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Electrohydrodimerization Reactions

VI. Rotating-Ring Disk Electrode and Macroscale Electrolysis Studies of the Second Reduction Wave of Diethyl Fumarate

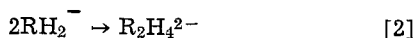
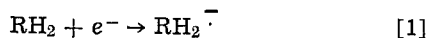
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ABSTRACT

The reactions occurring at potentials of the second reduction wave of diethyl fumarate (DEF) in dimethylformamide solutions, where a current dip is frequently observed in the voltammograms in the absence of added proton donors, was investigated. The over-all reaction order was determined by rotating disk electrode studies of the variation in the current at the dip with DEF concentration and theoretical results obtained by digital simulations. Analysis of products of macroscale electrolyses by NMR and mass spectroscopy was also undertaken. Several mechanisms are considered and one in which the electrogenerated dianion is protonated by the parent DEF to produce a carb-anion which can initiate formation of dimeric and trimeric species is proposed.

In recent years there have been numerous investigations dealing with the electrochemical reduction of deactivated olefins in aprotic media (1). For example, Baizer *et al.* (2) carried out polarographic, cyclic voltammetric, and macroscale electrolysis experiments and showed that the polarography of these compounds is characterized by two separate reduction waves. Numerous experimental studies of such systems (3-11), utilizing such electrochemical techniques as cyclic voltammetry, double potential step chronocoulometry, rotating-ring disk electrode (RRDE) voltammetry, and electron spin resonance (ESR) spectroscopy have shown that the predominant pathway of the electrohydrodimerization (EHD) reaction for reduction at the first wave consists of formation of the radical anion, RH_2^- , followed by dimerization and protonation



where RH_2 represents the deactivated olefin. Very little work has been reported on the processes occurring at the second reduction step. The polarographic curves for many of the compounds studied show a second reduction wave, while others, like diethyl fumarate (DEF), (*trans*- $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{CH}=\text{CH}\cdot\text{CO}\cdot\text{OC}_2\text{H}_5$) exhibit a current decrease or dip where a wave is expected (2). The presence of a dip where the dianion DEF^{2-} is supposed to be formed has been interpreted as oligo- or

polymerization initiated by the dianion. The mechanism of this reaction has not been established. By using cyclic voltammetric techniques and anhydrous working conditions with special steps taken to decrease the rate of the following homogeneous reaction(s) [through temperature reduction to -70°C in DMF (9, 10) or the use of the low electrophilic solvent liquid ammonia at -43°C (11)], the DEF dianion will exist for a sufficient time in the vicinity of the electrode surface to allow its observation. Its reactivity toward incoming parent molecules apparently can also be decreased by adding a proton source to the solution; the protonation of the doubly charged species then takes place, leading to the protonated species, RH_4 . In this case, the dip at the second polarographic wave is suppressed and a definite wave is produced. Thus the final distribution of reaction products depends on the concentration of proton source present in the solution, including accidental sources, such as residual water. Cyclic voltammetric and ESR studies show that a third species, probably one formed after the first step, undergoes a reduction at a more negative potential (3, 9, 12). When stationary electrodes are used, the chemical reaction involving the dianion appears to produce some filming of the electrode surface, hindering complete usage of the experimental behavior following the first step for elucidation of the reaction path. However the forced radial convective flux near the electrode surface of the RRDE apparently sweeps away the products quickly enough to avoid these filming difficulties.

This work is aimed at extending the study of the reduction mechanism of DEF in *N,N*-dimethylformamide (DMF) at the second reduction step. The polarographic behavior exhibited by DEF has been sometimes encountered before with other redox systems and

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qualitatively interpreted. However, no quantitative treatment of this behavior at the RRDE has been reported. Because of the reactivity of the dianion toward any proton source, especially careful drying and purification procedures for the solvent and the electrolyte were employed. The second part of this paper deals with the identification of products obtained through bulk electrolysis and a proposed mechanism for the reaction.

Experimental

The general experimental techniques were the same as those reported previously (3-5).

Materials.—The solvent, DMF, was purified as previously described. The supporting electrolyte, *tetra*-*n*-butylammonium iodide (TBAI), polarographic grade (Southwestern Analytical Chemicals, Austin, Texas) was dried under vacuum and stored under an inert atmosphere. Diethyl fumarate, puriss. (Aldrich Chemical Company, Incorporated, Milwaukee, Wisconsin), was used as received without further purification.

Apparatus.—Coulometric and preparative electrolysis experiments were carried out with a PAR Model 170 Electrochemistry System (Princeton Applied Research Corporation, Princeton, New Jersey). For the RRDE experiments, a Tacussel Electronique potentiostat Model BIPAD-2 was used. A Wavetek function generator provided the potential ramp for voltammetric studies recorded on a Mosley Model 2D-2 X-Y recorder. The RRDE, manufactured by the Pine Instrument Company (Grove City, Pennsylvania) was the same one as previously used (13); the platinum disk in it had a radius of 0.145 cm and was embedded in Teflon. It was driven with a Motomatic Model E 150 tachometer/generator motor (Electrocraft Corporation, Hopkins, Minnesota) using feedback control. The entire motor-electrode assembly was encased in a vacuum-tight mount, equipped with electrical feedthroughs to the motor and electrodes (13). The electrochemical cell used in the RRDE experiments had five glass joints leading to the working electrode assembly, the auxiliary electrode, and the reference compartment, with the remaining joints being devoted to solvent and solute transfers. The cell had a 50 ml capacity. A silver wire isolated in a compartment closed with a fine porosity sintered-glass disk was used as a reference electrode; its potential in the DMF-TBAI system was quite stable during each experiment. The auxiliary electrode was a platinum wire. The electrochemical cell used in preparative electrolysis and coulometric experiments comprised four compartments (auxiliary, intermediate-buffer to prevent catholyte contamination, reference, and working, the last having a 150 ml capacity). A mercury pool electrode was used as a working electrode; the auxiliary and reference electrodes were the same as those described above.

All the experiments were carried out in a glove box filled with a positive pressure of high purity helium (99.995% Matheson Gas Products, La Porte, Texas) and care was taken that neither purified solvent nor supporting electrolyte was ever in contact with the atmosphere following their purification. Furthermore, the following additional procedure was undertaken before each experiment to diminish the concentration of residual water or dissolved air in the solution. A weighed amount of supporting electrolyte was dissolved in the solvent under inert gas pressure and poured into a transfer vessel. After freezing and pumping of the solution, 5 ml of spectrograde benzene were added. Three freeze-pump-thaw cycles were performed and the water-benzene azeotrope was eliminated through vacuum distillation. The solution was then transferred under vacuum into the electrochemical cell, brought to atmospheric pressure with helium, and allowed to equilibrate. Before assembly the electrochemical cell was pumped down for about 1 hr and the platinum disk electrode polished with alumina. The same procedure

for purifying the solvent was used for the bulk electrolysis experiments. The catholyte solution had a volume of 120 ml and was saturated with supporting electrolyte (for TBAI, about 0.5M). Up to 0.2M depolarizer was added in several fractions and the electrolysis was conducted until each fraction had been converted before adding the next fraction. The basicity of the solution increased during electrolysis, and to avoid possible contamination a glass-embedded, rather than Teflon stirring bar, was used. After completion of the experiment, protonation of the remaining reactive species was achieved by pouring about 20 ml water into the solution. The mixture was then evaporated, the residue extracted with ether, washed with water, and the organic layer dried with anhydrous sodium sulfate. The solvent was removed by distillation and the analysis of the reaction products carried out.

Results

A typical RRDE voltammogram of DEF is shown in Fig. 1. The disk curve exhibits a one-electron reduction wave, with $E_{1/2} = -0.76V$ vs. the silver wire-reference electrode (Ag-RE), followed by a dip commencing at approximately $-1.60V$ vs. Ag-RE. After the short plateau, characterized by the current $i_{d,1}$, the disk current, i_d , increases, due to the background limiting reduction of the DMF-TBAI system on platinum. For the same working conditions, the $i_{d,1}$ value is reproducible within the experimental error and no appreciable filming of the electrode surface seems to occur, since two consecutive runs are essentially superimposable. On the same figure, curve b represents the ring current, i_r , as a function of disk potential, E_d , with the ring potential, E_r , held at 0.0V vs. Ag-RE. In absence of kinetic complication, the ratio i_r/i_d (the collection efficiency, N) is only a function of the geometry of the electrode and can be calculated theoretically. In the case of RRDE curves of DEF, the experimental value of N for the first reduction wave equals its theoretical value (0.555 for this electrode), because the second-order rate constant, k_2 , of the EHD reaction involving the DEF^- radical anion, [2], is so small that appreciable reaction of DEF^- does not occur during its transit from the disk to the ring [$k_2 = 44$ liter/msec (3-6)]. At more negative E_d values, however, the concomitant decrease of i_d and especially i_r , which finally drops to zero, shows evidence of the high instability of the electrogenerated species.

The i_d value in that potential region is proportional to the concentration at the disk surface of species able to undergo reduction, DEF and DEF^- . Hence, the decrease of i_d in a region where the dianion, DEF^{2-} , is presumably formed (by comparison with the behavior

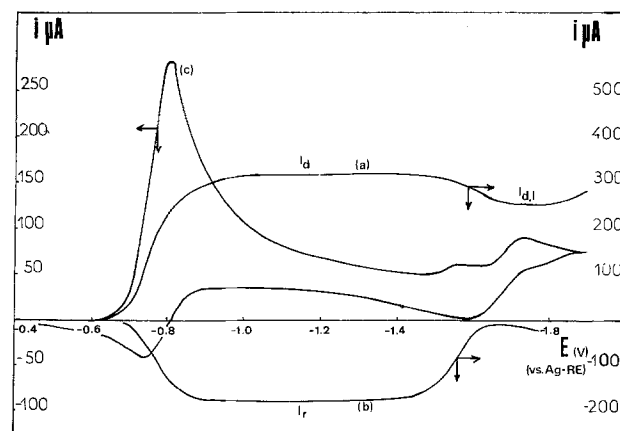


Fig. 1. Diethyl fumarate voltammograms in 0.1M TBAI-DMF solutions. RRDE voltammograms. $\omega = 45 \text{ sec}^{-1}$; $C = 9.4 \text{ mM}$. (a) i_d vs. E_d , (b) i_r vs. E_d with $E_r = 0.0V$ vs. Ag-RE. Cyclic voltammogram (c) 200 mV/sec, $C = 12 \text{ mM}$.

of olefins of similar structure) reveals the existence of a chemical stage involving the interception of incoming parent molecules by the dianion and/or by species formed after reactions of it. Thus the reaction kinetics are concentration dependent, so that for a sufficient concentration of DEF, the $i_{d,1}$ value is lowered to a value smaller than that of the first diffusion plateau. A study of the variation of $i_{d,1}$ with concentration of DEF, C , can then provide information about the nature and the kinetics of the reactions in this potential region. The "information content" of such an $i_{d,1}$ vs. C plot is not sufficiently high that the elementary steps or their rate constants can be determined individually. What can be obtained is the over-all reaction order and rate constant. Our approach was to use digital simulations (14) of different reaction sequences involving the dianion assumed to be produced in the region of the dip. We assumed that no further reduction of the dianion at the electrode occurred at these potentials and that the predominant reaction of the dianion was that with DEF. Thus the rate of disappearance of the monomer DEF, by reaction with the dianion could be expressed as

$$-d[\text{DEF}]/dt = k_n[\text{DEF}^{2-}][\text{DEF}]^n \quad [4]$$

where $n + 1$ represents the order of the equivalent over-all reaction and k_n is a composite rate constant, which is a function of the rate constants of the elementary bimolecular reactions involved in the reaction mechanism, as described later in this paper.

Digital simulation procedure.—A digital simulation of $i_{d,1}$ for different values of k_n and n was undertaken. The general procedure involved the same theoretical treatment as that used previously for a variety of electrochemical and RRDE problems (3-5, 14-17). Its extension to the study of the DEF second reduction wave process of the RDE is fairly straightforward. The program written previously by Prater (15, 16) needed some modifications, with the diffusion and hydrodynamic parts remaining unaltered. The expression for the flux at the electrode surface, and accordingly the normalized current, was written to take care of the new boundary conditions involved in the two-step reduction. To do the simulation in terms of dimensionless parameters, it is convenient to define the current by the ratio of $i_{d,1}$ over the value of twice the limiting current of the first reduction step. This ratio was called CONID. Another dimensionless variable used was $XKTC^n$, defined as

$$XKTC^n = (0.51)^{-2/3} \nu^{1/3} D^{-1/3} k_n \omega^{-1} C^n \quad [5]$$

which contains the rate constant k_n and the DEF concentration, C . We assumed the same diffusion coefficients for all of the species, D . The other parameters have their usual meaning. The digital program was tested by the simulation of an electrochemical process characterized by two separate reduction steps without kinetic complications. Simulated working curves were obtained for CONID as a function of $\log(XKTC^n)$ for several values of n . One difficulty which often arises in the simulation of electrochemical systems with coupled chemical reactions with large rate constants is that the reaction layer thickness becomes much less than that of the diffusion layer so that only a few elements describe the concentration profile and the accuracy is diminished. In the present study this difficulty was overcome by determining the limiting CONID value for $k_n \rightarrow \infty$ (practically 10^7 - 10^8), i.e., by the simulation of a totally irreversible reaction of DEF^{2-} with n DEF molecules. Working curves spread across the whole range of normalized rate constants could be obtained by interpolating the accurate values at smaller rate constants toward the limiting one; typical working curves are shown in Fig. 2. From these results curves of CONID vs. $\log(C)$ for each n and for several values of $\log(XKT)$ (where $XKT = XKTC^n/C^n$) were obtained and compared with the corresponding experimental points (Fig. 3). In the experiment $i_{d,1}$ was taken

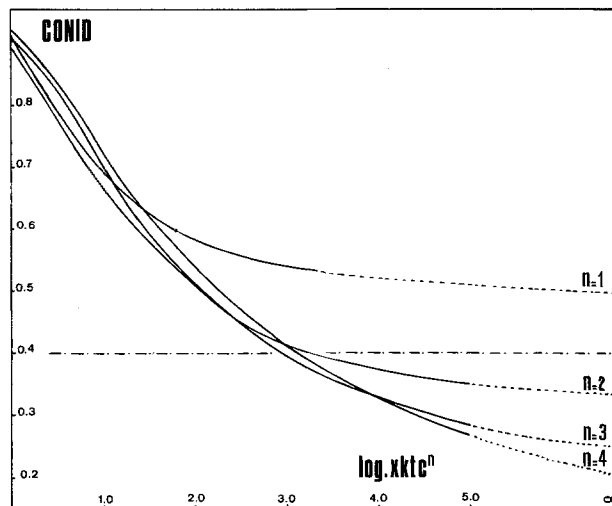


Fig. 2. Simulated CONID vs. $\log(XKTC^n)$ curves for several values of n .

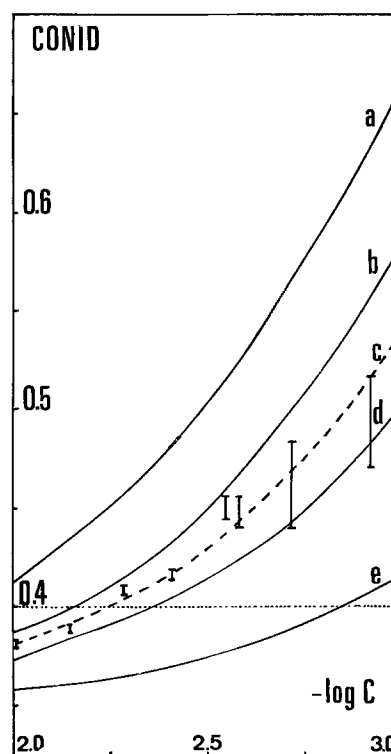


Fig. 3. Simulated CONID vs. $\log C$ curves for $n = 2$ and XKT values of: (a) 7×10^7 , (b) 3×10^7 , (d) 10^8 , (e) 10^9 . (c) (Dotted line) best fit to experimental results (yielding $XKT = 5.6 \times 10^7$).

at $E = -1.8\text{V}$ and the concentration was varied between 10^{-2} to 10^{-3}M . This concentration range proved to be the best for accurate measurements. At concentrations below 10^{-3}M side reactions of the dianion with impurity proton donors may be a problem. Measurements were difficult at the relatively high currents observed for concentrations greater than 10^{-2}M . The choice of the reaction order parameter was made as follows. The slopes of the simulated CONID vs. $\log C$ plots, such as Fig. 3 at a given point (e.g., $\text{CONID} = 0.4$) differ for different values of n . A plot of the slope for different values of $\log XKTC^n$ (Fig. 4) provides working curves which allow a more precise comparison of experimental and simulated data; this comparison leads, within the assumed mechanism, to an n of 2. Once n is known, the value of k_n can be estimated through the best fit between experimental and calculated CONID vs. $(-\log C)$ curves. The average value for k_n was $7 \times 10^8 \text{M}^{-1}\text{sec}^{-1}$.

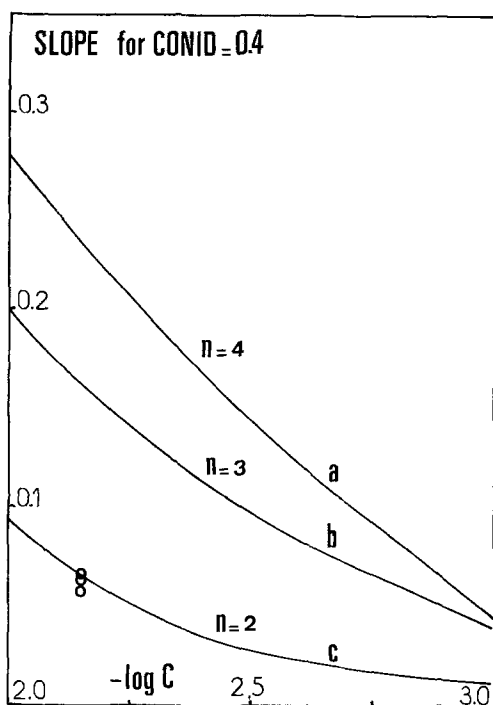


Fig. 4. Variation of the slope of CONID vs. $\log(XKTC^n)$ simulated curves at CONID = 0.4 vs. $\log C$ for several values of n . Circles indicate experimental data.

Macroscale electrolysis results.—Bulk electrolysis experiments were performed to identify reaction products. The same working conditions as the RRDE experiments were used. The reduction was carried out at a continuously stirred mercury pool cathode at a controlled potential of $-1.65V$ vs. Ag-RE in anhydrous DMF. For concentrations between 5×10^{-3} and $0.2M$, the apparent number of faradays per mole of DEF, n_{app} , was about the same as for the coulometric reductions performed after the first reduction wave. The vicinity of the third reduction peak and of the background reduction limit did not allow an accurate measurement of n_{app} , but most of the values fell in the range of 0.55-0.65. Thus n_{app} less than one is consistent with the existence of a reaction consuming parent molecules. During electrolysis, the working compartment solution showed a transient yellow color before turning gradually amber. The middle compartment remained colorless. Cyclic voltammograms taken during electrolysis showed a decrease of both reduction peaks with time. At all times during electrolysis no additional peaks were detected and the viscosity of the solution was apparently unchanged.

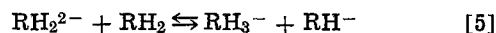
After completion of the electrolysis, no precipitate could be isolated, which might be formed by a polyaddition reaction initiated at the electrode and continuing in the bulk solution. Systematic attempts using gas chromatography to detect any ethanol (or ethanolate) that might be formed as a result of a subsequent reaction were unsuccessful. Such a possible pathway was first suggested by Nelson (18) to explain results based on ESR measurements. Recently, it was shown that a Dieckmann-type elimination of ethoxide stabilizes the dimeric cinnamate ester dianion (19, 20); however such a mechanism involves a different olefin under different working conditions. Our results demonstrate that EtO^- elimination from the DEF dianion does not occur. A proton NMR analysis was carried out on the isolated electrolysis products and the spectra compared with those of pure samples of hydrodimer, diethylsuccinate, and DEF. The results indicated that no dihydroproduct was formed. Moreover, no peak relative to protons carried by an sp^2 carbon could be detected. The spectra exhibited two major groups at

$\delta = 4.15$ ppm(CH_2) and $\delta = 1.30$ ppm(CH_3), arising from several nonequivalent ethyl groups. These major peaks were separated with numerous small groups in the CH and CH_2 region. Integration of this region led to a value of 1.2 nonethyl protons/ethyl group. These results were qualitatively confirmed with C-13 NMR. We attempted to obtain additional information about the molecular weight of the reaction products by using mass spectroscopic techniques. The mass spectrum of pure hydrodimer ($M = 346$) shows characteristic sequences of peak groups separated by loss of C_2H_5O units ($m/e = 45$) and C_2H_5COO units ($m/e = 73$) beginning with peaks at $m/e = 301$. The parent peak was absent. Qualitatively, the same type of spectra were obtained with the reaction products. The three first peak groups started, in the high range of m/e ratios, at 471, 472, 473-442, 443, 444 and 426, 427, 428. In the lower range, groups of peaks were positioned at m/e ratios arising from loss of units of 45 and 73. Since no peaks were detected at m/e values higher than the above limit, the mass spectra suggest formation of isomeric trimers as the predominant higher molecular weight species.

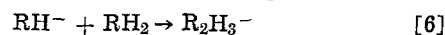
Discussion

The experimental results indicate that formation of the dianion does not lead to polymer formation and both the RDE results (showing $n = 2$) and the n_{app} results suggest predominant dimer and trimer formation. The absence of ethanol as a product demonstrates that a Dieckmann-type intramolecular cyclization does not occur. Three possible reaction schemes can be suggested, depending on the mode of reaction of the DEF dianion (RH_2^{2-}) with parent molecule (structures are shown in Fig. 5).

1. **Proton transfer scheme.**—The DEF dianion is a strong base and could abstract a proton from incoming parent monomer



This type of reaction between electrogenerated dianion (as a base) and a second molecule has been discussed by Baizer and co-workers (21, 22) and Iverson and Lund (23). The carbanion RH^- could then react with an additional molecule of incoming parent



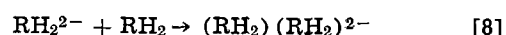
in a Michael reaction, with the dimeric species being protonated to yield R_2H_4 or reacting with yet another molecule of RH_2 to form the trimer, R_3H_6 . If [5] is rapid and [6] is the rate-determining step, a kinetic expression of the form of [4] would result, with $n = 2$. The n_{app} found for this scheme would depend upon the fate of the RH_3^- species and whether protonation of any of the intermediates (e.g., RH_3^- or $R_2H_3^-$) generates RH^- .

2. **Electron transfer scheme.**—The transfer of an electron between the dianion and parent is thermodynamically favored and would lead to two radical anions (reaction [7])



This route would lead to hydrodimer, R_2H_6 , via reactions [2] and [3]. Since the radical anion coupling reaction is relatively slow, about $44 M^{-1} \text{sec}^{-1}$ under these conditions (3-6), a large fraction of the $RH_2^{\cdot -}$ produced in the vicinity of the electrode will be reduced to dianion before coupling. The coupling intermediate $R_2H_4^{2-}$ cannot be the major source of the current decrease in the vicinity of the second wave, since it is also produced at the first wave as well.

3. **Direct addition scheme.**—The direct addition of the dianion to parent would lead to a species formally the same as that resulting from the coupling of two radical anions



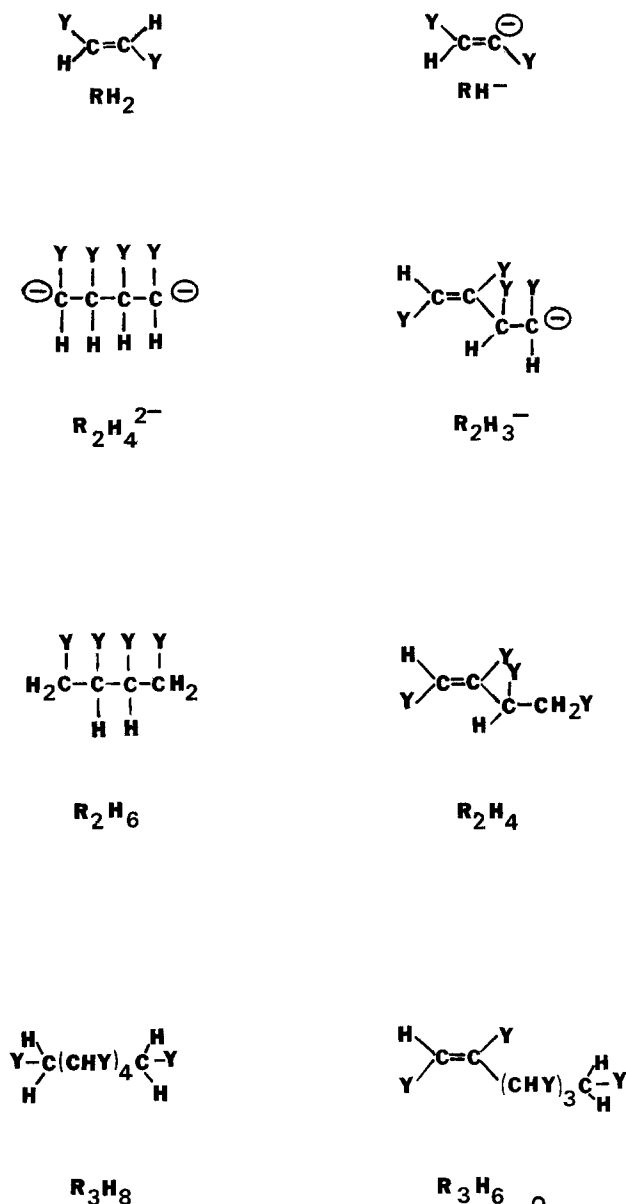
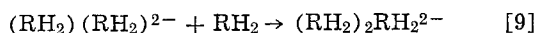


Fig. 5. Structures of various possible species. Y = $-\text{C}-\text{OEt}$

If this species were identical to the $\text{R}_2\text{H}_4^{2-}$ of reaction [2] appreciable reaction of it with parent, reaction [9], would not be expected. However if this species were different, at least for the time needed to undergo the



subsequent reaction, then production of the trimer, R_3H_8 , would be possible at potentials of the second wave. The sequence of reactions [8] (rapid) and [9] (rate determining) would lead to an equation of the form of [4] with $n = 2$. The way in which the two dimeric dianionic species may differ might be analogous to the difference in behavior found in the cross-coupling and self-coupling rates of the radical anions of the *trans*- and *cis*-pair diethyl fumarate and diethyl maleate (17, 24). In that case the *trans*-radical anion couples rather slowly and does not react with acrylonitrile (AN), while the *cis*-radical anion, which isomerizes quite rapidly to the *trans*-form (25, 26), couples about two orders of magnitude more rapidly and reacts with AN. This rather speculative suggestion, that the dimeric dianion has some memory of its origin, at least for a time long enough for it to react further, will require more definitive experiments, probably in a less complicated system, before it can be considered established.

At this time scheme 1, the proton transfer scheme, appears most reasonable, although we did not detect an ethylenic double-bond in the products by NMR analysis, as would be expected in the unsaturated dimer or trimer R_2H_4 or R_3H_6 . These species might also be reducible at potentials of the second wave, since they contain the basic DEF grouping, and thus undergo further reduction and protonation in the macroscale electrolysis experiments. Addition of proton donor, even a relatively weak one such as water, causes an increase in the current at the second wave by competing with RH_2 as a proton source. In the absence of RH^- interception of the incoming parent compound is avoided.

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