# Electrohydrodimerization Reactions

## II. Rotating Ring-Disk Electrode, Voltammetric and Coulometric Studies of Dimethyl Fumarate, Cinnamonitrile, and Fumaronitrile

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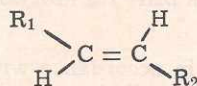*Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712*

## ABSTRACT

The reduction of the activated olefins dimethyl fumarate, cinnamonitrile, and fumaronitrile in tetra-n-butylammonium iodide-dimethylformamide solutions at a platinum electrode has been studied by rotating ring-disk electrode (RRDE) voltammetry, cyclic voltammetry, and coulometry. The results indicate that each compound undergoes a one-electron reduction to the anion radical which then undergoes a dimerization reaction. Rate constants for this dimerization reaction were found to be 110 (dimethyl fumarate), 880 (cinnamonitrile), and $7 \times 10^5$ (fumaronitrile) 1/mole-sec. Evidence of some bulk polymerization reaction was obtained from the coulometric results.

The general equation for electrohydrodimerization (or electrolytic reductive coupling) of an activated olefin, R, is shown in Eq. [1]

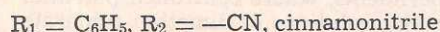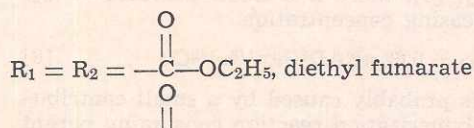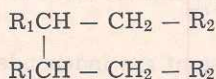$$2R + 2e + 2H^+ \rightarrow R_2H_2 \qquad [1]$$

The first paper in this series (1) dealt with the determination of the mechanism of this reaction for diethyl fumarate reduction in dimethylformamide (DMF) solutions. Results of

R (parent)                     $R_2H_2$ (hydrodimer)

$$\begin{array}{c} R_1 \\ \quad \diagdown \\ \quad\quad C = C \\ H \diagup \quad\quad \diagdown R_2 \end{array} \qquad \begin{array}{c} R_1CH - CH_2 - R_2 \\ | \\ R_1CH - CH_2 - R_2 \end{array}$$

$R_1 = R_2 = -\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5$, diethyl fumarate

$R_1 = R_2 = -\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$, dimethyl fumarate

$R_1 = C_6H_5$, $R_2 = -CN$, cinnamonitrile

$R_1 = R_2 = -CN$, fumaronitrile

double potential-step chronoamperometry experiments showed that the reduction proceeded by coupling of the electrogenerated radical anions (mechanisms I)

$$R + e \rightarrow R^- \qquad [2]$$

$$2R^- \overset{k_2}{\longrightarrow} R_2^{2-} \qquad [3]$$

rather than by reaction of the radical anion with parent and subsequent electron transfer (mechanism II)

$$R^- + R \overset{k_{2'}}{\longrightarrow} R_2^- \qquad [4]$$

$$R_2^- + e \rightarrow R_2^{2-} \qquad [5]$$
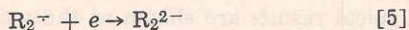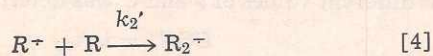
[and variations of this mechanism (2)] or initial formation of a dianion (mechanism III)

$$R + 2e \rightarrow R^{2-} \qquad [6]$$

$$R^{2-} + R \overset{k_{2''}}{\longrightarrow} R_2^{2-} \qquad [7]$$
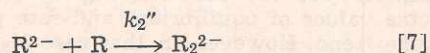
We assume throughout that protonation can occur at any stage of the reaction sequence, ultimately leading to $R_2H_2$, but that the protonation steps are not rate determining.

* Electrochemical Society Active Member.
  Key words: reductive coupling, electrochemical dimerizations, rotating disk electrode, coulometry, cyclic voltammetry.

In this paper we extend the study of the mechanism of electrohydrodimerization to the compounds dimethyl fumarate, cinnamonitrile, and fumaronitrile, with special emphasis on the application of rotating ring-disk electrode (RRDE) techniques, which have been shown to be particularly useful in distinguishing among mechanisms I, II, and III (2). Previous studies of these compounds [(3-6) and references therein] have verified that hydrodimers are the major products of the electroreduction. Since the lifetimes of the electrogenerated intermediates for these compounds span the range of millisecond to second, these studies also provide a useful test of the application of RRDE techniques over a wide range of reaction rates.

## Experimental

*Reagents.*—Dimethylformamide (DMF), obtained from Baker Chemical Company, was purified by the method of Faulkner and Bard (7) and was stored under He. Solvent purity was ascertained by voltammetric analysis of a DMF solution of tetrabutylammonium iodide (TBAI). Southwestern Analytical Chemical's polarographic grade TBAI was used as received. Fumaronitrile (Aldrich Chemical Company) was sublimed twice prior to use. Dimethyl fumarate, twice sublimed, and cinnamonitrile, used as received, were obtained from K. and K. Laboratories, Inc. All reagents were stored over Drierite.

*Apparatus.*—A Model 170 Electrochemistry System (Princeton Applied Research Corporation, Princeton, New Jersey) was employed throughout the study. A regulated power supply was used as a constant current source. The current was determined by measuring the potential developed across a 10 kohm ($\pm$ 0.025%) resistor with a digital multimeter. The electrochemical cell and dispensing vessel are shown in Fig. 1. 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 N-value for this electrode was determined from the geometry and by experimental measurements on electrochemical systems unperturbed by reactions of the disk generated species (e.g., azobenzene) and was found to be 0.555 $\pm$ 0.001. The electrode was rotated using a Motomatic Model E-550 motor and controller (Electrocraft Corporation, Hopkins, Minnesota). Electrical contact to the shaft was made using two sets of silver graphalloy brush and leaf assemblies. A platinum wire spiral served as the auxiliary electrode. The reference electrode was either a saturated calomel electrode (SCE) (coulometric experiments only) or a silver wire spiral (Ag-RE). The working electrode in the coulometric experiments was
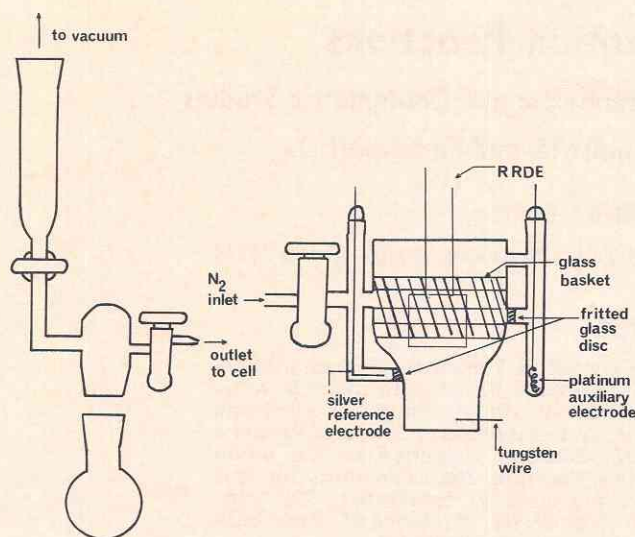
Fig. 1. Electrochemical cell and dispensing vessel

**Table I. Typical rotating-disk electrode data for the first reduction waves[a]**

| Concentration, $C$ (mM) | Limiting disk current, $i_{d,1}$ ($\mu$A) | Rotation rate, $\omega$ (sec$^{-1}$) | $i_{d,1}/\omega^{1/2}C$ |
|---|---|---|---|
| **A. Dimethyl fumarate** | | | |
| 3.00 | 149 | 47.6 | 7.19 |
| 3.30 | 158 | 47.6 | 6.96 |
| 3.54 | 168 | 47.6 | 6.90 |
| 4.45 | 207 | 47.6 | 6.75 |
| 6.20 | 213 | 27.0 | 6.61 |
|      | 276 | 47.6 | 6.45 |
|      | 330 | 67.2 | 6.48 |
|      | 398 | 98.6 | 6.48 |
|      | 491 | 149 | 6.48 |
|      | 568 | 202 | 6.45 |
| **B. Cinnamonitrile** | | | |
| 1.25 | 58.0 | 47.6 | 6.72 |
| 2.12 | 99.0 | 47.6 | 6.77 |
| 2.50 | 122 | 47.6 | 7.07 |
|      | 140 | 67.2 | 6.83 |
|      | 167 | 98.6 | 6.75 |
|      | 198 | 149 | 6.49 |
|      | 227 | 202 | 6.39 |
|      | 252 | 253 | 6.34 |
|      | 276 | 305 | 6.32 |
| 3.13 | 138 | 47.6 | 6.39 |
| 3.26 | 153 | 47.6 | 6.80 |
| 11.3 | 497 | 47.6 | 6.38 |
| **C. Fumaronitrile** | | | |
| 0.42 | 29.4 | 202 | 4.93 |
| 0.92 | 63.3 | 202 | 4.84 |
| 1.92 | 125 | 202 | 4.59 |
| 2.18 | 67 | 47.6 | 4.45 |
|      | 81 | 67.2 | 4.53 |
|      | 98 | 98.6 | 4.54 |
|      | 119 | 149 | 4.47 |
|      | 130 | 179 | 4.44 |
|      | 136 | 202 | 4.39 |
| 3.18 | 191 | 202 | 4.24 |
| 3.94 | 226 | 202 | 4.04 |

[a] The solutions were all 0.1M TBAI in DMF. The RDE radius was 0.187 cm.

either a mercury pool or a platinum wire gauze. Cyclic voltammograms were recorded on a Tektronix, Type 564 storage oscilloscope. All experiments were carried out at 24°C. Dissolved oxygen was removed from the solution by the freeze-pump-thaw technique. The dispensing vessel was then brought to atmospheric pressure with He. The solution was transferred to the electrochemical cell, which was continually being flushed with $N_2$, by the introduction of positive $N_2$ pressure. It was convenient to fill each compartment of the electrochemical cell separately. All experiments were conducted with a continuous stream of $N_2$ flowing over the solution surface. Impurities in the cinnamonitrile appeared as a irreversible reduction wave at the foot of the main cinnamonitrile reduction wave. This small wave was removed by carrying out exhaustive electrolysis at a potential on the plateau of this wave. The cinnamonitrile reduction current, after electrolysis of the impurity, equaled, within experimental error, the sum of the impurity and cinnamonitrile reduction currents prior to the pre-electrolysis. Limiting disk current ($i_{d,1}$) rotation rate ($\omega$) relationships were determined at several different potentials on the limiting current plateau. These $i_{d,1}$-values were determined both from voltammograms obtained at scan rates of 5 and 10 mV/sec and from currents obtained by stepping to potentials corresponding to the limiting current region. In all collection efficiency measurements a constant current was applied to the disk while the ring was maintained at a controlled potential. The ring was adjusted to a potential such that the ring current ($i_r$) was zero at the current sensitivity to be used in the measurement of $i_r$, when the disk current ($i_d$) equaled zero; this potential was always at a value where any radical anion being produced at the disk would undergo mass transfer controlled electrochemical oxidation at the ring. This procedure for measuring $i_r$ allowed the accurate determination of even very small values of $i_r$, and is most useful for studying short-lived disk generated species.

## Results

*Dimethyl fumarate.*—Rotating disk electrode (RDE) voltammograms ($i_d$ *vs.* $E_d$) taken at slow scan rates (5-10 mV/sec) for millimolar solutions of dimethyl fumarate in DMF-0.1M TBAI at $\omega$-values of 47.6-200 sec$^{-1}$ exhibit a reduction wave with $E_{1/2} = -0.75$V *vs.* Ag-RE followed by a dip in $i_d$ after development of a well-developed plateau. This dip develops into a second reduction wave on addition of water (6). The discussion of all results here are limited to processes occurring at the first reduction wave. Values of the Levich constant, $i_{d,1}/\omega^{1/2}C$, for different values of $\omega$ and $C$ are given in Table I. Although the values of the Levich

constant are independent of $\omega$, in accordance with the Levich equation [8], there is a small decrease of $i_{d,1}/\omega^{1/2}C$ with increasing concentration.

$$i_{d,1} = 0.62\, nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C \qquad [8]$$

This decrease is probably caused by a small contribution from a polymerization reaction consuming parent material. This polymerization is more strongly reflected in coulometric experiments, where controlled potential reduction of millimolar solutions of dimethyl fumarate at potentials on the plateau of the first reduction wave ($-1.625$V *vs.* SCE) yields an $n_{app}$ value ($n_{app}$ = number of faradays per mole of electroactive substance) of 0.62. Similar $n_{app}$ values were found for diethyl fumarate (1).

To obtain information about the mechanism of the reaction, RRDE experiments were undertaken, and the variation of the kinetic collection efficiency, $N_K$, where

$$N_K = |i_r/i_d| \qquad [9]$$

$i_r$ and $i_d$ are the ring and disk currents, respectively, as a function of the disk current, expressed as *CONI*, at different values of $\omega$ and $C$ was determined

$$CONI = i_d/i_{d,1} \qquad [10]$$

Typical results are shown as the points in Fig. 2. The trend of $N_K$ with *CONI*, i.e., $N_K$ decreasing with increasing *CONI*, has been shown to be characteristic of mechanism I (given in Eq. [2] and [3]) and excludes mechanisms II (it is possible that a nuance of mechanism II [see (2) case IId, Fig. 6] could exhibit, for some values of equilibrium and rate parameters, this same trend. However, in that case $N_K$ would vary as the square of the bulk concentration and the $N_K$ *vs.* 1-*CONI* trends could also be different for different concentrations of parent R), and III (2), as well as first order decomposition of R$^{\overline{\cdot}}$. Note these other reactions of R$^{\overline{\cdot}}$ may be occurring in parallel with the dimerization of R$^{\overline{\cdot}}$ (Eq. [3]), but dimerization must be the predominant pathway. The experimental points
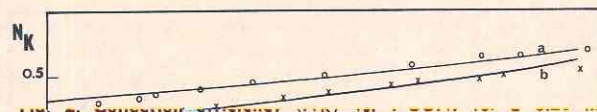
dimethyl fumarate solution at rotation rates ($\omega$) of 67.2 (o) and 47.6 (x) radians sec$^{-1}$. Solid lines are theoretical curves corresponding to mechanism I and (a) $XKTC = 0.16$ and (b) $XKTC = 0.25$, where $XKTC = (0.51)^{-2/3}\nu^{1/3}D^{-1/3}C\omega^{-1}k_2$.

were fit by simulating mechanism I for different values of $XKTC$, the dimensionless simulation

$$XKTC = (0.51)^{-2/3}\nu^{1/3}D^{-1/3}\omega^{-1}k_2C \qquad [11]$$

variable defined in Eq. [11]. For example, the line in Fig. 2 corresponds to an $XKTC$ value of 0.25. Values of $XKTC$ obtained by this method at different $C$ and $\omega$ are given in Table II, along with the normalized parameter $(XKTC)(\omega)/C$. Values of $k_2$ were calculated obtained from this data is $1.1 \pm 0.1 \times 10^2$ liters/mole-sec. This value can be compared to the dimerization

**Table II. Calculated rate constants for reactions of radical anions obtained from RRDE results[a]**

| $\omega$ (sec-1) | Concentration, $C$ (mM) | $XKTC$[b] | $\dfrac{(XKTC)(\omega)}{C}$ [b] | $k_2$ (liter/mole-sec)[c] | $k_2'$ (liter/mole-sec)[d] |
|---|---|---|---|---|---|
| A. Dimethyl fumarate | | | | | |
| 47.6 | 3.54 | 0.10 | $1.34 \times 10^3$ | $0.9 \times 10^2$ | |
| | 4.45 | 0.17 | 1.82 | 1.2 | |
| | 6.20 | 0.25 | 1.92 | 1.3 | |
| 67.2 | 3.54 | 0.06 | 1.14 | 0.8 | |
| | 6.20 | 0.16 | 1.73 | 1.1 | |
| 98.6 | 4.45 | 0.08 | 1.77 | 1.2 | |
| | 6.20 | 0.10 | 1.59 | 1.1 | |
| | | Avg. | $1.59 \times 10^3$ | $1.1 \times 10^2$ | |
| B. Cinnamonitrile | | | | | |
| | 3.13 | 0.88 | 1.34 | 8.9 | |
| | 3.26 | 0.91 | 1.33 | 8.8 | |
| | 3.67 | 1.01 | 1.33 | 8.8 | |
| | 7.46 | 2.25 | 1.44 | 9.6 | $0.6 \times 10^2$ |
| | 11.3 | 2.95 | 1.24 | 8.2 | $0.6 \times 10^2$ |
| 67.2 | 1.25 | 0.25 | 1.33 | 8.8 | |
| | 2.12 | 0.41 | 1.29 | 8.6 | |
| | 3.13 | 0.58 | 1.24 | 8.2 | |
| | 3.26 | 0.69 | 1.33 | 8.8 | |
| 98.6 | 1.25 | 0.25 | 1.33 | 8.8 | |
| | 2.12 | 0.27 | 1.26 | 8.3 | |
| | 3.13 | 0.46 | 1.45 | 9.6 | |
| | 3.26 | 0.47 | 1.42 | 9.4 | |
| | 3.67 | 0.46 | 1.24 | 8.2 | |
| | 4.72 | 0.61 | 1.27 | 8.4 | |
| | 5.38 | 0.77 | 1.41 | 9.4 | |
| | | Avg. | $1.33 \times 10^4$ | $8.8 \times 10^2$ | $0.6 \times 10$ |
| C. Fumaronitrile | | | | | |
| 201 | 0.42 | 24.5 | $1.2 \times 10^7$ | $7 \times 10^5$ | $10 \times 10^3$ |
| | 0.42 | 28.5 | 1.4 | 8 | 10 |
| | 3.18 | 160 | 1.0 | 5 | 2 |
| | 3.94 | 150 | 0.8 | 4 | 3 |
| | | | $1.1 \times 10^7$ | $6 \times 10^5$ | $6 \times 10^3$ |

[a] The solutions were all 0.1M TBAI in DMF. The RRDE had $r_1 = 0.187$ cm, $r_2 = 0.200$ cm, and $r_3 = 0.332$ cm.
[b] $XKTC = (0.51)^{-2/3}\nu^{1/3}D^{-1/3}C\omega^{-1}k_2$, $\nu = 0.00849$ cm$^2$/sec.
[c] For reaction $2R^- \rightarrow R^{2-}$.
[d] For reaction $R^- + R \rightarrow R_2^-$.

rate found previously for diethyl fumarate by double potential step chronoamperometry of about 34 liters/mole-sec.

*Cinnamonitrile.*—The rotating disk electrode voltammetry with $CONI$ were also carried out; typical results are shown in Fig. 3. Again the behavior is characteristic of mechanism I, and best fit values of $XKTC$ and $k_2$ are listed in Table II. The average value of $k_2$ for dimerization of cinnamonitrile was $8.8 \pm 0.1 \times 10^2$ liter/mole-sec. For concentrations of cinnamonitrile of 7.5 mM or higher a better fit to the experimental data was obtained by carrying out the simulation with the inclusion of some reaction of $R^-$ by the reaction of Eq. [4]. Simulations of this scheme, simultaneous occurrence of mechanisms I and IIa (2), assuming only $R^-$ was oxidized at the ring, gave the same $k_2$ values as found at lower concentrations and $k_2'$ values of $0.6 \times 10^2$ liters/mole-sec.

*Fumaronitrile.*—RDE voltammetry of fumaronitrile duction wave is expected. Values of the Levich constant listed in Table I are quite constant with $\omega$, but show a strong dependence on concentration. The coulometric $n_{app}$ values for reduction of 1 to 3 mM solutions at the first reduction wave are $0.44 \pm 0.02$. These results suggest some polymerization of fumaronitrile occurs. The Levich constant for fumaronitrile is smaller than expected, based on the values for dimethyl fumarate and cinnamonitrile. Similar results this result could be ascribed to polymerization, the constancy with $\omega$ and with time, as well as the trend with $C$ lead to an explanation based on some fumaronitrile in a dimeric form in rapid equilibrium with monomeric form. This point will be discussed more fully in a later communication.

The anion radical of fumaronitrile is the least stable of the compounds studied here. For example, no
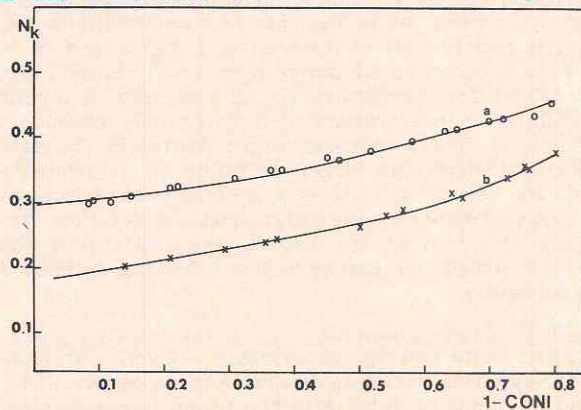


Fig. 3. Collection efficiency ($N_K$) vs. 1-$CONI$ at $\omega = 47.6$ radian sec$^{-1}$ for a 3.00 (o) and 7.46 (x) mM cinnamonitrile solution. Solid lines are theoretical curves corresponding to mechanism I and (a) $XKTC = 0.88$ and (b) $XKTC = 2.25$.

Table III. Cyclic voltammetric data and calculated rate constants[a]

| Scan rate $v$ (V/sec) | $\dfrac{i_{pc}[b]}{v^{1/2}C}$ | $\dfrac{i_{pa}}{i_{pc}}$ | $\tau^c$ | $\omega^d$ | $k_2^e$ (liter/mole-sec) |
|---|---|---|---|---|---|
| **A. Dimethyl fumarate (C = 4.46 mM)** | | | | | |
| 0.05 | 91 | 0.33 | | | |
| 0.10 | 98 | 0.39 | | | |
| 0.20 | 100 | 0.43 | | | |
| 0.50 | 99 | 0.58 | 0.68 | 2.4 | $1.9 \times 10^3$ |
| 1.00 | 97 | 0.74 | 0.34 | 0.84 | $1.3 \times 10^3$ |
| 2.00 | 100 | 0.78 | 0.17 | 0.60 | $1.9 \times 10^3$ |
| 5.00 | 91 | 0.98 | | | |
| 10.0 | 86 | 1.02 | | | |
| 20.0 | 82 | 1.04 | | | |
| **(C = 6.20 mM)** | | | | | |
| 0.05 | 90 | 0.35 | | | |
| 0.10 | 95 | 0.38 | | | |
| 0.20 | 97 | 0.43 | | | |
| 0.50 | 101 | 0.54 | 0.68 | 4.2 | $1.8 \times 10^3$ |
| 1.0 | 90 | 0.72 | 0.34 | 2.1 | $1.1 \times 10^3$ |
| 2.0 | 77 | 0.76 | 0.17 | 1.0 | $1.1 \times 10^3$ |
| 5.0 | 91 | 0.89 | 0.25 | 0.42 | $1.4 \times 10^3$ |
| | | | | Avg. | $1.6 \times 10^3$ |
| **B. Cinnamonitrile (C = 3.46 mM)** | | | | | |
| 0.05 | 94 | 0.31 | | | |
| 0.10 | 93 | 0.33 | | | |
| 0.20 | 91 | 0.39 | | | |
| 0.50 | 89 | 0.49 | 0.60 | 4.5 | $8.5 \times 10^2$ |
| 1.0 | 86 | 0.56 | 0.30 | 2.2 | 8.0 |
| 2.0 | 83 | 0.70 | 0.15 | 1.1 | 8.0 |
| 5.0 | 82 | 0.84 | 0.06 | 0.34 | 7.0 |
| 10.0 | 78 | 0.95 | | | |
| 20.0 | 82 | 1.00 | | | |
| | | | | Avg. | $7.9 \times 10^2$ |
| **C. Fumaronitrile (C = 1.76 mM)** | | | | | |
| 0.05 | 55.3 | | | | |
| 0.10 | 53.6 | | | | |
| 0.20 | 51.9 | | | | |
| 0.50 | 50.6 | | | | |
| 1.0 | 51.4 | | | | |
| 2.0 | 50.8 | | | | |
| 10.0 | 50.3 | | | | |
| 20.0 | 49.6 | | | | |

[a] Solutions contained 0.1M TBAI and DMF. The platinum working electrode area was 0.11 cm².

[b] $i_{pc}$ = cathodic peak current for first reduction wave ($\mu$A), $v$ = scan rate (V/sec), $C$ = concentration (mM).

[c] $\tau = (E_\lambda - E^\circ)/v$, where $E_\lambda$ is the switching potential, $E^\circ$ is the formal electrode potential, and $v$ is the scan rate.

[d] $\log \omega = \log 2k_2C\tau + 0.034\ (a\tau - 4)$, $a = (nF/RT)v$ [see Ref. (8)].

[e] Note that Nicholson et al. (8) define the rate constant for reaction in Eq. [3] in terms of loss of R⁻, i.e., $d[\text{R}^-]/dt = -k_{2N}[\text{R}^-]^2$, while we define $k_2$ in terms of formation of the dimer $d[\text{R}_2^{2-}]/dt = \dfrac{-1}{2}\,d[\text{R}^-]/dt = k_2[\text{R}^-]^2$. Therefore, $k_2 = \dfrac{1}{2}\,k_{2N}$.

reversal wave is observed in cyclic voltammograms for scans of up to 500 mV/sec (see below) and only very small ring currents are measured during generation of R⁻ at the disk. However, by using the technique of adjustment of $E_r$ to a potential where $i_r = 0$ for $i_d = 0$, and then determining $i_r$ at high current sensitivity for increasing $i_d$ values, precise values of $i_r$ could be determined. Typical results of $N_K$ vs. $CONI$ for a 0.92 mM fumaronitrile solution are given in Fig. 4; note the small $N_K$ values. As in the case of cinnamonitrile, the trend is clearly that of mechanism I, but a best fit to the data is obtained by assuming a small contribution (ca. 1-2%) for mechanism IIa. A summary of results for different concentrations of fumaronitrile are shown in Table II. The somewhat larger scatter in the data probably reflects the larger deviation in determining small $N_K$ values, as well as a greater perturbation of the measurements by the polymerization reaction. Assuming the data at the lowest concentration is the least perturbed, we can give the following estimated rate constants

$$k_2 = 7 \times 10^5 \text{ liters/mole-sec}, \quad k_2' = 10^4 \text{ liters/mole-sec}.$$

*Cyclic voltammetry experiments.*—Cyclic voltammetric experiments were undertaken to obtain additional evidence pertaining to the proposed mechanism and to confirm the RRDE simulations. Typical cyclic voltammograms of the three compounds are shown in Fig. 5. Cyclic voltammetric treatments of dimerization reactions like that in mechanism I have been given by
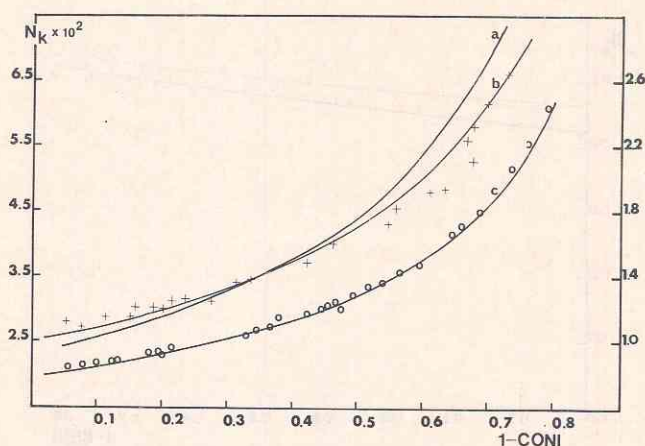


Fig. 4. Collection efficiency ($N_K$) vs. 1-$CONI$ at $\omega = 202$ radians/sec for 0.92 (o) and 1.92 (+) mM fumaronitrile solutions. Solid lines are theoretical curves corresponding to (a) mechanism I, $XKTC = 133$, (b) mechanism I, $XKTC = 92$, and mechanism IIa, $XKTC = 1.0$, considered as parallel paths, and (c) simultaneous consideration of mechanism I, $XKTC = 50$, and mechanism IIa, $XKTC = 0.5$. The right scale applies to curves a and b whereas, the left to curve c.
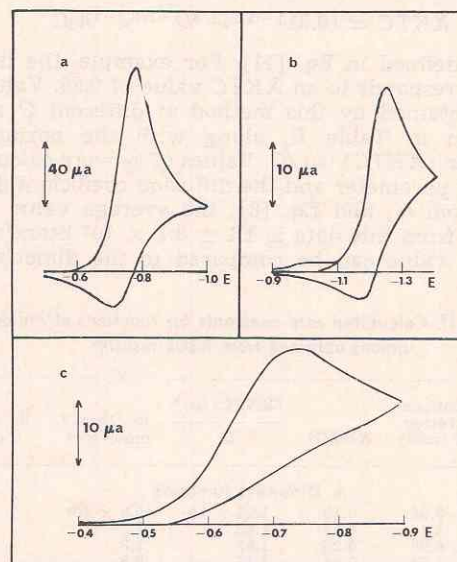


Fig. 5. Cyclic voltammograms at 100 mV/sec. of (a) 4.45 mM dimethyl fumarate, (b) 1.09 mM cinnamonitrile. Note the small impurity wave prior to the cinnamonitrile reduction wave. This wave was removed upon pre-electrolysis at $-$ 0.98V vs. Ag-RE, and (c) 1.92 mM fumaronitrile solution.

both Nicholson and co-workers (8) and Saveant and co-workers (9). Second order ECE reactions, such as shown in mechanism II, have also been considered (9). Qualitatively, both mechanisms show $i_{pa}/i_{pc}$ ratios [$i_{pa}$ and $i_{pc}$ are anodic (reversal) and cathodic peak currents, respectively] which increase with increasing scan rate, $v$. However, the mechanisms differ in the behavior of the current function $i_{pc}/v^{1/2}C$ with scan rate (1, 9). For the EC dimerization (mechanism I) $i_p/v^{1/2}C$ decreases with increasing $v$, while the ECE process (mechanism II) shows the opposite trend. Typical cyclic voltammetric data for the three compounds are given in Table III. The current function trend characteristic of mechanism I can be discerned in the data for cinnamonitrile and fumaronitrile, while the data for dimethyl fumarate shows this trend at faster scan rates, but is considerably more scattered. A similar trend has also been observed for diethyl fumarate (1). If one assumes that mechanism I is occurring, then the $i_{pa}/i_{pc}$ values can be employed to calculate the dimerization rate constant, $k_2$, following

the procedure of Nicholson *et al.* (8). This procedure was carried out for dimethyl fumarate and cinnamonitrile in the region where $i_{pa}/i_{pc}$ is most sensitive to variations in $k_2$. The $i_{pa}$ values for fumaronitrile were too small to allow precise calculations from cyclic voltammetric data. The results and some intermediate factors used in the calculations are shown in Table III. The $k_2$ values obtained for dimethyl fumarate and cinnamonitrile are $1.6 \times 10^2$ and $7.9 \times 10^2$ liters/mole-sec, respectively.

## Discussion

The results obtained here support the previous studies (1) and point to the major pathway in the electrohydrodimerization of these compounds as involving initial production of the anion radical followed by a coupling step. Other aspects of the mechanism, the protonation steps, the nature of the polymerization reaction, and the reactions at the later waves, which sometimes lead to secondary radicals (10), still await elucidation.

In examining the results, we see that dimethyl fumarate, which undergoes dimerization at the slowest rate of the three compounds, shows the most scatter in the $k_2$ value calculated from RRDE results and only fair agreement with that obtained by cyclic voltammetry. Several factors contribute to this. Because the radical ion disappearance is slow on the RRDE time scale, $N_K$ values are close to those for an unperturbed collection efficiency, and the observed slopes are rather insensitive to small changes in $XKTC$. Moreover, the small value of $k_2$ necessitates use of high dimethyl fumarate concentrations, which increases the polymerization side reaction.

The RRDE results for cinnamonitrile fall into the sensitive $N_K$ *vs.* $CONI$ region for our electrode and the reaction is unperturbed by polymerization. The $k_2$ values determined by RRDE measurements over a wide range of $C$ and for differing $\omega$ show good precision and agree very well with the value determined by cyclic voltammetry. This good agreement between a steady-state and transient technique also is suggestive of lack of involvement of adsorption of parent or intermediates in the reaction mechanism.

The fumaronitrile RRDE experiments were performed near the upper limit of determinable $k_2$ values with our RRDE. For this reaction, for concentrations of 0.4 to 4 mM, $N_K$ values of only 0.020-0.006 ($CONI = 1$) were found. For both the cinnamonitrile and fumaronitrile reactions the data suggest some contribution from a reaction of the anion radical with parent, although in both cases this contribution was relatively small. It is interesting that even this small contribution can be noticed and accounted for in the analysis of the data, although other processes removing anion radical, such as a first order ECE reaction leading to $RH_2$, may also account for the small deviations from a close fit to mechanism I.

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