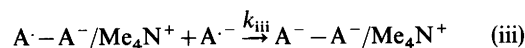
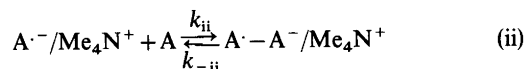


Mechanisms of the Electrohydrodimerization of Activated Olefins. III.* The Mechanism in Proton Donor Poor Solvents, a Revelation

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The mechanism of the electrohydrodimerization of diethyl fumarate, one of the most actively investigated model substances, in acetonitrile in the near absence of water consists of a variation of the anion radical–substrate coupling scheme. In the presence of tetramethyl ammonium ion the mechanism of the reaction is described by equations (i) to (iii). The reaction orders with respect to anion radical ($A^{\cdot -}$), substrate (A), and Me_4N^+ were



demonstrated by linear sweep voltammetry and derivative cyclic voltammetry kinetic studies. When the counter ion is Me_4N^+ , a linear Arrhenius plot was observed with an apparent activation energy of 5.0 kcal/mol. The low apparent E_a was suggested to be a consequence of a negative temperature dependence on equilibrium (i). In the presence of $(hexyl)_4N^+$, the temperature dependence is more complex and the rate is nearly independent of temperature between +7 and –17 °C. The inconsistencies in the large body of previous mechanistic work on electrohydrodimerization is discussed.

Dimer forming reactions hold a prominent position among electrode reactions. Electrohydrodimerization, following the pioneering work of Baizer,³ is surely the most actively studied organic electrode

process both from the preparative^{3–18} and mechanistic aspects.^{19–40} Although the initial studies^{19,20} resulted in different conclusions, later studies^{21–40} have generally agreed that the reactions involve, as the primary step, the coupling of two anion radicals (eqn. 1). This conclusion has in turn



fostered the belief that the ion radical–substrate coupling reaction (eqn. 2), one of the pathways favored by Baizer,¹⁸ is unfavorable relative to (1) and does not take place. We have recently presented



compelling evidence that the primary step in the dimer forming reaction of 4,4'-dimethoxystilbene (D) cation radical is the radical–substrate reaction (eqn. 3).⁴¹ The latter paper describes the first clear



evidence for the ion radical–substrate coupling mechanism and two recent papers^{42,43} on the coupling of $D^{\cdot +}$ led to the conclusion that the mechanism involves the simple dimerization of cation radicals.

Our work⁴¹ on the coupling mechanism of $D^{\cdot +}$ cast doubt on the universal occurrence of ion radical dimerization in coupling reactions of olefinic ion radicals and called for a re-examination of the evidence leading to the general acceptance of the latter. Perusal of the papers published during the last decade on the mechanism of electrohydrodimerization resulted in what appeared to the author

* See Refs. 1 and 2 for other parts in this series.

as glaring inconsistencies. Some of these inconsistencies are pointed out in the following paragraphs.

Bard and coworkers^{21,22} report a second order rate constant of $44 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C for the dimerization of the anion radical of diethylfumarate in *N,N*-dimethylformamide (DMF). An activation energy equal to 4.2 kcal/mol was reported for the

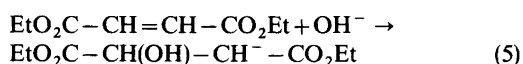


same reaction.^{21,39} Diffusion controlled reactions have activation energies of $3-4 \text{ kcal/mol}$.⁴⁴ Thus, the rate constant-activation energy relationship reported for the dimerization of $\text{DEF}^{\cdot-}$ (eqn. 4) appears to be completely incompatible with the simple dimerization mechanism.

The Bard²¹ and Savéant^{28,29} groups observe that the addition of water enhances the rates of some electrohydrodimerizations but both groups conclude that the mechanism is the same in anhydrous and wet solution. In some cases²⁹ linear sweep voltammetry slopes, $dE^p/d \log C_{\text{H}_2\text{O}}$, of about 20 mV/decade were observed. This appeared to the author to be a clear indication that water is kinetically involved and that the reactions are first order in the proton donor. It also appears to be very questionable to discuss data obtained in anhydrous solutions. Our work⁴⁵⁻⁴⁸ has shown that it is very difficult to remove residual water from solvent-electrolyte systems and one case, the reduction of azobenzene anion radical, showed that our purification procedures allowed for the observation of the dianion while the vacuum techniques⁴⁹ similar to those used in the "anhydrous" electrohydrodimerizations²¹ resulted in completely irreversible voltammetry for the azobenzene anion radical-dianion couple due to rapid protonation of the dianion by residual water.⁴⁸ Thus, before the present investigations were undertaken, no evidence was available for the mechanism of electrohydrodimerization of activated olefins in the absence of water. Furthermore, the interpretation^{21,29} that the mechanism is the same in the presence and absence of proton donors appeared to be on very loose grounds.

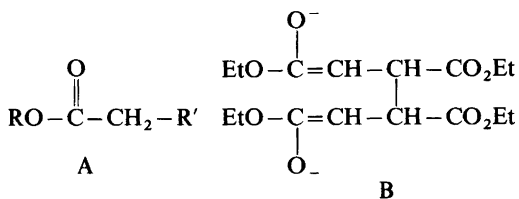
Bard and coworkers^{21,22} observed coulometric n values considerably less than unity and attributed this to polymerization of the 1,2-disubstituted olefins. This interpretation did not seem reasonable to the author since 1,2-disubstituted olefins do not readily undergo polymerization and even vinyl compounds which are much more likely to poly-

merize can be converted to the hydrodimers in excellent yield.¹⁸ Perhaps, even more remarkable in terms of the proposed polymerization, the addition of Li^+ resulted in n values of 1.0. No meaningful explanation was proposed for this phenomenon. These data led the author to suspect that the low n values were simply due to a competing reaction, the nucleophilic attack by OH^- (eqn. 5) since ionic reactions are well-known⁵⁰ to be rapid in



DMF and two mol of hydroxide ion are produced for each mol of hydrodimer. The function of Li^+ could then be simply to act as a hydroxide ion scavenger.

Discussions by the Bard²² and Maloy⁴⁰ groups concerning protonation reactions of hydrodimer dianions appeared to be inconsistent with what is known about proton transfer reactions. Esters of structure A have $\text{p}K_a$ values of the order of 25.⁵¹ The conjugate acid of the dimer dianion B would be expected to show similar acid-base properties.



Proton transfer from oxygen acids (water in this case) to strong bases are exceedingly rapid with rate constants of about 10^8 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁵² Thus, protonation of B by water is expected to be nearly diffusion controlled. It is difficult to see how Li^+ ion²² could make the protonation reaction even faster and thus decrease the degree of polymerization. Bezilla and Maloy⁴⁰ propose that reactions (6) and (7) account for the mechanism of cinnamic

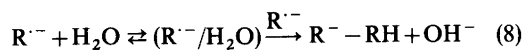


acid ester reactions as first suggested by Klemm and Olsen.⁵³ Values of the order of 10^2 M^{-1} and 10 s^{-1} were suggested for K_6 and k_7 , respectively.⁴⁰ Under the reaction conditions equilibrium (6) was proposed to be established. The latter is clearly inconsistent

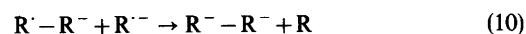
with the expected behaviour of the dianion in the presence of the trace amounts of water no doubt present in the solvent–electrolyte system. Under the reaction conditions $R^- - R^-$ would very rapidly be protonated and converted to products precluding the observation of slow kinetics.

In the opinion of the author, it is unbelievable that so much material relating to the mechanism of electrohydrodimerization has been published with so many apparent inconsistencies, some of which are discussed above. The published work has produced a general misconception about the relative ease of ion radical dimerization and ion radical substrate coupling.² The role of water in enhancing the rate of hydrodimerization has not been completely understood.^{21,29}

The inconsistencies noted above led the author to undertake a systematic investigation of this important class of reactions. In a preliminary communication, the hydrodimerization of DEF in DMF was shown to be first order in water and the key step in the coupling was observed to be the reaction of an anion radical–water complex with an uncomplexed anion radical (eqn. 8).¹ When water is effectively removed by carrying out voltammetric experiments over active neutral alumina, a



change in mechanism is observed with the key step involving the coupling between an anion radical and the substrate (eqn. 9) which is followed by rate determining electron transfer reaction (10).



In this paper, a detailed account of the mechanism of the hydrodimerization of diethyl fumarate in “anhydrous” acetonitrile is presented. More details on the reactions in the presence of proton donors will appear later.

RESULTS

General comments on kinetic measurements. All kinetic measurements employed derivative cyclic or linear sweep voltammetry using experimental techniques which have recently been developed.^{54–56} The general kinetic approach was that

developed by the author^{57,58} and is based upon relationship (11) where R'_1 refers to the ratio of the

$$R'_1 = f(k_{app}/v) \quad (\text{for a first order reaction}) \quad (11)$$

derivatives of the currents on the backward and forward scans of a cyclic voltammogram and v is the voltage sweep rate. The important feature of the method is that if R'_1 is held constant while changing some feature of the reaction conditions, the change in v required is equal to the change in k_{app} brought about by the change in the conditions. Thus, reaction orders, activation energies and kinetic isotope effects can be obtained directly from experimental parameters without resort to any theoretical calculations. When v in (11) is v_1 , the value required to maintain R'_1 at 0.500, the rate constant can be calculated from theoretical data if the mechanism is known.⁵⁸

For linear sweep voltammetry studies, mechanism analysis can readily be carried out without any theoretical calculations as well.⁵⁹ The response is determined by the reaction orders of the species involved and can be predicted from the rate equation (12), where the superscripts are the reaction orders, A is the substrate, B the electrode generated

$$\text{Rate} = k_{obs} C_B^b C_A^a C_X^x C_I^i \quad (12)$$

intermediate, X is an additional reactant and I is a species formed during the process that participates further in the reaction. In the present study, the linear sweep voltammetry slope which can be used to distinguish between the radical–radical and radical–substrate coupling mechanisms is the substrate concentration dependence which is given by equation (13).⁵⁹ The rate law for the radical–radical reaction is (14) and that for the radical–substrate is given by (15).

$$-dE^p/d \log C_A = ((a+b+x+i-1)/(b+1))RT/nF \quad (13)$$

$$\text{Rate} = k_{obs} C_B^2 \quad (14)$$

$$\text{Rate} = k_{obs} C_B^2 C_A \quad (15)$$

Application of (13) on these two rate laws results in slopes of $-(1/3)RT/F$ and $-(2/3)RT/F$ or -19.7 and -39.4 mV/decade, respectively, when the temperature is 298 K.

Kinetics in electrolyte solutions passed over neutral alumina. The data in Table 1 show the effect of

Table 1. Kinetics of the electrohydrodimerization of diethyl fumarate in "anhydrous" acetonitrile.^a

C_A ^b /mM	$v_{\frac{1}{2}}$ ^c /V s ⁻¹	$(v_{\frac{1}{2}}/C_A)$ /V s ⁻¹ mM ⁻¹
1.00	4.70	4.70
2.00	10.1	5.05
4.00	23.5	5.88
8.00	50.0	6.25

^a At an Au electrode in solvent containing Me₄NBF₄ (0.05 M) at 21 °C. Measurements conducted on solutions passed through neutral alumina. ^b Concentration of diethyl fumarate. ^c The voltage sweep rate at which the ratio of the derivative peaks was equal to 0.500.

substrate concentration on $v_{\frac{1}{2}}$, which is proportional to k_{obs} , for the reaction of DEF in solvent-electrolyte solution which had been passed through a column containing neutral alumina immediately before the measurements were made. The supporting electrolyte was Me₄NBF₄, which was used throughout this study. The feature of interest in the data is the steady increase in $v_{\frac{1}{2}}/C_A$ with increasing C_A . An 8-fold increase in C_A was accompanied by

Table 2. The Effect of tetramethylammonium ion concentration on the kinetics of electrohydrodimerization of diethyl fumarate in "anhydrous" acetonitrile.^a

[Me ₄ NBF ₄]/M	$v_{\frac{1}{2}}$ /V s ⁻¹	$(v_{\frac{1}{2}} - 0.8)$ /V s ⁻¹
0 ^b	0.80	0
0.015	2.20	1.40
0.030	3.60	2.80
0.060	5.00	4.20

^a At an Au electrode in solvent over neutral alumina at 21 °C. Diethylfumarate concentration = 1.00 mM. ^b The electrolyte was Hx₄NClO₄ (0.1 M).

Table 3. Electrolyte effects on the electrohydrodimerization of diethyl fumarate in "anhydrous" acetonitrile at constant ionic strength.^a

[Hx ₄ NClO ₄]/M	[Me ₄ NBF ₄]/M	$v_{\frac{1}{2}}$ /V s ⁻¹ at C_A /mM		
		1.00	2.00	4.00
0.10	0	0.54	1.48	4.44
0.09	0.01	0.80	2.42	6.00
0.08	0.02	1.08	3.20	7.50
0.06	0.04	2.25	5.60	15.2
0.02	0.08	5.90	15.4	40.0

^a At an Au electrode at 22 °C. Measurements conducted over neutral alumina.

a 1.33-fold increase in the ratio which indicates a higher order rate law than (14). In the presence of water, $v_{\frac{1}{2}}/C_A$ has previously been shown to be constant which is consistent with rate law (14).^{1,2} The fact that the increase in the ratio with increasing concentration is less pronounced than was observed during the reduction of methyl cinnamate² is a consequence of the lower concentration of water when the experiments are conducted with alumina in the cell.

Effect of tetramethylammonium ion concentration on the kinetics. Data are summarized in Table 2 from several kinetic runs carried out in electrolyte solutions over active neutral alumina in which the Me₄NBF₄ concentration was varied. The first entry is for when tetrahexylammonium perchlorate (Hx₄NClO₄) was the electrolyte. The last column in Table 2 represents the contribution of Me₄N⁺ to the rate of the reaction, estimated by subtracting out the rate when only the larger cation is present. These data indicate an approximate reaction order of one for Me₄N⁺.

Effect of Me₄N⁺ ion at constant ionic strength. A criticism of the data in Table 2 is that the ionic strength varied in the series of experiments and the observed rate dependence could be due to a salt effect. For this reason, a large number of kinetic runs were conducted in which both the substrate concentration and the Me₄N⁺ concentration were varied while keeping the ionic strength constant by the appropriate addition of Hx₄NClO₄. The data are summarized in Table 3. The features of interest in the data are that doubling C_A results in an approximate 3-fold increase in $v_{\frac{1}{2}}$ independent of the concentration of Me₄N⁺ and that the rate is dependent upon the latter. The dependence of the rate of the reaction on [Me₄N⁺] is seen most clearly from the tabulation in Table 4. Here again,

Table 4. The effect of tetramethylammonium ion concentration on the electrohydrodimerization of diethyl fumarate in "anhydrous" acetonitrile at constant ionic strength.^a

[Me ₄ NBF ₄]/M	[v _{1/2} - v _{1/2} (Hx ₄ N ⁺)] ^b /V s ⁻¹ at			
	C _A /mM	1.00	2.00	4.00
0	0	0	0	0
0.01	0.26	0.94	1.56	1.56
0.02	0.54	1.72	3.06	3.06
0.04	1.71	4.12	10.8	10.8
0.08	5.36	13.9	35.6	35.6

^aData from Table 3. ^bNormalized values obtained by subtracting v_{1/2} for the case where the electrolyte was Hx₄NClO₄ (0.10 M).

the contribution of Me₄N⁺ to the reaction rate is obtained by subtracting out v_{1/2} for the case where the electrolyte was only Hx₄NClO₄. The data indicate that the reaction order in [Me₄N⁺] is very nearly unity at concentrations lower than 20 mM and appears to approach 2 at higher concentrations.

Apparent activation energies for the hydrodimerization of DEF. Temperature effects on the reaction rate were determined both in the presence and absence of Me₄N⁺ ion. In the former case, a reasonably linear Arrhenius plot was obtained with an apparent activation energy of 5.0 kcal/mol with a correlation coefficient of 0.978. Measurements were made at only three temperatures in the absence of Me₄N⁺ and the plot of the data was clearly not linear with nearly the same apparent rate constants

Table 5. The effect of temperature on the kinetics of the electrohydrodimerization of diethyl fumarate in "anhydrous" acetonitrile.^a

[Me ₄ NBF ₄]/M	[Hx ₄ NClO ₄]/M	T/K	v _{1/2} /V s ⁻¹
0.04	0.06	295.2	13.0 ^b
0.04	0.06	286.1	10.9 ^b
0.04	0.06	278.8	9.2 ^b
0.04	0.06	272.7	7.2 ^b
0.04	0.06	266.3	5.0 ^b
0.10	0	295.2	4.5
0.10	0	280.8	2.0
0.10	0	256.3	1.5

^aMeasurements at an Au electrode in solvent over neutral alumina with C_A equal to 5.00 mM. ^bArrhenius activation energy of 5.0 kcal/mol with a correlation coefficient of 0.978.

Table 6. The effect of the counter ion and temperature on reversible electrode potentials for the reduction of diethyl fumarate in "anhydrous" acetonitrile.^a

T/°C	C _{electrolyte} /M	-E _{zc} ^b with electrolytes	
		Me ₄ NBF ₄	Hx ₄ NClO ₄
21.2	0.05	572.5(0.1)	570.1(0.4)
6.5	0.05	561.3(0.1)	563.5(0.4)
-12.5	0.05	546.2(0.3)	541.4(0.2)
21.2	0.02	590.0(0.1)	—
21.2	0.04	577.3(0.0)	—
21.2	0.08	570.5(0.1)	—

^aAt an Au electrode in solvent containing diethyl fumarate (0.5 mM). ^bThe second harmonic *a.c.* quadrature component measured at 300 Hz with a *d.c.* voltage sweep rate of 40 mV s⁻¹. Potentials refer to a potentiostat bias setting of -1.200 V vs. Ag/Ag⁺ in acetonitrile.

being observed at +7 and -17 °C. Unusual temperature effects during electrode processes have recently been discussed and attributed to complex reaction mechanisms.⁶⁰

Temperature and electrolyte effects on reversible electrode potentials. The change in reversible electrode potential (ΔE_{rev}) brought about by the association of supporting electrolyte cations (M⁺) with an anion radical formed by reduction of a neutral organic compound is given by eqn. (16) where K refers to the association constant for (17).⁶¹

$$\Delta E_{\text{rev}} = (RT/nF) \ln(1 + K[M^+]) \quad (16)$$



Thus, ion pairing can be detected by electrode measurements providing that the product K[M⁺] is significant relative to unity. The most accurate measurement of reversible potentials in systems where reactions of the electrode generated intermediate are taking place is phase selective second harmonic *a.c.* voltammetry.^{62,63} The theoretical relationships have recently been verified for rapidly reacting organic systems.⁶⁴

Data for the 2nd harmonic *a.c.* quadrature component (E_{zc}) in the presence of both Me₄N⁺ and Hx₄N⁺ are summarized in Table 6. The object of comparing the two electrolyte cations was that the large Hx₄N⁺ ion is not expected to ion pair with the radical anion while Me₄N⁺, in analogy to hydrocarbon anion radicals,⁶⁵ was expected to be more prone to do so. The data show that there is very

Table 7. Linear sweep voltammetry mechanism analysis of the electrohydrodimerization of diethyl fumarate in "anhydrous" acetonitrile.^a

$v/\text{mV s}^{-1}$	$-E^p$ at C_A/mM			$dE^p/d \log C_A^b$
	0.50	1.00	2.00	
100	367.9(0.1)	358.3(0.2)	347.8(0.1)	-33.4
200	371.0(0.2)	359.9(0.2)	349.2(0.2)	-36.2
400	375.8(0.2)	364.0(0.3)	352.9(0.1)	-38.0
1000	382.6(0.1)	370.4(0.1)	358.3(0.2)	-40.3

^a In solvent containing Me_4NBF_4 (sat.) at 22 °C at an Au electrode. Potentials are in mV relative to a potentiostat bias setting of -1.420 V vs. Ag/Ag^+ in acetonitrile. ^b In mV/decade, correlation coefficients of 0.9997, 1.0000, 0.9998 and 1.0000 for 100, 200, 400 and 1000 mV s^{-1} , respectively.

little difference in the potentials measured over a 34 degree temperature range in the presence of the two cations. The latter precluded a possible concentration dependence test at constant ionic strength. The effect on E_{rev} brought about by changing $[\text{Me}_4\text{N}^+]$ in the range from 0.02 to 0.08 M was observed to be a decreasing trend at low concentration which appears to level off as the cation concentration approaches that limited by solubility. The most reasonable conclusion is that the observed effect is due to a medium change in going from low to higher ionic strength and that the effect brought about by ion pairing is negligible.

Linear sweep voltammetric substrate concentration dependence. As mentioned earlier, the value of $dE^p/d \log C_A$ differs by a factor of 2 for the radical-radical and radical-substrate coupling mechanisms. The data in Table 7 show that in a solution saturated in Me_4NBF_4 (~ 0.1 M), the value of the slope observed on a 4-fold concentration change is close to that expected for the radical-substrate coupling mechanism. The value, -37.0 ± 2.9 mV/decade is within experimental error of the theoretical value, -39.0 mV at 22 °C. On the other hand, the voltage sweep rate dependence does not show linear behaviour and calculated slopes are less than the theoretical value, 19.5 mV/decade, and show a decreasing trend as the concentration is increased. In order to test for a possible reason for this behaviour, the derivative cyclic voltammetric peak current ratios were measured in the voltage sweep rate range where the linear sweep voltammetry data were obtained. The values of R'_i observed were 0.323, 0.288, 0.282, 0.297 and 0.351 at 80, 100, 200, 400 and 1000 mV s^{-1} , respectively. This is a clear indication of an additional complication in the mechanism. The increasing trend in R'_i with decreas-

ing sweep rate below 200 mV s^{-1} is indicative of a reversible reaction producing radical anion which is only observed when the sweep rate is low. A very similar situation has recently been encountered during the reduction of anthracenes substituted with electron withdrawing groups. The stable dimeric dianions formed by coupling of the anion radicals undergo dissociation which can be observed at low sweep rates.⁶⁶

The reaction of diethyl fumarate with hydroxide ion in DMF. It was mentioned in the introduction that the reaction between hydroxide ion and DEF could possibly explain the low coulometric n values observed in DMF.^{21,22} In order to test this hypothesis, attempts were made to study the kinetics of the reaction between OH^- and DEF in DMF in the presence and absence of lithium ion. The kinetic method consisted of the recording of derivative cyclic voltammograms for the reduction of DEF at 100 V s^{-1} at 1 s intervals while vigorously stirring by bubbling nitrogen through the solution. Both solutions contained DEF (5.0 mM) in DMF containing Bu_4NBF_4 (0.1 M) and one solution contained LiClO_4 (25 mM). The solution containing Li^+ was used as a model for the case where coulometric n values of 1.00 were obtained.²² The experiments were initiated by injecting Bu_4NOH (5.0 mM) by means of a syringe. In the case where no Li^+ was present, the first cyclic voltammogram recorded indicated about 50 % conversion of DEF and the second showed only traces of the substrate left. With Li^+ present no decrease in the reduction current for DEF was observed upon injection of the Bu_4NOH solution.

After adding the base, the observation was that there were no species present in solution that were electroactive in the region where DEF is reduced.

This means that $\text{EtO}_2\text{C}-\text{CH}(\text{OH})-\text{CH}=\text{CO}^-$ (OEt) is not reduced in this potential range.

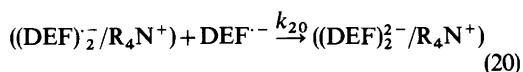
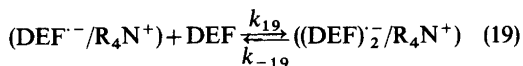
From the above experiments, the conclusion can be drawn that the rate of reaction (5) under the conditions of the measurements is as great as the rate of mixing the reagents together and that a five-fold excess of Li^+ completely inhibits the reaction. From the experiment in the absence of Li^+ we can estimate a minimum value of the second order rate constant for (5) to be equal to $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The reaction is probably even faster since the observed rate is partially or more likely nearly completely controlled by the mixing rate.

DISCUSSION

Before going into a discussion of the mechanism, a brief summary of the data presented in the previous sections is called for. The data in Table 1 under conditions less stringent toward the exclusion of water than that in the remaining Tables, indicate that when the water concentration is finite but low, the reaction order in substrate is greater than that predicted by the simple dimerization rate law. The data in Tables 2 and 3 show that the rate is dependent upon the concentration of Me_4N^+ and that doubling C_A results in a three-fold increase in the apparent rate constant. The data in Table 4 show that the reaction order in Me_4N^+ is very nearly 1 at low concentration and approaches 2 at higher concentrations. The apparent activation energy for the reaction in the presence of Me_4N^+ is low, 5.0 kcal/mol (Table 5), and in the presence of Hx_4N^+ the non-linear Arrhenius plot cannot be related to an activation energy. Reversible electrode potential measurements (Table 6) show no apparent effect of the nature of the counter ion and no evidence for ion pairing was obtained. The linear sweep voltammetry data, in spite of some problems to do with the reversibility of the reaction which can be observed at low sweep rates is in agreement with the radical-substrate coupling mechanism.

The simple radical-substrate coupling mechanism (eqns. 9 and 10) accounts for all of the kinetic

data with the exception of the dependence of the rate on $[\text{Me}_4\text{N}^+]$.* The latter may appear to contradict the fact that ion-pairing could not be detected by the second harmonic *a.c.* electrode potential measurements. This is not the case, but rather tells us something about the magnitude of K in eqn. (16). The failure to observe a significant electrolyte concentration effect on E_{rev} means that $K[\text{M}^+]$ does not exceed about 0.1 and hence the maximum value of K can be estimated to be of the order of 1.0 or smaller. Thus, in order to accommodate all of the data, reaction (18) must be incorporated and the mechanism is then described by (18)–(20).



The very low activation energy is readily explained by the complex reaction scheme (eqns. 18–20) providing that any of the individual steps show inverse temperature dependence. In this respect it is of interest to note that if the data in Table 3 are treated assuming the simple dimerization mechanism, the calculated rate constants are of the order of 10^2 greater than reported by Bard²¹ and still the observed activation energy is somewhat greater. As mentioned earlier, these very low activation energies are inconsistent with the simple dimerization and are indicative of complex reaction schemes such as reactions (18)–(20).

Product adsorption on the electrode is observed at high concentration in the absence but not in the presence of water and must be due to the low solubility of the dianion formed in (20) which would not be expected to have a finite lifetime in the presence of water. Some indication that this could be the case comes from hydrolysis reactions of DEF in "anhydrous" acetonitrile using Bu_4NOH . A precipitate is formed on addition of the base which dissolves upon the addition of small amounts of water. The anions are not the same in the two reactions but there are similarities in their structures.

At higher concentrations of Me_4N^+ , the reaction appears to be tending toward second order in the cation in the mixed electrolyte (Table 3) but not

* The kinetic data, for example in Tables 3 and 7, do not exactly correspond to the radical-substrate coupling mechanism but indicate that under the reaction conditions, that mechanism predominates. The anion radical-water complex mechanism (Ref. 1) as well as anion radical dimerization are likely minor competing mechanisms.

when Me_4N^+ is the only cation present. It also appears that the reaction is somewhat slower, at the same substrate and Me_4N^+ concentrations, when Hx_4NClO_4 is present. This suggests a possible inhibiting effect of Hx_4NClO_4 but as mentioned earlier the experiments are not directly comparable because the one series varies in ionic strength while the other does not. It is clear that further work is needed on the effect of the electrolyte in these reactions.

The experiments on the reaction between DEF and OH^- in DMF conclusively show that the production of hydroxide ion during electrohydrodimerization of DEF will be accompanied by competing reaction (5). If all of the base produced participates in (5) the coulometric n value would be expected to be equal to 0.5. In fact values as low as 0.55 and commonly 0.65 were reported.²² Thus, it is clear that the suggestion of polymer formation²² is incorrect and the low n values are due to competing (5). It is also interesting that when Li^+/DEF ratios of 5 were used in the hydrolysis experiments, no reaction could be detected. Lithium ion is apparently a very effective hydroxide ion scavenger in DMF.

In view of referee comments on this and related papers dealing with competing mechanisms of electrode generated intermediates, a reminder regarding the factors determining which mechanism predominates is in order. It is *not* the relative rate constants that are most important in determining whether the ion radical dimerization or the ion radical-substrate coupling mechanism predominates. These reactions are relatively slow processes and are associated with a relatively thick reaction layer. There are steep concentration gradients of both ion radical and substrate in the reaction layer and the concentration of the substrate is much higher than that of the ion radical in all regions with the exception of a very thin layer close to the electrode. Thus, the relative concentrations play a major role in controlling the course of the reactions. This appears to be a major source of misunderstanding of mechanisms of this type.

In conclusion, this study has shown that the inconsistencies noted in the introduction are primarily due to the failure to account for the proton donors in "anhydrous" solutions. The ion radical-substrate coupling mechanism of electrohydrodimerization is a favourable reaction pathway when proton donors are kept at a very low concentration.

EXPERIMENTAL

The instrumentation, electrodes, cells, data handling procedures and solvent and electrolyte purification were the same as described recently.⁶⁷ Diethyl fumarate was reagent grade and used as received.

The kinetic techniques described in the results section are discussed in more detail in Refs. 58 and 59.

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