

Electrohydrodimerization Reactions

III. Rotating Ring-Disk Electrode, Voltammetric and Coulometric Studies of Mixed Reductive Coupling of Dimethyl Fumarate in the Presence of Cinnamitrile and Acrylonitrile in Dimethylformamide Solution

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ABSTRACT

The electrohydrodimerization reaction of dimethyl fumarate in the presence of cinnamitrile and acrylonitrile was studied in dimethylformamide solution by rotating ring-disk electrode, voltammetric and coulometric techniques. At potentials where only dimethyl fumarate is electroactive, the rate and mechanism of decay of the dimethyl fumarate anion radical are only slightly perturbed from the results obtained in the absence of cinnamitrile and acrylonitrile. This is an indication that little or no cross-coupling was occurring. At potentials where both dimethyl fumarate and cinnamitrile are electroactive evidence for the occurrence of a solution oxidation-reduction reaction consuming cinnamitrile anion radical and dimethyl fumarate parent was obtained. In addition, the role of *cis-trans* isomerization of radical anions in electrohydrodimerization reactions is discussed. Differences in the cyclic voltammograms of diethyl maleate in the presence of acrylonitrile when compared with those obtained in the absence of acrylonitrile and for dimethyl fumarate in the presence of acrylonitrile are observed.

We have previously reported (1) the use of rotating ring-disk electrode (RRDE) voltammetry, cyclic voltammetry, and coulometry in the elucidation of the mechanism of the electrohydrodimerization (electrolytic reductive coupling) of the three di-substituted olefins dimethyl fumarate (DF), cinnamitrile (CN), and fumaronitrile (FN) in anhydrous dimethylformamide (DMF) solution. Potential-step chronoamperometry has also been employed to determine the electrohydrodimerization mechanism of diethyl fumarate (2). These studies showed that these hydrodimerizations proceed predominantly via a one-electron reduction

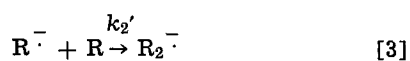


followed by a radical ion dimerization (EC reaction scheme) for each olefin

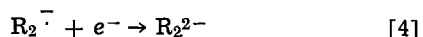


It is also of interest to examine the hydrodimerization reaction of a disubstituted olefin in the presence of a second activated olefin (R') by RRDE voltammetry (3) and coulometric techniques. The aim was to explore the conditions under which formation of cross-coupled products can occur, thus obtaining more insight into the mechanism of electrolytic reductive coupling.

This approach was first undertaken by Baizer *et al.* (4-7). These investigators discovered cross-coupled products of the form $R'RH_2$ after electrolysis of aqueous-DMF solutions at mercury electrodes containing high concentrations (up to 5M) acrylonitrile (AN) at potentials where R , but not R' , was electroactive. They attributed these results, on the basis of this as well as cyclic voltammetric evidence (8), to the occurrence of an ECE mechanism; *i.e.*, a one-electron reduction (Eq. [1]) followed by nucleophilic attack by the radical anion on the parent molecule

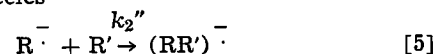


to form the electroactive species R_2^- which can undergo further reduction to yield the



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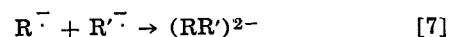
nonelectroactive species R_2^{2-} . They surmised that in the presence of a second olefin R' , because of its greater concentration at the electrode surface when compared with R , nucleophilic attack by R^- on R' to form the electroactive species



$(RR')^-$ occurs. This species can undergo further reduction to yield a cross-coupled product (9)



The ratio of cross-coupled product to simple dimer (R_2H_2) would be dependent on the concentration ratio of R and R' , on the rate of formation of the cross-coupled product relative to the rates of formation of the simple dimers (R_2H_2 and R'_2H_2), and on the rates of formation of the simple dimers relative to each other. They also found that the yield of cross-coupled product was substantially increased when electrolysis was conducted at potentials where both R and R' were reduced; this is an indication that cross-coupling via a radical ion-radical ion-coupling mechanism was occurring at a faster rate than the ECE



mechanism postulated in Eq. [5] and [6].

Dimethyl fumarate was chosen to serve as the species R . Its radical decay rate constant (*i.e.*, dimerization rate constant) is at the lower limit of rate constants measurable with the particular RRDE used and thus any increase in the velocity of that reaction, as explained above, would still result in reasonable current levels at the ring. Also, the $E_{1/2}$ of its first reduction occurs well before that of cinnamitrile and acrylonitrile (AN), the two species which would function as the R' species. CN was chosen because its hydrodimerization has been studied (1), because its second-order rate constant is only eight times that of dimethyl fumarate, and because it is more difficult to reduce than dimethyl fumarate. Acrylonitrile was chosen because of its use in previous studies (4-7). The mechanism and rate of dimerization of AN, however, have not been determined because the electrogenerated product reacts very quickly (9).

The diagnostic criteria which were used to determine the reaction path consisted of a qualitative examina-

tion of the dependence of the ring current (i_r) on disk potential (E_d) at constant ring potential (E_r), a quantitative examination of the dependence of the kinetic collection efficiency, N_K , on the rotation rate and concentration (XKTC) (10-12), where

$$XKTC = (0.51)^{-2/3} \nu^{-1/3} D^{1/3} C^0 \omega^{-1} k_2 \quad [8]$$

and ν is the kinematic viscosity, D is the diffusion coefficient, C^0 is the initial concentration, ω is the rotation rate, and k_2 is the second-order homogeneous rate constant, on the behavior of N_K with various disk currents (CONI) (3)

$$CONI = i_d/i_{d,l} \quad [9]$$

where i_d is the disk current and $i_{d,l}$ is the disk current at the limiting current plateau, and finally, controlled potential coulometric analysis.

Experimental

Reagents.—N,N-dimethylformamide (DMF), obtained from Baker Chemical Company, was purified by vacuum distillation and stored under He. Solvent purity was ascertained by cyclic voltammetric analysis of DMF solutions of tetrabutylammonium iodide (TBAI) obtained from Southwestern Analytical Chemicals, Inc. TBAI and tetrabutylammonium perchlorate (TBAP), also obtained from Southwestern Analytical Chemicals, Inc., were vacuum dried and stored over Drierite. Dimethyl fumarate (DF), sublimed prior to use, and cinnamionitrile, used as received, were obtained from K. and K. Laboratories. Acrylonitrile, Matheson, Coleman and Bell Chemicals, was used as received.

Apparatus.—A Tascussel Electronique Bipotentiostat, Model Bipad 2, was used for all RRDE experiments. A Digitec digital voltmeter, Model 204, and a Fairchild digital multimeter, Model 7050, were used to measure the steady-state ring and disk currents simultaneously. A Wavetek function generator provided a d-c potential ramp for voltammetric experiments recorded on a Mosley Model 2D-2 X-Y recorder. The platinum-Teflon rotating ring-disk electrode, having a disk radius (r_1) of 0.187 cm and inner (r_2) and outer (r_3) ring radii of 0.200 and 0.332 cm, respectively, was constructed by Pine Instrument Company, Grove City, Pennsylvania. The maximum collection efficiency, N , for the RRDE used in these experiments was 0.555 (1). The electrochemical cell, dispensing vessel, and motor and controller used to rotate the RRDE have been described previously (1). The reference electrode was a silver wire spiral (Ag-RE) whose potential was dependent on the identity and concentration of the supporting electrolyte. TBAI was used as supporting electrolyte in all RRDE experiments. A Model 170 Electrochemistry System (Princeton Applied Research, Princeton, New Jersey) was employed for all controlled potential coulometric experiments. A conventional coulometry cell was used. In these experiments, a platinum gauze served as the working electrode and a platinum spiral as the auxiliary. A saturated calomel electrode (SCE) was used as the reference electrode. The reference and auxiliary compartments were separated from the cathode compartment by medium porosity glass frits.

Procedure.—DMF, dispensed from the storage vessel into the dispensing vessel by positive He pressure, together with supporting electrolyte and, in most cases, the depolarizer, was subjected to a minimum of three freeze-pump-thaw cycles. In experiments where CN was present, it was first necessary to conduct a pre-electrolysis to remove an electroactive impurity present in the CN prior to addition of the DF. This was carried out at a Hg pool electrode in the RRDE electrochemical cell. In these experiments the DF concentration was determined from a working curve of the disk limiting current ($i_{d,l}$) vs. concentration. This curve was compiled from measurements on solutions of dimethyl fumarate in the absence of cinnamionitrile and validated with known mixtures of DF and CN.

Results

Dimethyl Fumarate-Cinnamionitrile

Electrochemical generation of the DF radical ion.—RDE voltammograms of DF and CN are illustrated in Fig. 1 and 2. DF (Fig. 1a) exhibits a one-electron reduction with half-wave potential, $E(i = i_{d,l}/2)$ of $-0.8V$ vs. silver reference electrode (Ag-RE) followed by a current dip commencing at approximately $-1.55V$. This dip has been shown to occur at potentials corresponding to formation of the dianion and has been interpreted as resulting from polymerization initiated by that ion (8). Curve b is a ring current (i_r) vs. disk potential (E_d) trace with the ring potential (E_r) maintained at a constant value of $0.0V$ vs. Ag-RE. The ring current increase results from oxidation of the DF radical anion being formed at the disk electrode. At sufficiently negative disk potentials ($E_d > -1.55V$) reduction of DF to the dianion begins and the ring current decreases because of instability of the dianion in solution.

Figure 2 curves a and b, which describe the CN system, are analogous in interpretation to curves a and b in Fig. 1, respectively. The CN dianion participates to a lesser extent in polymerization reactions than does the DF dianion, thus an increase in cathodic current and a reduction wave 1.5 times the height of the first wave results. The half-wave potentials of the one- and two-electron reductions for CN are -1.21 and $-1.83V$, respectively.

Figure 3, curve a, shows a disk current-potential trace of the mixed DF-CN system in $0.15M$ TBAI-DMF. For convenience this voltammogram will be considered as consisting of four regions, as shown. Comparison with Fig. 1 and 2 reveals that reductions occurring in regions 1 and 3 can be ascribed to DF reductions, whereas those in regions 2 and 4 are CN reductions. The DF one-electron reduction limiting current is, within experimental error, unchanged upon addition

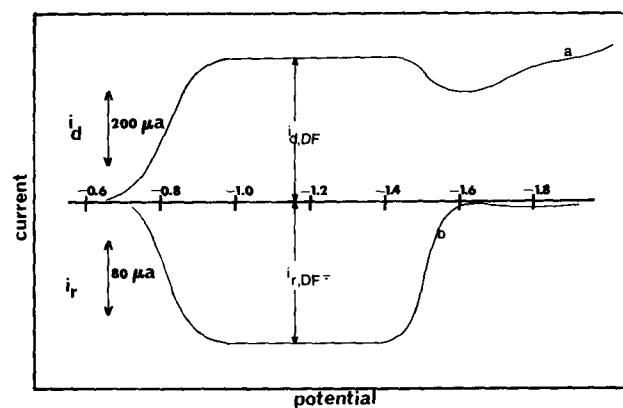


Fig. 1. Dimethyl fumarate (8.2 mM) RRDE voltammograms in $0.15M$ TBAI-DMF solution. $\omega = 47.6 \text{ sec}^{-1}$; (a) i_d vs. E_d and (b) i_r vs. E_d , $E_r = 0.0V$.

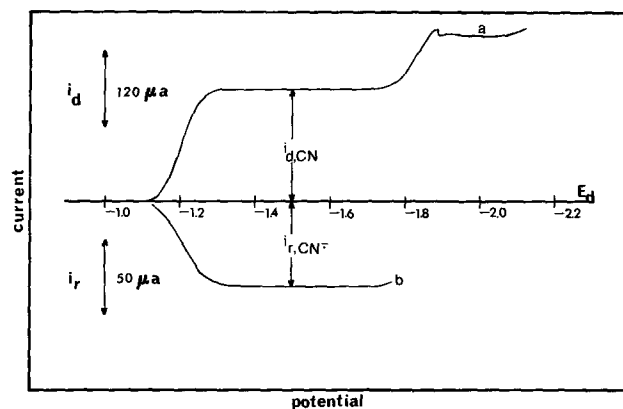


Fig. 2. Cinnamionitrile (3.8 mM) RRDE voltammograms determined at $\omega = 47.6 \text{ sec}^{-1}$; (a) i_d vs. E_d and (b) i_r vs. E_d , $E_r = 0.0V$.

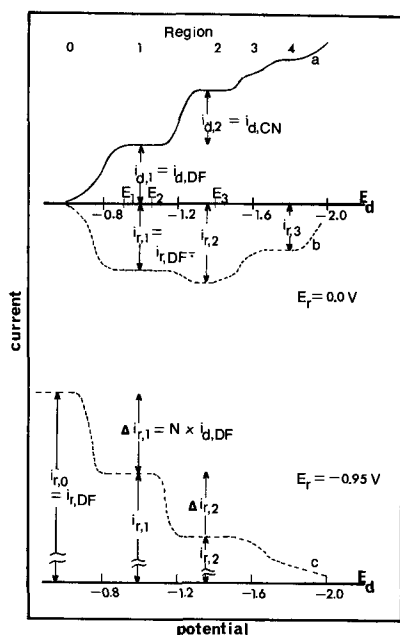


Fig. 3. Typical DF-CN RRDE voltammograms: (a) i_d vs. E_d ; (b) i_r vs. E_d , $E_r = 0.0V$; and (c) i_r vs. E_d , $E_r = -0.95V$.

of CN. Further, the disk limiting current plateau (curve a, region 1), as well as the ring current plateau (curve b, region 1), exhibits essentially zero slope; evidence that processes occurring at the potential denoted E_1 do not differ from those at E_2 . These results differ from those obtained from product analysis after exhaustive electrolysis of diethyl maleate (DEM) (6), where it was found that the products varied as a function of the working electrode potential and it was concluded that the processes occurring on the DEM limiting current plateau are a function of the applied potential in the mixed system.

Determination of N_K as a function of $CONI$ for $i_d < (i_{d,1})_a$, where $(i_{d,1})_a$ is the DF limiting disk current in region 1, resulted in the experimental data shown in Fig. 4 and tabulated in Table I. This trend, N_K increasing with increasing $1-CONI$, is the one reported to be characteristic of the EC dimerization mechanism

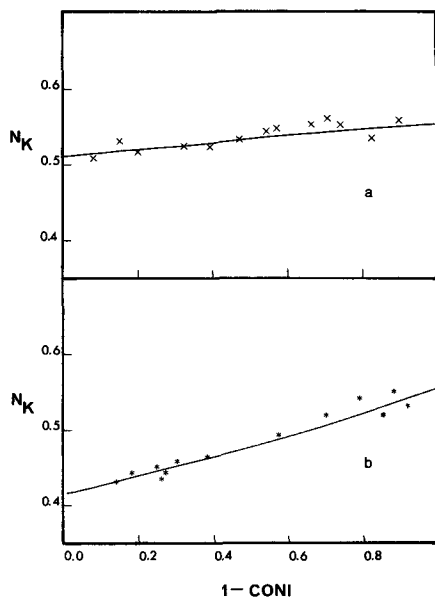


Fig. 4. Dimethyl fumarate collection efficiency (N_K) vs. $1-CONI$ at $\omega = 47.6 \text{ sec}^{-1}$ in the presence of cinnamionitrile: (a) DF = 1.85 mM and CN = 3.85 mM; (b) DF = 7.3 mM and CN = 3.8 mM. Solid lines are theoretical curves corresponding to mechanism I and (a) $XKTC = 0.06$ and (b) $XKTC = 0.25$.

Table I. Collection efficiency (N_K) for dimethyl fumarate reduction as a function of the disk current

Compound (conc-mM)		ω (sec^{-1})	i_r (μA)	i_d (μA)	N_K	$CONI$
Olefin R	Olefin R'					
Dimethyl fumarate (1.85)	Cinnamionitrile (3.85)	47.6	4.4	8.0	0.550	0.080
			8.8	16.4	0.536	0.164
			14.4	26.0	0.554	0.260
			20.8	37.6	0.553	0.376
			24.8	45.6	0.544	0.456
			30.8	59.0	0.522	0.590
			35.6	68.0	0.524	0.680
			40.8	79.0	0.517	0.790
			45.2	89.0	0.508	0.890
			46.8	93.0	0.503	0.930
Dimethyl fumarate (8.19)	Acrylonitrile (200)	98.6	17	42	0.405	0.080
			40	88	0.454	0.169
			70	140	0.500	0.268
			91	186	0.489	0.356
			105	222	0.473	0.425
			137	288	0.476	0.552
			152	336	0.452	0.644
			166	378	0.439	0.724
			179	418	0.428	0.800
			188	452	0.416	0.866
218	518	0.421	0.992			

(Eq. [2]), but not of ECE mechanisms II and III (3). N_K vs. $1-CONI$ theoretical curves for the EC mechanism with $XKTC$ equal to 0.06 and 0.25 are also given in Fig. 4. Calculation of the second-order rate constant for dimerization of DF anion radicals yields a value of $1.1 \pm 0.1 \times 10^2$ liter/mole-sec; the same value is obtained in the absence of CN (1).

A theoretical curve depicting the dependence of N_K on $XKTC$ for the EC (I) mechanism, together with experimental values of N_K measured at potentials on the DF limiting current plateau and determined as functions of the rotation rate, are presented in Fig. 5. It can be seen that the experimental points closely fit the curve generated for the radical ion dimerization mechanism; this provides additional evidence that mechanism I is the path of choice, even in the presence of a second olefin.

These similarities, both qualitative and quantitative, which appear in the RRDE experimental dimethyl fumarate currents measured in the presence and in the absence of cinnamionitrile, are also evident from cyclic voltammetric studies. Figure 6 shows cyclic voltammograms of DF (curve a), CN (curve b), and the mixed DF-CN system (curves c and d). As with the RRDE data, curves c and d can be compared with curves a and b for purposes of assignment. The first reduction of DF exhibits a sizable anodic current on

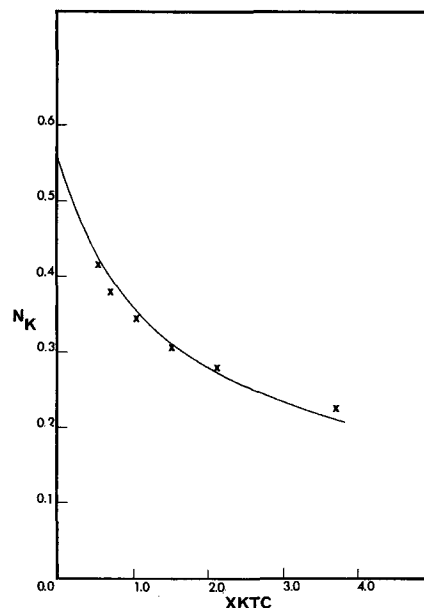


Fig. 5. Dimethyl fumarate (1.8 mM) collection efficiency (N_K) vs. $XKTC$ plot in the presence of cinnamionitrile (3.8 mM). Solid line corresponds to the theoretical curve depicting the behavior of N_K for mechanism I.

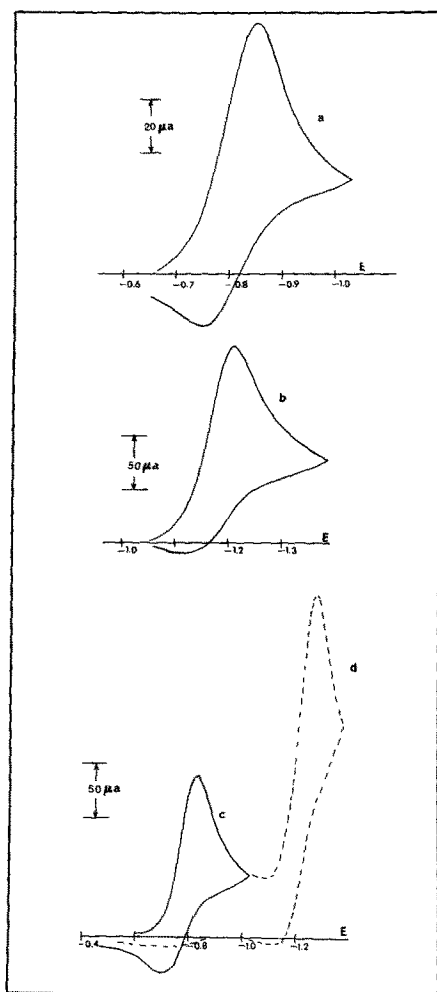


Fig. 6. Cyclic voltammograms recorded at 0.1 V/sec; (a) dimethyl fumarate (3.5 mM); (b) cinnamionitrile (2.6 mM); (c) dimethyl fumarate (1.8 mM), cinnamionitrile (3.8 mM); and (d) same as (c).

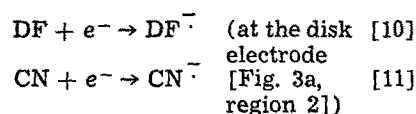
reversal (curve a) even in the presence of cinnamionitrile (curve c). The ratio of peak currents ($i_{p,DF^-}/i_{p,DF}$) and the peak current function ($i_{p,DF}/C_{DF}^0V^{1/2}$) were found to be 0.38 and $96 \mu A/mM V sec^{-1}$, respectively, in the absence, and 0.42 and $99 \mu A/mM V sec^{-1}$ in the presence of CN.

In addition, coulometric analysis at $-1.425V$ vs. SCE, a potential on the DF first reduction current plateau but positive of potentials necessary for reduction of CN, resulted in an n_{app} -value of 0.63 for an equimolar DF-CN solution. The n -value predicted by each of the postulated hydrodimerization mechanisms is one (3). An n_{app} -value less than one results because of the occurrence of polymerization side reactions during the time scale of the coulometric experiment. Coulometry at $-1.625V$ vs. SCE in the absence of cinnamionitrile yielded an n_{app} -value of 0.62. If the ECE mechanism involving reactions [5] and [6] occurred, the n_{app} in

the presence of CN should have been greater than 0.62, and possibly even greater than one.

Simultaneous electrochemical generation of the dimethyl fumarate (DF^-) and cinnamionitrile (CN^-) radical anions.—To determine the extent of cross-coupling arising from a radical ion-radical ion mechanism (Eq. [7]), an examination of the DF-CN mixed system at potentials where both DF and CN undergo reduction to form their respective radical anions was undertaken.

Ring current vs. disk potential voltammograms where $E_r = 0.0V$ (curve b) and $E_r = -0.95$ (curve c) are shown in Fig. 3. Curve b shows the oxidation of electroactive species being formed at the disk during processes shown in Fig. 3a or of any electroactive species being formed from reactions of disk products. From the study of the DF radical anion alone, we know that the ring current in region 1 under the electrode conditions imposed to obtain curve b [denoted $(i_{r,1})_b$] results solely from oxidation of the DF^- radical anion. If there were no interaction in the bulk between DF parent or radical anion and CN parent or radical anion, the measured ring current, $(i_{r,2})_b$, would simply equal the sum, $i_{r,s}$, of the DF and CN ring currents measured independently (i.e., the ring currents i_{r,DF^-} and i_{r,CN^-} illustrated in Fig. 1 and 2, respectively). This is not the case and $i_{r,s}$ is greater than $(i_{r,2})_b$. Typical experimental values are given in Table II. These experimental values were collected at various concentrations and rotation rates. To determine the magnitude of the current contribution to $(i_{r,2})_b$ from oxidations other than that of the DF^- radical anion, the experiment recorded as Fig. 3c was conducted. The ring current $(i_{r,0})_c$, results from reduction of DF at the ring electrode. At disk potentials sufficiently negative (e.g., $E = E_1$, shown in Fig. 3a), DF reduces at the disk and a decrease, $\Delta(i_{r,1})_c$, in the cathodic current measured at the ring electrode results because of a decrease in the amount of DF reaching the ring. This is termed shielding and $\Delta(i_{r,1})_c$ equals N times $(i_{d,1})_a$, the DF disk limiting current shown in Fig. 3a, region 1. The DF^- radical anion is not oxidized at the potential applied at the ring electrode and is, therefore, not detected. At more negative disk potentials (i.e., Fig. 3a, $E = E_3$) both DF and CN are reduced at the disk electrode to the respective radical anions



and a second decrease in the ring current, $(\Delta i_{r,2})_c$ is observed. The measured current, $(i_{r,2})_c$, is the sum of two currents; a cathodic current component resulting from the one-electron reduction of DF and an anodic current component resulting from the oxidation of the CN radical anion

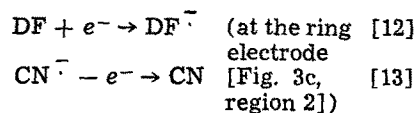


Table II. Disk and ring currents at different values of E_d and E_r^*

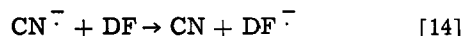
Concentration (mM)		ω	$(i_{d,1})_a$	$(i_{d,2})_a$	$(i_{r,1})_b$	i_{r,CN^-}	$(i_{r,2})_b$	$(i_{r,3})_b$	$(i_{r,s})_b$	$\Delta(i_{r,1})_c$	$\Delta(i_{r,2})_c$
DF	CN										
1.62	2.46	47.6	112	123	55	30	74	47	—	—	68
1.62	2.46	67.2	133	137	66	42	88	54	79	—	78
2.20	4.42	47.6	152	226	69	52	87	65	96	—	92
2.20	4.42	98.6	208	311	98	91	148	108	104	—	158
2.85	3.10	47.6	143	144	68	—	94	52	78	—	63
3.78	3.58	47.6	178	174	84	44	104	60	104	—	82

* DMF solution containing 0.15M TBAI. See Fig. 3 for definition of terms. All currents in microamperes.

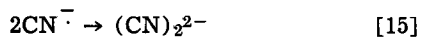
At the applied ring potential, neither the CN parent nor the DF radical are electroactive. The current decrease, $|\Delta(i_{r,2})_c|$, cannot result simply from oxidation of the cinnamionitrile radical anion, since $|\Delta(i_{r,2})_c| > |(i_{r,CN^{\cdot-}})|$, where $i_{r,CN^{\cdot-}}$ is the ring current resulting from oxidation of CN radical anion in the absence of DF (Fig. 2b and Table II). For example, item 6 in

Table II shows that the $CN^{\cdot-}$ ring current (i.e., $|i_{r,CN^{\cdot-}}|$) for $C = 3.58 \text{ mM}$ and $\omega = 47.6 \text{ sec}^{-1}$ in the absence of DF is $44 \mu\text{A}$. The decrease in the ring current, $\Delta(i_{r,2})_c$, is $82 \mu\text{A}$. One would have anticipated a decrease less than or equal to $44 \mu\text{A}$, but not greater than this if

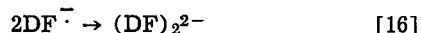
oxidation of $CN^{\cdot-}$ were the only additional process occurring in this region. Radical ion-radical ion cross-coupling could occur but this would decrease the stability of the CN and DF radical anions, leading to a smaller value of $\Delta(i_{r,2})_c$. One must also take into account, however, the occurrence of the electron transfer reaction



In the absence of any other kinetics (e.g., dimerization) contributing to the instability of the species $CN^{\cdot-}$ and DF, the occurrence of reaction [14], in terms of measured ring current at $E_r = -0.95$, would have no observable effect and $\Delta(i_{r,2})_c$ would equal N times $i_{d,CN}$, where $i_{d,CN}$ is the CN disk limiting current. However, in this case both $DF^{\cdot-}$ and $CN^{\cdot-}$ undergo further dimerization reactions ([15] and [16]). Moreover, the rate constant of the CN dimerization reaction



is about eight times larger than that of the DF dimerization reaction (1)



Hence, the effect of reaction [14], if its rate is much larger than that of reaction [15], is to remove a less stable intermediate ($CN^{\cdot-}$) and form a more stable one ($DF^{\cdot-}$) in transit from disk to ring. This leads to a smaller amount of DF available for reduction at the ring and hence a larger-than-expected value of $\Delta(i_{r,2})_c$. This hypothesis, i.e., the effect of the oxidation-reduction represented in Eq. [14], is supported by digital simulation of the RRDE experimental conditions.

This program assumed that the disk electrode was maintained at a potential where reduction of DF (Eq. [10]) and CN (Eq. [11]) to their respective radical anions proceeded at mass transfer controlled rates. The ring electrode was maintained at a potential where mass transfer controlled oxidation of the CN radical anion (Eq. [13]) and reduction of DF parent (Eq. [12]) occurs. Three homogeneous reactions were assumed to occur in the gap region: the radical ion-radical ion dimerizations of DF (Eq. [16]) and CN (Eq. [15]), and the oxidation-reduction reaction represented in Eq. [14]. The rate constants for the DF (1.1×10^2 liters/mole-sec) and CN (8.8×10^2 liters/mole-sec) dimerizations, together with the specific experimental conditions (e.g., concentrations, diffusion constant, etc.), were used to calculate the appropriate XKTC values. The oxidation-reduction reaction was assumed to occur at a diffusion-controlled rate. The simulation output parameters of interest were a dimensionless current parameter proportional to the disk current, and dimensionless current parameters proportional to the currents resulting from reduction of the DF and from oxidation of the CN radical anion at the ring electrode.

The current decrease, $\Delta(i_{r,2})_c$, was found to occur totally from a decline in the cathodic current due to loss of DF parent species in transit to the ring electrode, and with essentially no contribution to the cur-

rent decrease from anodic current resulting from oxidation of the $CN^{\cdot-}$ species. That is, the velocity of the reaction represented in Eq. [14] is of such a high order of magnitude that the CN dimerization does not successfully compete with that reaction and all the $CN^{\cdot-}$ is consumed in reaction [14]. Under these conditions, the simulation accounted for approximately 90% of the experimentally measured current, $\Delta(i_{r,2})_c$.

Cyclic voltammograms of the DF-CN system show no oxidizable species other than the DF and CN radical anions that were observed. In addition a coulometric experiment, in which a solution of DF and CN, in approximately equimolar concentrations, electrolyzed at -1.90 V vs. SCE was carried out. This potential is sufficient to produce both the DF and CN radical anions but not negative enough to produce the DF dianion. An over-all n_{app} -value of 0.81 was obtained. The average n_{app} -value obtained for the CN reduction in the absence of DF was 0.96. Assuming $n = 1.0$ for the CN reduction, the n_{app} -value for DF in the presence of CN is 0.64, essentially the same value obtained in the absence of CN. This value is less than that anticipated if the cross-coupling reaction [Eq. 7] was occurring to an appreciable extent, since this should reduce the extent of polymerization and result in $0.62 < n_{app} < 1.0$. The unchanged n_{app} -value for DF suggests that the DF radical anion is effectively insensitive to the presence of CN parent and the CN radical anion being electrochemically generated. The equivalents vs. time (t) and the current (i) vs. time curves for this experiment are shown in Fig. 7. The presence of two slopes in the equivalent vs. t curve and the break in the i vs. t curve indicate the possible existence of two consecutive reductions as opposed to two simultaneous reductions, although simultaneous reduction of DF and CN is occurring at the potential of the working electrode. The coulometric data can be explained by the occurrence of the oxidation-reduction reaction (Eq. [14]) in

the bulk solution. The $CN^{\cdot-}$ produced at the electrode reacts with DF parent to yield CN parent and $DF^{\cdot-}$. Until a sizable amount of the DF parent has been consumed, the electrolysis is completely characteristic of a DF electrolysis, but at a faster rate than the controlled potential electrolysis of DF alone because of the additional coulometric titration of DF by $CN^{\cdot-}$. Thus, the coulometric, as well as the RRDE, results point to the importance of the oxidation-reduction reaction represented in Eq. [14], in the over-all reaction scheme.

Simultaneous electrochemical generation of the dimethyl fumarate dianion (DF^{2-}) and the cinnamionitrile radical anion.—In the DF-CN mixed system, the current dip anticipated at potentials where formation of the DF dianion commences, Eq. [17] does not occur, but instead additional cathodic current (Fig. 3a, re-

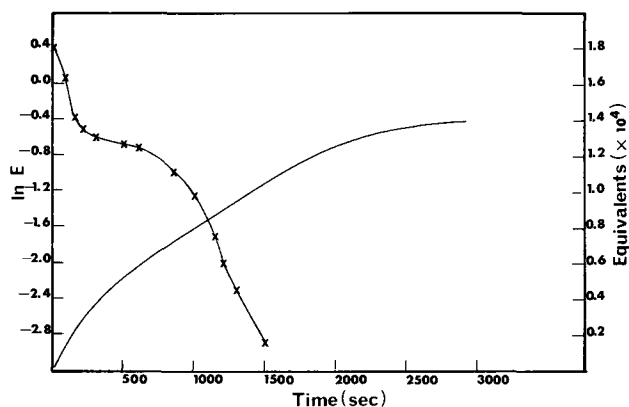
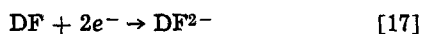
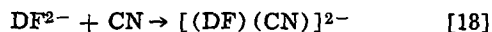


Fig. 7. Dimethyl fumarate (3.3 mM), cinnamionitrile (3.7 mM) equivalents electrolyzed vs. time (t) and current (i) vs. time experimental curves.

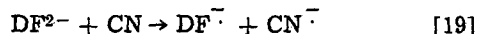
gion 3) results.



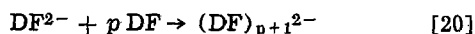
A possible explanation for the increase in cathodic current here is either the formation of an electroactive cross-coupled dimer



or the occurrence of the redox reaction



Either [18] or [19] would be expected to compete with polymerization of DF



resulting in increased currents.

Dimethyl Fumarate-Acrylonitrile

Dimethyl fumarate in the presence of acrylonitrile (AN).—Figure 8 illustrates typical disk current-potential (curves a, b, and c) as well as ring current-disk potential (curves d and e) scans obtained at constant ring potential ($E_r = 0.0V$ vs. Ag-RE) for DF in the absence (curves a, b, and d) or presence (curves c and e) of AN. The significance of curve a has been explained. Curve b is a voltammogram of a quiescent solution ($\omega = 0$). Curve c is a repeat of curve a following the addition of 0.2M AN. Curves d and e represent the ring current recorded as a function of disk potential while the disk electrode is simultaneously undergoing the processes shown in curves a and c, respectively. Values of N_K measured in the absence and in the presence of AN are given in Table III. In approximately equimolar concentrations there is no apparent perturbation. When AN is present in large excess, the rate of decay of the dimethyl fumarate radical is seen to increase as a function of DF concentration, but not to the extent anticipated were the ECE mechanism a major path. The N_K vs. $1-\text{CONI}$ plots for $i_d < i_{d,DF}$ are consistent with the trend predicted by digital simulation techniques for the EC dimerization (mechanism I) being the primary reaction path (Fig. 9).

Cyclic voltammetric studies reveal that the $\text{DF}^{\cdot-}$ has a measurable lifetime even in the presence of 0.2M AN

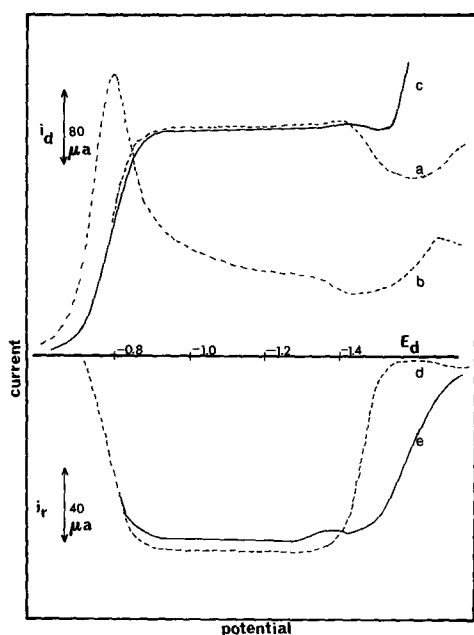


Fig. 8. Dimethyl fumarate (4.8 mM) RRDE voltammograms; (a) i_d vs. E_d , $\omega = 47.6 \text{ sec}^{-1}$; (b) i_d vs. E_d , $\omega = 0$; (c) i_d vs. E_d , $\omega = 47.6 \text{ sec}^{-1}$, AN (0.2M) present; (d) i_r vs. E_d , $E_r = 0.0V$, $\omega = 47.6 \text{ sec}^{-1}$; and (e) i_r vs. E_d , $E_r = 0.0V$, $\omega = 47.6 \text{ sec}^{-1}$; 0.2M AN present.

Table III. RRDE collection efficiency data for the dimethyl fumarate radical anion

Concentration (mM)		ω (sec^{-1})	N_K
DF	AN		
4.0	0	47.6	0.480
		67.2	0.501
4.0	~4	47.6	0.475
		67.2	0.500
4.8	0	47.6	0.436
4.8	200	47.6	0.422
8.2	0	47.6	0.394
8.2	200	47.6	0.356

(Fig. 10). The $(E_p)_c$ remained unchanged but $(i_p)_c$ exhibited a 5% decrease.

Controlled potential coulometric experiments employing potentials sufficient to reduce DF to the radical anion but insufficient to reduce AN were undertaken. The results are presented in Table IV. The n_{app} -values given for a single solution were obtained by the addi-

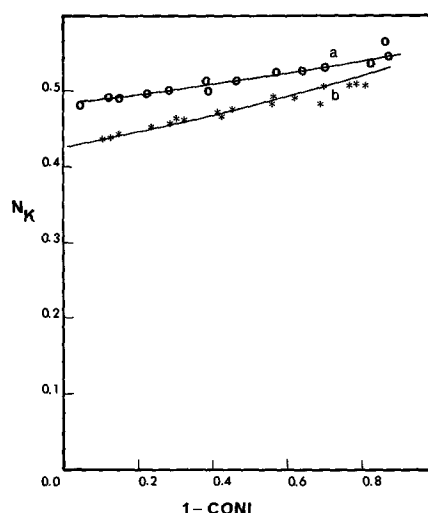


Fig. 9. Collection efficiency (N_K) vs. $1-\text{CONI}$ at $\omega = 47.6 \text{ sec}^{-1}$ for 4.0 mM (o) and 4.8 mM (*) dimethyl fumarate solution in the presence of 0.2M acrylonitrile. Solid lines are theoretical curves corresponding to mechanism I and $XKTC =$ (a) 0.12 and (b) 0.25.

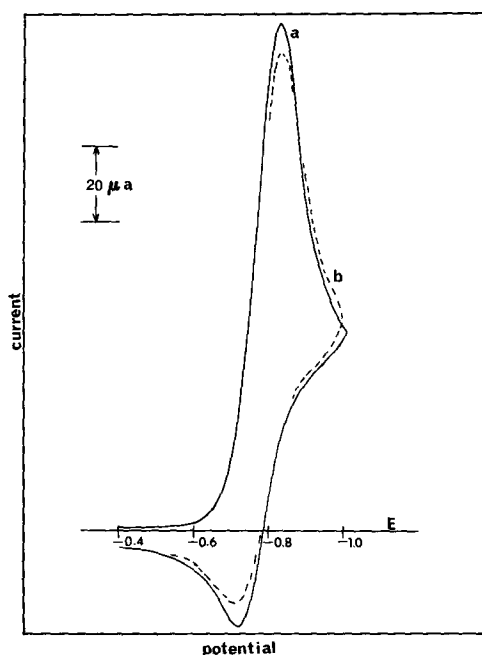


Fig. 10. Dimethyl fumarate (4.8 mM) cyclic voltammograms recorded at 0.1 V/sec; (a) acrylonitrile absent, (b) acrylonitrile (0.2M) present.

Table IV. Coulometric results for mixtures of dimethyl fumarate and acrylonitrile^a

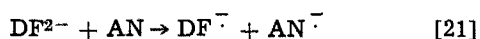
Solution	E (vs. SCE)	Moles present		n_{app} -value
		DF ($\times 10^4$)	AN	
1	-1.625	0.66	0	0.62
2	-1.450	1.10	Equimolar	0.62
	-1.600	0.98	Equimolar	0.76
	-1.525	1.07	Equimolar	0.78
	-1.450	1.02	Equimolar	0.79
3	-1.750	1.09	Large excess	0.77
	-1.550	1.00	Large excess	0.80

^a The solution was 0.15M TBAI in DMF and the working electrode was Pt.

tion of a DF sample following exhaustive electrolysis of the previous sample. The average n_{app} was 0.78. Thus, the presence of AN does perturb, on the coulometric time scale, the following reaction of the DF radical. Whether this perturbation in the n_{app} results from some cross-coupling or from interference by the AN in some other manner with the reactions which result in the n_{app} -value less than one in the absence of AN (e.g., polymerization), it is difficult to determine with the experimental evidence at hand. Were n_{app} greater than one, cross-coupling by an ECE path would have been probable.

Electrochemical generation of the DF dianion.—The DF-AN system differs from the DF-CN system in that formation of the DF dianion occurs prior to the first reduction step of the R' species (AN), as can be seen by comparing curve a to c (Fig. 8). Further, the DF radical anion is detected by the ring electrode over a greater potential range in the presence of AN (Fig. 8e) when compared with the potential range for detection of the radical anion in the absence of AN (Fig.

8d). In other words, in the presence of AN, DF⁻ is being generated in a potential region normally associated with formation of the DF dianion. The anodic current measured at the ring electrode (curve e) is now seen to decrease at disk potentials corresponding to reduction of AN (curve c) at potentials more negative than those necessary to form the DF dianion (curve a). A possible explanation is the occurrence of a rapid oxidation-reduction reaction consuming dimethyl fumarate dianion and acrylonitrile parent and yielding the radical anions of DF and AN



Thus, the amount of DF radical anion reaching the ring electrode remains relatively unchanged up to disk potentials corresponding to reduction of AN. Other possible explanations of this occurrence include the stabilization of the DF dianion by AN toward fragmentation or polymerization. However, no oxida-

tions other than the oxidation of DF⁻ were observed on varying the ring potential in RRDE voltammetry or on reversal in cyclic voltammetric experiments. In addition, the fact that the ring current does not change significantly at the more negative potentials is another indication that the identity of the species in transit to the ring is not a function of potential. Another possible explanation for this occurrence is the stabilization of the DF parent toward acceptance of the second electron. This, too, however, does not seem likely, since one would likewise expect stabilization of the DF parent species to acceptance of the first electron, and this is not observed.

Discussion

The mixed system results indicate that the mechanism which serves as the primary route for the disappearance of the dimethyl fumarate radical anion is not altered appreciably by the presence of a second olefin which is itself not electroactive at potentials

sufficient to produce the DF radical anion under the conditions of our experiment. Further, the velocity of the radical decay remains, within experimental error, unchanged from the velocity measured in the absence of the second olefin when the second olefin is present in amounts about equal to that of DF; when AN is

present in large excess, DF⁻ decay increases to some extent. Considering the arguments presented, these RRDE results confirm the conclusion (1) that the major pathway in the electrodimmerization of dimethyl fumarate in anhydrous DMF is the EC dimerization path (Eq. [16]).

The interpretation of the processes following the first DF reduction wave is more difficult. In the case of the DF-CN system, the CN one-electron reduction occurs prior to the DF two-electron reduction and appears unperturbed up to potentials necessary for formation of the dimethyl fumarate dianion. Analysis of the ring currents at various ring electrode potentials

reveals that the stability of the CN⁻ is decreased from its value in the absence of DF. This additional instability is attributed mainly to the electron transfer reaction between DF parent and CN radical anion, forming DF radical anion and CN parent. This hypothesis is supported by results of controlled potential coulometry conducted at electrode potentials where the radical anions of both DF and CN are formed which qualitatively indicate the occurrence of two independent reactions and quantitatively indicate little or no change in the coulometric n_{app} -value for the reduction of DF.

In the DF-AN system, the reduction of DF to the dianion occurs prior to reduction of AN. Thus, simultaneous generation of the DF and AN radical anions is not possible. The DF current-potential curve does not exhibit a dip at the second reduction potentials when AN is present. Further, the ring current resulting from oxidation of the DF radical anion extends into the region of disk potential normally associated with formation of the DF dianion and falls off only when the AN reduction commences. Here again the possibility of a redox reaction, this time involving the DF dianion, seems likely. That the ring current plateau does not change significantly at these potentials from its value in the disk potential region where formation of the DF radical anion occurs would lead one to conclude that the DF radical anion is the electroactive species being produced.

It is necessary to compare the results found here with previous studies of cross-coupling (4-7, 13). Our findings demonstrate that the DF-CN and DF-AN systems do not follow the path where cross-coupling occurs when the radical ion of only one species is produced in the presence of an equimolar concentration of the second olefin. For DF-AN concentration ratios of approximately 1 to 40 and 1 to 25, a slightly accelerated decay of the DF radical ion is observed, perhaps due to cross-coupling. Certainly, the cross-coupling reaction will be favored by very high concentrations of the second olefin. When radical ions of both reactants are produced, then the electron transfer reaction must be considered in addition to, or as a path to, the cross-coupling reaction. Baizer and co-workers (6) studied the cross-coupling reaction of the *cis*-isomer diethyl maleate (DEM) and AN and showed appreciable cross-coupled product formation at potentials where only the DEM radical ion is produced. Baizer also found coupling of DEF with AN under conditions of a very high ratio of AN to DEF (DEF added dropwise to AN containing tetraethylammonium *p*-toluene-sulfonate and a small amount of water) (4). Baizer and Chruma (14) have recently repeated this experiment and found substantial quantities of cross-coupled product (about one-fifth of the amount of the hydrodimer of DEF, tetraethylbutane tetracarboxylate) and no AN reduction products. The amount of cross-coupled product when DEM and AN are used

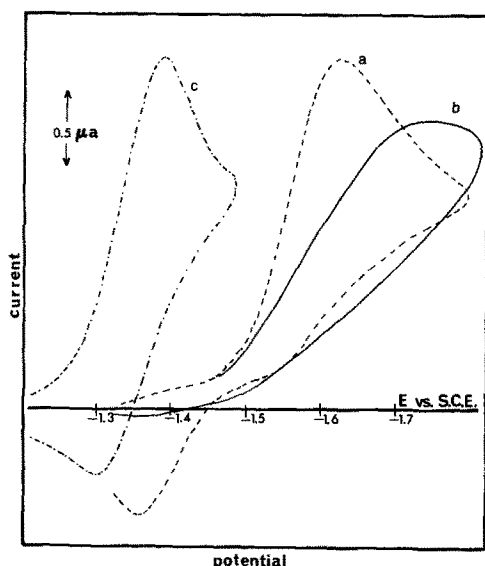


Fig. 11. Cyclic voltammograms at 200 mV/sec on a Pt working electrode: (a) diethyl maleate (3.9 mM), TBAP (0.15M), DMF; (b) diethyl maleate (3.9 mM) after the addition of AN (0.2M); (c) dimethyl fumarate (3.7 mM) in the presence of diethyl maleate and AN.

appears higher (6). On preliminary consideration, one would predict that the DEF-AN and the DEM-AN reactions would follow identical pathways, since DEF and DEM ultimately produce the same radical anion on reduction (15). However, recent results in our laboratory have shown that the behavior of DEM is very different from that of DEF. DEM is more difficult to reduce than its *trans*-isomer form, DEF; in addition, the diethyl maleate radical anion undergoes fast isomerization to form the diethyl fumarate radical and it appears that the direction of the isomerization lies exclusively toward the *trans* form (16, 17). Figure 11 is a cyclic voltammogram of a DEM-TBAP-DMF solution illustrating this isomerization. Following addition of excess AN, the wave shape becomes altered and no anodic current is observed on reversal (Fig. 11b). However, a cyclic voltammogram of the solution taken after the addition of dimethyl fumarate shows that the DF wave shape is qualitatively unaltered from that reported (1) and that anodic current is observed on reversal. One must conclude on the basis of this series of voltammograms that the *cis*-radical anion reacts with AN prior to isomerization, whereas the *trans*-radical anion is more stable with respect to re-

action with AN. Cross-coupling of diethyl maleate and AN at potentials where only the diethyl maleate is electroactive and indeed, the occurrence of increasingly greater amounts of cross-coupled product with increasingly negative electrode potential when electrolyzing a mixture of DEM and DEF in the presence of AN can be explained in the light of the above observations. Further experiments are currently under way to uncover the nature of the difference between the reactivity of the *trans*- and *cis*-isomers. In conclusion these experiments demonstrate that cross-coupling will compete with dimerization only when the ratio of the second olefin (e.g., AN) to the reduced olefin (DEF) is very large, and that cross-coupling can probably be carried out more efficiently by reducing both reactants (7).

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