  $k_b$  tends toward zero as the water concentration is increased. This is compatible with the dissocia-

tion rate constants for the mono- or disolvated dimers being small as compared to  $k_{-0}$ . Let us assume that these two rate constants are effectively negligible. This leads to a simplified expression for  $k_b$  given by eqn. (13).

$$k_b \approx k_{-0} / (1 + K_{D,1}[\text{H}_2\text{O}] + K_{D,1}K_{D,2}[\text{H}_2\text{O}]^2) \quad (13)$$

The two anionic centers in the  $^{\ominus}\text{A}-\text{A}^{\ominus}$  dimer can be regarded as independent and chemically identical as far as complexation by water is concerned. Thus

$$K_{D,2} \approx K_{D,1}/4$$

where the (1/4) factor results from a symmetry entropic term.<sup>16</sup> This leads to a simplified expression for  $k_b$  given by eqn. (14).

$$k_b = k_{-0} / (1 + K_{D,1}[\text{H}_2\text{O}] + (K_{D,1}^2/4)[\text{H}_2\text{O}]^2) \quad (14)$$

which depends only on  $K_{D,1}$ . Fig. 2 shows that such an expression, with  $k_{-0} = 4.16 \text{ s}^{-1}$  and  $K_{D,1} = 0.27 \text{ M}^{-1}$  is in good agreement with the experimental data. It cannot, however, be excluded more than one water molecule complex for each anionic center of the  $^{\ominus}\text{A}-\text{A}^{\ominus}$  dimer. A slightly better fit is indeed obtained if such reactions are taken into account.

The example of ANCN thus shows that the effect of water is not restricted to the "anion radical-water complex mechanism". The radical-radical coupling of two complexed anion radicals also interferes. At this point, it is worth recasting earlier data obtained with other organic molecules. With *p*-methylbenzylidene malonitrile ( $p\text{-CH}_3\text{-C}_6\text{H}_4\text{-CH=C(CN)}_2$ ) a cyclic voltammetry investigation of the reduction in acetonitrile<sup>2f</sup> showed that the standard potential varies by more than 30 mV per log unit of water concentration between 0.17 and 5.7 M indicating a rather strong complexation of the anion radical by water. It, however, appears that the dimerization rate constant is practically insensitive to the increase in water concentration in this range. We may thus conclude, on the basis of the above equation giving  $k_b$ , that the prevalent dimerization pathway involves the coupling of complexed anion radicals, there predominating, at equilibrium, over the bare anion radicals. This is also compatible with the observation that at preparative scale concentrations ( $\sim 0.1 \text{ M}$ ), a decrease of

the rate of the dimerization process and a change of the overall kinetics are observed when the water concentration falls in the same range as the olefin concentration.<sup>2c</sup>

With acetophenone in acetonitrile,<sup>14</sup> the dimerization process is again accelerated by the addition of water. The standard potential becomes more positive upon addition of water by more than 90 mV per log unit of water concentration. This indicates the involvement of complexes containing more than one water molecule per anion radical.

The examples of 9-cyanoanthracene, *p*-methylbenzylidene malonitrile and acetophenone show that the "anion radical-water complex mechanism" is by no means a unique pathway accounting for the effect of water on the reductive electro-dimerization of organic molecules in aprotic solvents. Other pathways such as dimerization of two complexed anion radicals or even dimerization of complexes involving more than one water molecule per anion radical may well be occurring depending upon the nature of the anion radical and the water concentration. *Specific solvation of the anion radicals by water* thus appears as a sounder and more general description of the effect of water addition on reductive electro-dimerization processes.

#### METHODOLOGICAL ASPECTS. THE ELECTRODIMERIZATION OF 4-METHOXYBIPHENYL

The mechanistic investigation of electro-dimerization reactions raises important methodological questions. One of these is the applicability of reaction order analysis. There is ample precedence that such an approach is valid for reactions kinetically controlled by a *single rate-determining step*. However, these approaches are not suited to more complex reaction schemes in which the kinetics is controlled by more than one rate-determining step. Erroneous mechanistic conclusions can then be drawn as illustrated by examples taken in the analysis of the reductive electro-dimerization of 9-cyanoanthracene and of the oxidative electro-dimerization of 4-methoxybiphenyl. Procedures involving some more algebra and computation, for which ample theoretical and experimental background exists, should instead be used for reaching sound conclusions.

Homogeneous chemical steps coupled with electrode electron transfers interfere in electrochemical reactions in a heterogeneous manner in the sense that they are coupled with the diffusion of reactants, intermediates and products to and from the electrode surface. The kinetic analysis of such reactions is thus somewhat more complex than for purely homogeneous processes. The time-dependent differential equations describing the homogeneous kinetics have to be replaced by time and space dependent partial derivative equations; boundary conditions at the electrode surface and in the bulk of the solution have to be taken into account. This explains why, in a first stage, analysis of this type of electrochemical kinetics and application to mechanism diagnosis and rate constant determination have been restricted to simple kinetic behaviours, *i.e.*, those in which the overall kinetics is controlled by a single rate-determining step. The latter does not necessarily follow or precede immediately the electrode electron transfer, but may be separated from it by other chemical steps remaining at equilibrium. The corresponding homogeneous rate law is introduced into the diffusion partial derivative equations, the resolution of which provides the description of the kinetics of the overall electrochemical process.

Considering, for example, reaction schemes in which the initial electron transfer step,  $A + e \rightleftharpoons B$ , is followed by homogeneous chemical steps involving B, situations of particular interest are met when the life-time of B is so short, with respect to diffusion, that "pure kinetic" conditions are achieved. These imply that a stationary state exists resulting from mutual compensation of the diffusion and chemical processes. The variations of the B concentration with time can then be neglected and the concentration profile of B is confined within a "reaction layer" vanishingly thin as compared to the diffusion layer. Under such conditions, the characteristics of the polarization curves are related in a rather simple manner to those of the homogeneous kinetics, namely reaction orders and overall rate constant, provided the initial electron transfer is sufficiently fast so as not to interfere kinetically. In cyclic voltammetry, these "pure kinetic" conditions give rise to totally irreversible waves. The peak potential,  $E_p$ , is then a linear function of the A/B standard potential and of the logarithms of

the overall rate constant ( $k$ ), sweep rate ( $v$ ), initial substrate concentration ( $C^\circ$ ) and, according to the case, of the concentration of electroinactive reactants ( $Z^\circ$ ). The  $\partial E_p / \partial \log v$ ,  $\partial E_p / \partial \log C^\circ$ ,  $\partial E_p / \partial \log Z^\circ$  are then simply related to the reaction orders of the homogeneous kinetic law. These expressions are obtained by integration of the space-dependent, time-independent, differential equations relative to B which do not require any numerical calculation. Mechanism analysis is then based upon the comparison between the experimental slopes and the values predicted for the limiting, single rate-determining step, kinetic behaviors. An early example of this type of mechanism analysis concerned radical-radical dimerization as illustrated experimentally by the reduction of benzaldehyde in a protic medium.<sup>13</sup> Since then, the method has been extended to a number of other reaction schemes<sup>12,15,17</sup> and applied to various electrochemical reactions such as electrodiminization of tropylium<sup>18a</sup> and immonium cations,<sup>18b</sup> carbonyl compounds,<sup>2e</sup> imines,<sup>18c</sup> activated olefins,<sup>2a,2b</sup> polyenic compounds,<sup>3d,3e</sup> electrocyclicisations,<sup>19</sup> electrohydrogenations.<sup>17c,18c,20</sup> Systematic mechanism analysis thus involves the comparison of the measured slopes with those predicted for all the limiting kinetic behaviors of all the possible mechanisms (see, *e.g.*, Refs. 2a, 2b). Numerical calculations are necessary for deriving the overall rate constant from the peak potential knowing the A-B standard potential independently. They are also required if one wants to use the information contained in the whole polarization curve rather than in the peak potential only. This allows more efficient discrimination between the various limiting kinetic behaviors. Measurement of the peak width or fitting of the whole polarization curve may be used in this connection as well as other procedures such as convolution of the current with the linear diffusion characteristic  $(\pi t)^{-1/2}$  function.<sup>2f,21</sup> Numerical calculation then consists in the computation of the convolution integral from the experimentally determined current.<sup>2f,21</sup>

The relationship between the homogeneous kinetics and the electrochemical response is somewhat more complex when, still dealing with a single rate-determining step, the chemical process is not sufficiently fast as compared to diffusion for the "pure kinetic" conditions to be achieved. The partial derivative equations can no



longer be simplified into space-dependent, time-independent, derivative equations. The dependence of the electrochemical response upon substrate concentration, electroinactive reactant concentration, time-scale (*i.e.*, sweep rate in cyclic voltammetry) can however be predicted for any given limiting behavior by dimension analysis of the system.<sup>12b,12c,17a,17c,17e</sup> It thus appears that the interplay between diffusion and chemical processes is dependent upon a single dimensionless parameter  $\lambda$ . If, for example, the reaction orders of the homogeneous process are  $\alpha$  for A,  $\beta$  for B and  $\zeta$  for an electroinactive reactant, Z,

$\lambda = (RT/F)k(C^\circ)^{(\alpha+\beta-1)}C_z^\circ \zeta / \nu$  in cyclic voltammetry<sup>12b,12c,17a,17c,17e</sup> (or, equivalently,  $\lambda = k(C^\circ)^{(\alpha+\beta-1)}(C_z^\circ)^\zeta / \nu$ , in potential step chronoamperometry) where  $k$  is the overall rate constant,  $\nu$  the sweep rate and  $t$  the time.

When looking for the reaction mechanism, a first test is thus to check that the electrochemical response does follow the concentration and sweep rate (or time) dependence predicted, through  $\lambda$ , for the hypothesized limiting behavior: since the electrochemical response depends only upon  $\lambda$ , it should remain the same when varying  $C^\circ$ ,  $C_z^\circ$  and  $\nu$  so as  $(C^\circ)^{(\alpha+\beta-1)}(C_z^\circ)^\zeta / \nu$  remains constant. This is, however, not sufficient in most cases since different limiting kinetic behaviors may well give rise to the same concentration and sweep rate (or time) dependence. A further step will be then to compare the experimental and predicted shapes of the electrochemical response= $f(\lambda)$  relationship. This requires the calculation of the corresponding working curve by algebraic or numerical integration of the partial derivative equation system. For one-electron processes, such as electrodimersizations, adequate electrochemical responses are obtained from current ratios in cyclic techniques such as cyclic voltammetry,<sup>22a</sup> derivative cyclic voltammetry<sup>11c</sup> or double potential step chronoamperometry.<sup>1a,22b</sup>

An early extension of the capabilities of mechanism analysis beyond the above described cases, was provided by the treatments in which the reversibility of the coupled chemical reaction was taken into account involving the participation of both the forward and the backward reactions to kinetic control.<sup>12b,12c,23</sup> More recently, a number of more complex reaction schemes have been analyzed involving the competition between two or even three rate-limiting steps.

Methods were thus described which allow to predict the influence of the operational parameters, sweep rate (or time, or diffusion layer thickness), concentrations, on the overall kinetics, particularly how their variations shift the system toward limiting behaviors. This has been applied to a variety of electrochemical processes, under various micro- and macroelectrolysis regimes: two-electron processes involving competing heterogeneous and homogeneous electron transfers,<sup>24</sup> electrocatalysis of chemical reactions,<sup>25</sup> homogeneous catalysis of electrochemical reactions,<sup>26</sup> competition between H-atom and electron transfers,<sup>27</sup> between radical-radical and radical substrate dimerization and between dimerization and further electron transfer.<sup>28</sup> These treatments can be extended to other reaction schemes and/or other electrochemical techniques. Ample background is thus available for analyzing rather complex mechanisms.

This reminder of the previously acquired knowledge in the field of electrochemical mechanism analysis seemed necessary in view of the recently proposed "reaction order" approach of the problem.<sup>6,7,11,29</sup> As far as limiting kinetic behaviors are concerned, this approach is essentially the same as the previously described methods mentioned above. Being actually based on the rigorous relationships established in previous work by other authors, its application to practical situations is anticipated to lead to correct conclusions as far as their range of applicability is respected, *i.e.*, as far as single rate-determining step kinetic behaviors are dealt with. However, the use of this approach has also been repeatedly advocated for more complex reaction schemes and applied to such experimental situations.<sup>6,7,11c,29b-29d</sup> Overlooking the abundant previous work relative to this type of situations,<sup>24-28</sup> the kinetic interplay between diffusion and homogeneous chemical reactions was then either ignored, as if the homogeneous process was functioning by itself,<sup>29b-29d</sup> or taken into account on questionable intuitive grounds.<sup>11c</sup> It is anticipated that this may lead to erroneous mechanism diagnostics. This was shown above to be the case for the mechanism analysis of the electrodimersization of anthracenes substituted with electron-withdrawing substituents. We give hereafter a second example concerning the anodic electrodimersization of 4-methoxybiphenyl in acetonitrile<sup>11c</sup> which is an illustrative example of

the general problem of the competition between radical-radical and radical-substrate coupling in electrodimmerization reactions.

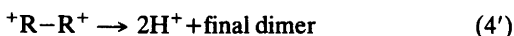
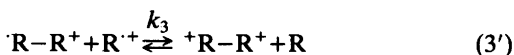
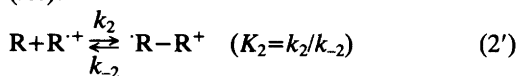
The kinetic data obtained using derivative cyclic voltammetry (DCV)<sup>11c</sup> are summarized in Fig. 6 under the form of a log-log plot of the variations of  $v_{1/2}$  with the substrate concentration  $C^\circ$ ,  $v_{1/2}$  being the value of the sweep rate necessary for the ratio of the derivative peaks on the backward and forward scans of the cyclic voltammogram to equal 0.5. It is seen that  $v_{1/2}$  is proportional to  $C^\circ$  at high values of  $C^\circ$ , and to  $(C^\circ)^2$  at low  $C^\circ$  values. It was concluded<sup>11c</sup> from these observations that the dimerization mechanism involves the competition between a radical-radical coupling (rrc) and a radical-substrate coupling (rsc) reaction (eqn. 0'-4').



(rrc):



(rsc):



(R=4-methoxybiphenyl). More precisely, the forward reaction (1') was regarded as the rds in the rrc reaction which fits the  $C^\circ$  proportionality found at high  $C^\circ$ 's, while forward reaction (3') was regarded as the rds of the rsc reaction with reaction (2') remaining at equilibrium which fits the  $(C^\circ)^2$  proportionality observed at low  $C^\circ$ 's. Intuitively, it is predicted that the corresponding limiting rrc behavior will predominate at low  $C^\circ$ 's and the rsc behavior at high  $C^\circ$ 's, opposite to what is found experimentally concerning the variations of  $v_{1/2}$  with  $C^\circ$ . This discrepancy was explained by hardly controllable qualitative reasoning on the differences existing between the purely homogeneous process and the electrochemical process where the homogeneous reactions are coupled with diffusion. What is the actual answer to the question as results from a rigorous

treatment of the hypothesized competition between the two mechanisms in the context of diffusion to and from the electrode? The problem can be formulated in dimensionless terms as described by eqns. (15)–(17).

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \cdot \frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \frac{2RT}{F} \frac{k_1 C^\circ}{v} b^2 \left(1 + \frac{K_2 k_3}{k_1} C^\circ a\right) \quad (15)$$

$$\tau=0, y \geq 0 \text{ and } y \rightarrow \infty, \tau > 0: a=1, b=0 \quad (16)$$

$$y=0, \tau > 0: (\partial a / \partial y) + (\partial b / \partial y) = 0, \\ a = b \exp[-(F/RT)(E - E^\circ)], \quad (17)$$

$$E = E_i + vt \text{ for } 0 \leq t \leq \theta, E = E_t - v(t - \theta) \text{ for } t \geq \theta$$

the current-time function being obtained as:

$$t_2 i = -\text{FSD}^{1/2} C^\circ (Fv/RT)^{1/2} (\partial a / \partial y)_0$$

with  $\tau = Fvt/RT$ ,  $y = x(Fv/RTD)^{1/2}$ ,  $a = [\text{R}]/C^\circ$ ,  $b = [\text{R}^+]/C^\circ$ ;  $t$ : time,  $x$ : distance from the electrode,  $C^\circ$ : bulk conc. of R,  $E$ : electrode potential,  $E^\circ$ :  $\text{R}/\text{R}^+$  standard potential,  $E_i$ : initial potential,  $E_t$ : scan inversion potential,  $\theta$ : scan inversion time,  $S$ : electrode surface area,  $D$ : diffusion coefficient of R and  $\text{R}^+$ . The calculations were carried out for  $(F/RT)(E^\circ - E_i) = 10$ ,  $E_i$  being then sufficiently negative to  $E^\circ$  for having practically no influence of the cyclic voltammogram.  $E_t$  was taken 300 mV positive to  $E^\circ$ , at 22 °C.

Since it is assumed that the rrc mechanism predominates at high  $C^\circ$ 's,  $k_1$  is found as equal to  $2.76 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (right-hand side asymptote in Fig. 6). Similarly  $K_2 k_3 = 1.28 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$  as derived from the rsc behavior assumed to predominate at low  $C^\circ$ 's (left-hand side asymptote in Fig. 6). The above system and thus the ratio of the derivative peaks are thus functions of only two parameters,  $v$  and  $C^\circ$ . For each value of  $C^\circ$ , the value of  $v$ ,  $v_{1/2}$ , for which this ratio equals 0.5 was numerically obtained from an explicit finite difference resolution of the above system.<sup>30</sup> The resulting  $v_{1/2} - C^\circ$  working curve is shown in Fig. 6 (dashed-line) in comparison with the experimental data.

It is clearly seen that the predicted kinetics is in complete disagreement with the experimental data, showing that the proposed rrc-rsc competi-

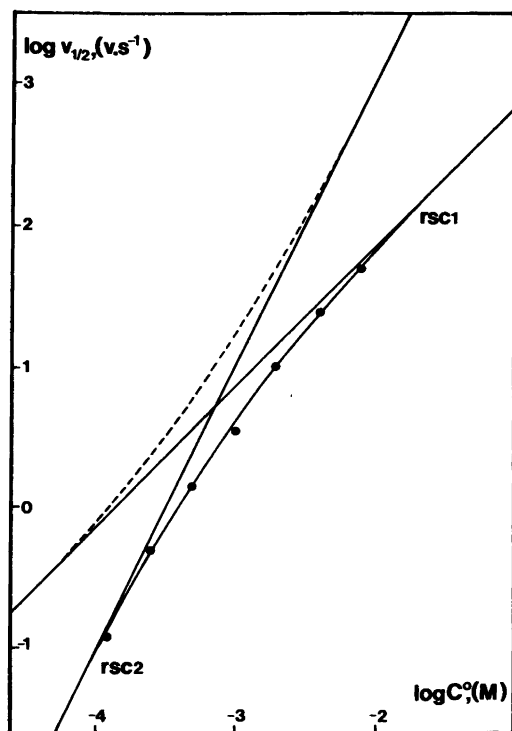


Fig. 6. Anodic electrodimersation of 4-methoxybiphenyl. Comparison between experimental kinetic data (●) (from Table 1 in Ref. 11c) and predicted kinetics for an rrc-rsc2 competitive mechanism (---) and an rsc mechanism (—).  $v_{1/2}$ : sweep rate value necessary for the ratio of the derivative peaks on the backward and forward scans to equal 0.5.  $C^{\circ}$ : 4-methoxybiphenyl bulk concentration.

tive mechanism is certainly wrong. This casts severe doubts on the contention that the process going on at high concentrations involves the radical-radical coupling of two cation radicals.<sup>11c</sup> Important consequences concerning the chemistry of electrodimersation in general ensue. The dimerization reaction occurring at high concentration in the oxidation of 4-methoxybiphenyl was indeed taken as the prototype of radical-radical coupling in the ion-radical series, a reaction claimed to occur very scarcely<sup>7, 11c</sup> in contrast with the conclusions of past investigations. In this connection, the activation energy of the reaction, 10.6 K cal/mol, was regarded as a minimum value for the rrc of all ion radicals, serving as a piece of evidence against the reality

of previously postulated rrc processes for which the activation energies are smaller.<sup>11c</sup> All these reasonings now become very doubtful since the very existence of an rrc process in the oxidation of 4-methoxybiphenyl in the high concentration range appears itself as doubtful. On the other hand, rrc of ion radicals may well involve activation energies significantly smaller than 10 Kcal/mol as discussed above.

Since the rrc-rsc competitive mechanism is clearly ruled out by proper analysis of the experimental data, the question arises of the actual nature of the mechanism of the oxidative electrodimersation of 4-methoxybiphenyl. Let us consider that the rrc pathway is negligible, *i.e.*, that dimerization totally proceeds along the rsc mechanism. In this context, we remove the restriction that (3') is the rds with (2') remaining at equilibrium. In other words, it is considered that both steps may participate to the kinetic control of the overall rsc process. There are then two limiting kinetic behaviors, one in which (2') is the rds and another in which (3') is the rds with (2') acting as a pre-equilibrium. These limiting behaviors will be named rsc1 and rsc2, respectively. For rsc1,  $v_{1/2}$  is proportional to  $C^{\circ}$  while for rsc2 it is proportional to  $(C^{\circ})^2$ . Passing from rsc2 to rsc1 implies that reaction (3') becomes more and more efficient as opposed to backward reaction (2'). An increase of  $C^{\circ}$  is anticipated to produce this effect since reaction (3') is second order and backward reaction (2') is first order. This is similar to what occurs in disproportionation processes where the chemical step interposed between the electrode electron transfer and the solution electron transfer is a first order reaction in both directions.<sup>24a</sup> In more quantitative terms, the overall process is described by the following system (eqns. (18), (19)) which involves the stationary state assumption concerning  $R-R^+$ .

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} \quad (18)$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \frac{2RT}{F} \frac{k_2 c^{\circ}}{v} \frac{ab^2}{b + \frac{k_{-2}}{k_3 C^{\circ}}} \quad (19)$$

with the same initial and boundary conditions as for the rrc-rsc2 mechanism and the same symbolism. The rsc1 behavior is obtained for  $k_3 C^{\circ} \gg k_{-2}$ ,

*i.e.*, at the high concentration limit. It ensues that  $k_2$  can be estimated as  $k_2 = 3.55 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The rsc2 behavior is reached when  $k_3 C^\circ \ll k_{-2}$ , *i.e.*, at the low concentration limit. We then obtain an estimation of  $k_2 k_3 / k_{-2}$ ,  $k_2 k_3 / k_{-2} = 1.28 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ . The system and thus the ratio of the derivative peaks are thus a function of the two parameters  $\nu$  and  $C^\circ$ . For each value of  $C^\circ$ , the value of  $\nu$ ,  $\nu_{1/2}$ , for which this ratio equals 0.5 was then numerically obtained according to the same computation procedure as for the rrc-rsc2 case. The resulting  $\nu_{1/2} - C^\circ$  working curve is shown in Fig. 6 (solid line) in comparison with the experimental data; the best fitting with the experimental data leads to the following values:  $k_2 = 4.07 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_3 k_2 / k_{-2} = 1.65 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ .

It is seen that the agreement between the predicted and experimental kinetic behaviors is now excellent. The rsc mechanism is thus compatible with the DVC data. For the following reasons, some caution should, however, be exerted as to the conclusion that this is the actual mechanism of the reaction. We attempted to check that the linear sweep voltammetric peak variations with sweep rate and concentration predicted for such a mechanism are indeed followed. In the low range of concentrations ( $C^\circ = 0.1 \text{ mM}$ ) this implied the use of rather low sweep rates ( $\nu < 0.01 \text{ V s}^{-1}$ ) in order that the wave becomes irreversible, *i.e.*, that "pure kinetic" conditions be achieved. It was also of interest to raise the concentration so as to attempt to reach the region where the rsc1 behavior predominates which corresponds to  $\partial E_p / \partial \log \nu = -30 \text{ mV}$  and  $\partial E_p / \partial \log C^\circ = 30 \text{ mV}$  as opposed to  $-20$  and  $20 \text{ mV}$ , respectively, for the rrc mechanism. In our hands, these experimental conditions led to poor accuracy and reproducibility of peak potential measurements, resulting most probably from product adsorption. It was suspected that the deprotonated dimer could itself be oxidized in the same potential region as the starting compound possibly leading to polymeric products. Whether these reactions are or are not a part of the process taking place under DCV conditions is not clear at present. More generally, the exact nature of the reaction products formed under these conditions is not ascertained as compared to what is obtained under preparative scale conditions.<sup>31</sup>

In conclusion, it appears worthwhile to again

emphasize the dangers of using "reaction order, without calculations" approaches to mechanism analysis outside of their actual range of validity, *i.e.*, in the case of reactions that are kinetically controlled by more than one step. On a plea of avoiding mathematical complexity, these approaches thus ignore the availability of sound theoretical background which would allow the right mechanistic conclusions to be drawn. In this sense, they amount to a regression with regard to the present capabilities of mechanism analysis of electrochemical reactions.

## CONCLUDING REMARKS

1. Contrary to recent contention,<sup>7</sup> radical-radical coupling of anion radicals does not appear as an uncommonly followed pathway. The reductive electrodimmerization of 9-substituted anthracenes do follow this type of mechanism. The results obtained with these molecules showed that steric factors should be taken into account when comparing the activation energy with the rate constant at a given temperature. Erroneous conclusions recently drawn in this respect were founded on the misconception that the activation energy of the reaction should be compared to the activation energy of the diffusion limiting process.<sup>7,11c</sup> This implicitly assumes that the pre-exponential factors are the same for both processes since, actually, the rate constants should be compared through:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_{\text{dif}}} + \frac{1}{k_{\text{act}}}$$

and not directly the activation energies. In other words, such a procedure amounts to the neglecting of steric factors in all cases, taking the perfect gas collision frequency as pre-exponential factor.

In the case of activated olefins, radical-radical coupling also appears as a rather common pathway except in very dry aprotic media. In the latter case, some evidence exists that a radical-substrate coupling pathway prevails although this is still not a fully demonstrated conclusion.

2. Acceleration of the dimerization reaction by addition of water appears to be related in a number of cases to specific solvation of the anion radicals rather than to protonation by water. The "anion radical-proton donor complex mechanism",<sup>6b</sup> is a possible mode of the role of

water under particular circumstances. It is by no means a unique pathway accounting for the effect of water. Other pathways such as dimerization of two complexed anion radicals or even dimerization of complexes involving more than one anion radical may well occur, depending upon the nature of the starting molecule and the water concentration.

3. The danger of using "reaction order, without calculation" approaches to the analysis of electrochemical mechanisms not controlled by a single rate-determining step should be emphasized. Far from being "capable of unravelling many of the complexities of ion radical reactions"<sup>29d</sup> or of showing "their true power in such situations"<sup>29c</sup> these oversimplified approaches actually lead to erroneous mechanistic conclusions. They should be replaced by correct kinetic analyses for which a large background is now available as illustrated by the above discussion. Besides the reduction of 9-substituted anthracenes, the oxidative dimerization of 4-methoxy biphenyl<sup>11c</sup> is a typical illustration of the shortcomings of such oversimplified treatments of the kinetic data. Important consequences as to the chemistry of cation radicals ensue.

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