

Reductive Coupling and Isomerization of Electrogenerated Radical Ions of *cis*- and *trans*-Isomers

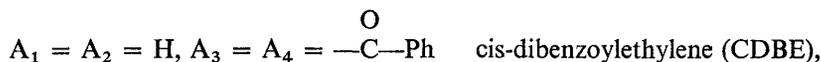
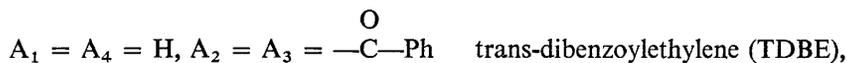
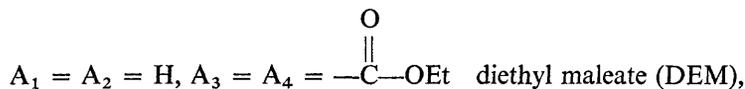
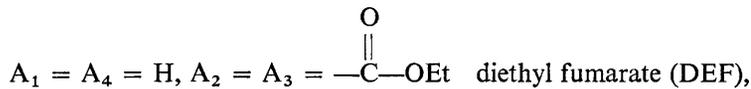
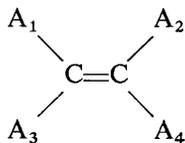
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The electrochemical behaviour of the *cis*-*trans*-pairs: diethyl maleate (DEM), diethyl fumarate (DEF) and *cis*- and *trans*-dibenzoyl ethylene (CDBE and TDBE) in *N,N*-dimethylformamide solutions was investigated using cyclic and rotating ring-disc electrode (RRDE) voltammetry and bulk electrolysis. In both cases the *cis*-isomer is reduced at more negative potentials than the *trans*-isomer. Although the radical anion formed from the *trans*-isomer is fairly stable, that of the *cis*-isomer undergoes a rapid isomerization to form the *trans*-radical anion and also reacts more rapidly in either self- or cross-coupling reactions. The electron spin resonance (e.s.r.) spectra obtained by electrolytic reduction of either DEM or DEF has been re-interpreted as being caused by different conformations of the *trans*-radical anion. Identical e.s.r. spectra are also obtained from reduction of CDBE and TDBE; this is attributed to a single conformation of TDBE radical anion.

There has been much interest in the electrochemical behaviour of activated olefins (R)



especially because these molecules undergo hydrodimerization (or reductive coupling) upon electroreduction, leading to the formation of R_2H_2 .¹ Previous studies of the mechanism of these reactions in dimethylformamide (DMF) solutions by rotating ring-disc electrode (RRDE) voltammetry, cyclic voltammetry, double potential-step chronocoulometry and electron spin resonance (e.s.r.) spectroscopy on molecules such as DEF, cinnamionitrile and fumarionitrile, have shown that the reaction path

involves the initial formation of the radical anion ($R^{\cdot-}$) followed by coupling (1) and protonation²⁻⁵:



Of particular interest is the difference of behaviour of cis- and trans-isomers upon electroreduction to the radical ions with respect to isomerization, coupling and mixed coupling (where the radical anion of one olefin reacts with the parent molecule of a second olefin).

The study of the comparative behaviour of the cis-trans-pair, diethyl maleate (DEM) and diethyl fumarate (DEF), is of particular interest, since the radical anions derived from these have often been assumed to behave similarly. Nelsen⁶ produced the radical anions of DEF and DEM by electroreduction in DMSO and showed that the same e.s.r. spectrum was obtained from both and that it consisted of signals from two separate species. He concluded, by comparison with the behaviour of diethyl phthalate, that these were the cis- and trans-anion radicals. However, electrochemical studies in these laboratories,^{3b} as well as those of Il'yasov and Kargin and co-workers⁷ demonstrated rapid conversion of $DEM^{\cdot-}$ to $DEF^{\cdot-}$. We report here a detailed study of these species which provide a striking example of the strong influence of structure of electrogenerated intermediates on their behaviour. We also discuss the electrochemistry and e.s.r. spectra of trans- and cis-dibenzoylethylene (TDBE and CDBE) radical anions.

EXPERIMENTAL

Experimental apparatus and techniques followed previous studies.³ A Tacussel 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 disc currents simultaneously. A Wavetek function generator provided a d.c. potential ramp for voltammetric experiments recorded on either a Mosley model 2D-2 or Hewlett-Packard Autograf X-Y recorder. The Pt-Teflon RRDE had dimensions $r_1 = 0.187$ cm, $r_2 = 0.200$ cm and $r_3 = 0.332$ cm and was constructed by Pine Instrument Company. The maximum collection efficiency N for this RRDE is 0.555.³ Electrolysis for the purpose of removing electroactive impurities was performed at a mercury pool electrode in the RRDE cell. The reference and auxiliary electrodes were silver (Ag, R.E.) and platinum spirals, respectively, contained in compartments separated from the working electrode compartment by medium-porosity glass frits. Bulk electrolysis performed to study the isomerization process was carried out in a conventional coulometry cell utilizing a platinum-gauze working electrode, and platinum and S.C.E. auxiliary and reference electrodes, respectively. A model 170 Electrochemistry System (Princeton Applied Research Corp., Princeton, N.J.) was employed for all cyclic voltammetric and d.c. and a.c. polarographic experiments.

The dual electrode flow cell used porous silver disc working electrodes (Selas-Flotronics Co.) about 50 μ m thick with 3 or 5 μ m average pore size. They were separated by a 200 μ m thick Teflon screen cloth with a 0.2 cm² hole. Each disc working electrode was controlled with respect to its own Pt auxiliary electrode and S.C.E. reference electrode.

The cell used in e.s.r. experiments was that designed for simultaneous electrochemical-e.s.r. (SEESR) work, and comprises a Pt working electrode, tungsten auxiliary electrode and silver wire reference electrode.⁸ A Varian model V-4502 e.s.r. spectrometer was employed.

In preparing solutions, DMF, dispensed from the storage vessel into the dispensing, vessel by positive He pressure, together with supporting electrolyte and the depolarizer were subjected to a minimum of three freeze-pump-thaw cycles. The solution was then transferred to the electrochemical cells. However, in the experiment where CDBE was analyzed in the dark, the CDBE was not carried through the freeze-pump-thaw cycles, but was added directly to the contents of the electrochemical cell. In every case, acrylonitrile was added directly to the electrochemical cell.

N,N-dimethylformamide (DMF), obtained from Baker Chemical Co. or Matheson, Coleman and Bell, was purified by vacuum distillation⁹ and stored under He. Tetra-n-butylammonium iodide (TBAI) and fluoborate (TBAF), obtained from Southwestern Analytical Chemicals, Inc., were vacuum dried and stored over Drierite. DEF, obtained from K. and K. Laboratories, was sublimed prior to use. DEM, obtained from Matheson, Coleman and Bell, contained about 6% DEF as an impurity. The DEM was purified using preparative gas chromatography using a 6 m chromatographic column, 30% S.E. 30 on 60/80 Chromosorb P and a column temperature of 175°C. TDBE, purchased from Aldrich Chemical Co., exhibited a m.p. of 108°C and was used as received. CDBE was prepared from the trans-compound by photo-isomerization. The transformation was verified by n.m.r. analysis. The resultant cis product was in the form of white and brown needles having a m.p. of 132-134°C. Sublimation yielded white needles which had the same melting point. Acrylonitrile, purchased from Matheson, Coleman and Bell Chemicals, was used as received.

RESULTS

THE DEF+DEM SYSTEM

Previous studies^{2, 3} of the electroreduction of the trans-isomer, DEF, in DMF solutions, have shown that it undergoes a reversible one-electron reduction to the radical anion (fig. 1a, $E_p = -1.41$ V vs S.C.E.) followed by a coupling reaction, with a rate constant of about $34 \text{ M}^{-1} \text{ s}^{-1}$.



The cyclic voltammetry of the cis-isomer, DEM, at scan rates below 5 V s^{-1} , however, shows a somewhat broader reduction peak, with $E_p = -1.61$ V, and with no anodic

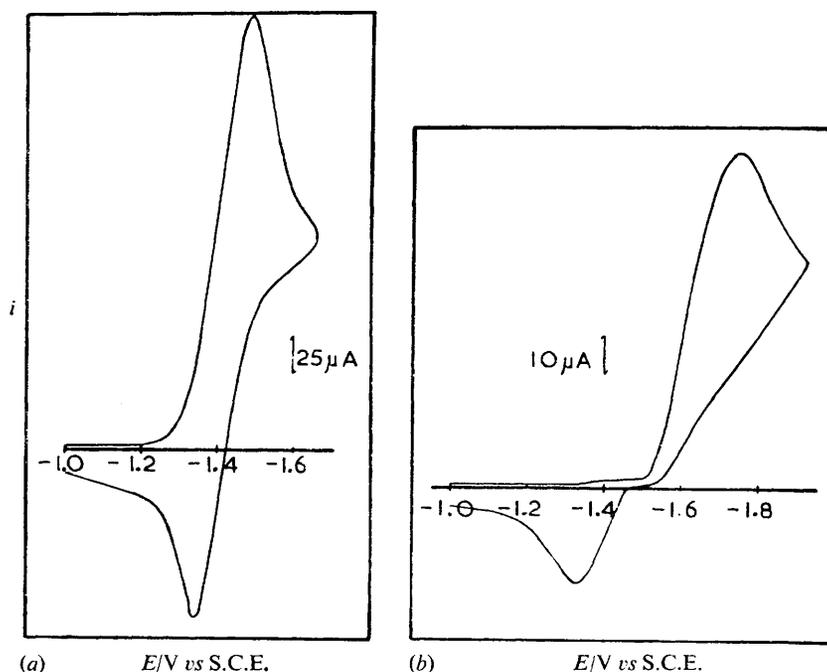


FIG. 1.—Cyclic voltammograms of (a) diethyl fumarate (scan rate 50 mV s^{-1}) and (b) 3 mM diethyl maleate (scan rate 5 V s^{-1}) in 0.1 M TBAF-DMF.

peak corresponding to this cathodic peak (fig. 1*b*). An anodic peak is observed at the same potentials where the oxidation of DEF^- occurs. At a scan rate of 50 V s^{-1} a small anodic peak is observed where DEM^- oxidation is expected. The current function for the reduction wave, $i_p/v^{1/2}C$, where i_p is the peak current, v is the scan rate, and C the concentration, is $63 \mu\text{A mM}^{-1} \text{ V}^{1/2} \text{ s}^{-1/2}$, slightly smaller than the current functions of reversible one-electron processes of similar molecules found with this electrode, of 80 to 95. A.c. polarography of DEM (fig. 2*a*) shows a broad peak at

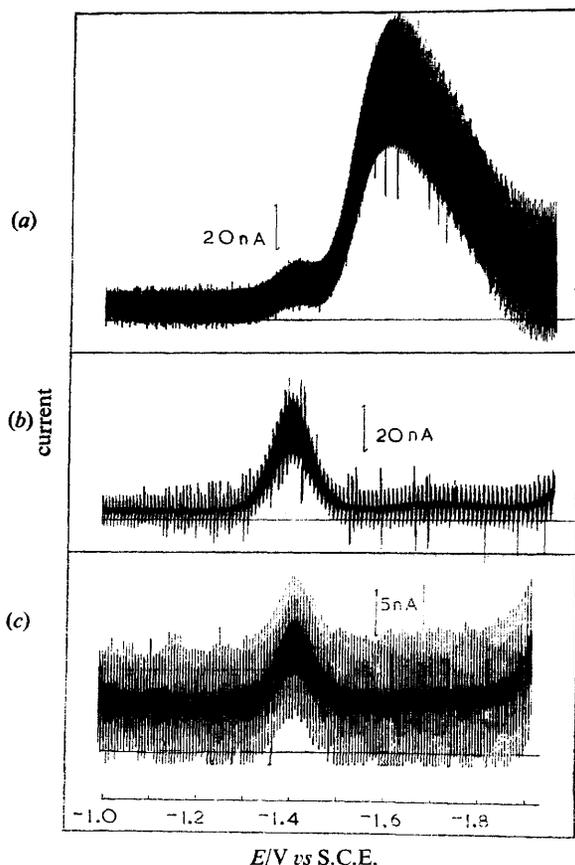


FIG. 2.—A.c. polarograms of (a) 1.2 mM diethyl maleate solution; (b) effluent from dual electrode flow cell for 1.2 mM DEM inlet solution at flow rate of 0.22 ml min^{-1} ; (c) effluent from dual electrode flow cell for 0.55 mM DEM inlet solution and flow rate *ca.* 0.1 ml min^{-1} , a.c., 100 Hz at 10 mV

potentials corresponding to the cyclic voltammetric reduction wave. The small pre-peak observed in both the cyclic voltammetry and a.c. polarography represents a small amount of DEF impurity contained in the DEM. These results can be explained by assuming an initial reversible formation of DEM^- followed by rapid isomerization to DEF^- ,



The rate constant of this isomerization is about 10 s^{-1} .

To demonstrate unequivocally that reduction of both DEF and DEM leads only to DEF^- , experiments were undertaken with a dual-electrode flow cell. This system, shown in fig. 3, consists of two closely-spaced porous electrodes with the potential

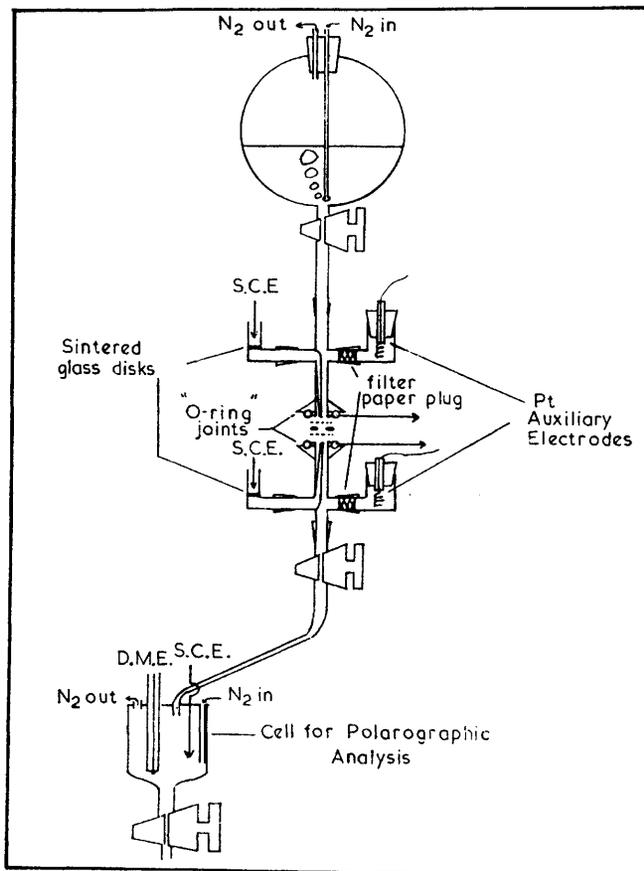
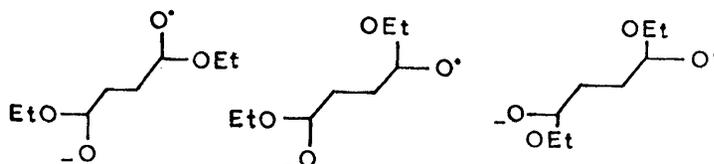


FIG. 3.—Dual electrode flow cell.

of each electrode being controlled with respect to separate reference electrodes and with solution flowing through the electrodes from one electrode to the other. A complete description of the construction and calibration of this apparatus is available.⁹ The experiment undertaken involves electrolysis of a substance at the upper (inlet) electrode, followed by flow of the product to the lower (outlet) electrode where a second electrolysis is carried out. The efficiency of the electrolysis, i.e., the fraction of substance electrolyzed, and the transit time between the electrodes, is governed by the flow rate of solution. The first experiment using the flow cell involved a 1.2 mM solution of DEM in DMF containing 0.1 M TBAF flowing first through the inlet electrode held at a potential where DEM reduction occurred and then to the lower electrode held at a potential where any radical anions would be oxidized, at a flow rate of 0.22 ml min^{-1} (interelectrode transit time of 1.4 s). The porous electrodes were shown to carry out electrolysis with greater than 99 % efficiency for flow rates below 2 ml min^{-1} . Analysis of the effluent solution by a.c. polarography (fig. 2b) showed the presence of only DEF. A similar experiment at a flow rate of less than 0.1 ml min^{-1} gave similar results (fig. 2c). When a similar experiment was performed

employing a 1.4 mM solution of DEF with reduction to $\text{DEF}^{\cdot-}$ at the inlet electrode and oxidation at the lower electrode, again, only DEF was found in the effluent. These results show that the reduction of either DEM or DEF leads to a solution containing only $\text{DEF}^{\cdot-}$ and that the different species observed in e.s.r. must be different conformers of the trans-radical anion,



The different reduction potentials for DEM and DEF and the rapid isomerization of $\text{DEM}^{\cdot-}$ leads to interesting behaviour on attempted removal of the small amount of DEF from the DEM sample by pre-electrolysis. When a sample of DEM containing DEF was electrolyzed at a platinum gauze electrode at $-1.425\text{ V vs S.C.E.}$, a potential corresponding to the mass transfer limiting current plateau of DEF but positive potentials for DEM reduction for 10 min, the cyclic voltammogram of the system shows a relative increase in the height of the DEF wave (fig. 4). Continued electrolysis

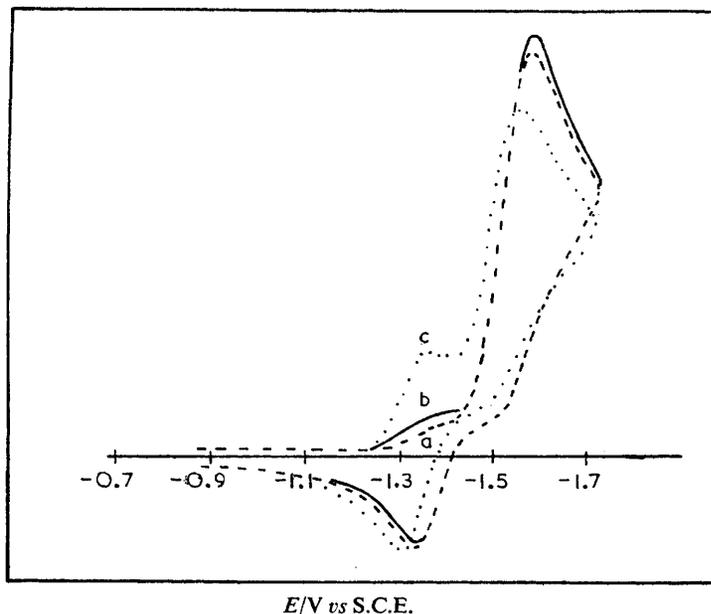


FIG. 4.—Cyclic voltammograms at 200 mV s^{-1} on a Pt working electrode, (a) diethyl maleate (4 mM) small (5–8 %) diethyl fumarate impurity in TBAP (0.15 M)-DMF initially and following, (b) 10 and (c) 45 min of bulk electrolysis at -1.425 V against S.C.E.

at this potential for an additional 35 min causes a further increase in the relative height of the DEF wave (fig. 4c). This apparently anomalous behaviour can be attributed to the reaction of $\text{DEF}^{\cdot-}$ with DEM,



Although the extent of this reaction is slight, the irreversible rapid isomerization of

DEM⁻ occurs, and the net effect of reactions (6) and (5) is the conversion of DEM to DEF catalyzed by DEF⁻.

RRDE studies on DEM were undertaken to compare with those of DEF.³ A plot of the disc current (i_d) against disc potential (E_d) generally follows the behaviour expected from CV studies, i.e., a small impurity wave for DEF at about -0.7 V vs Ag R.E. and a reduction wave for DEM with $E_{\frac{1}{2}}$ at -1.13 V vs Ag R.E. As with disc voltammograms reported for DEF³ a current depression is observed on the reduction plateau at potentials corresponding to those where di-anion formation is expected. The plot of ring current, i_r , vs E_d with the ring potential E_r held at -0.5 V vs Ag R.E. shows an anodic current where production of DEF⁻ and DEM⁻ occurs; i_r decreases where the dip in i_d commences. These current dips have been attributed to polymerization initiated by generation of the dianion. The dependence of i_r on E_r at different values of E_d is shown in fig. 5. Curve *a*, taken where $E_d = 0$ V, shows the current

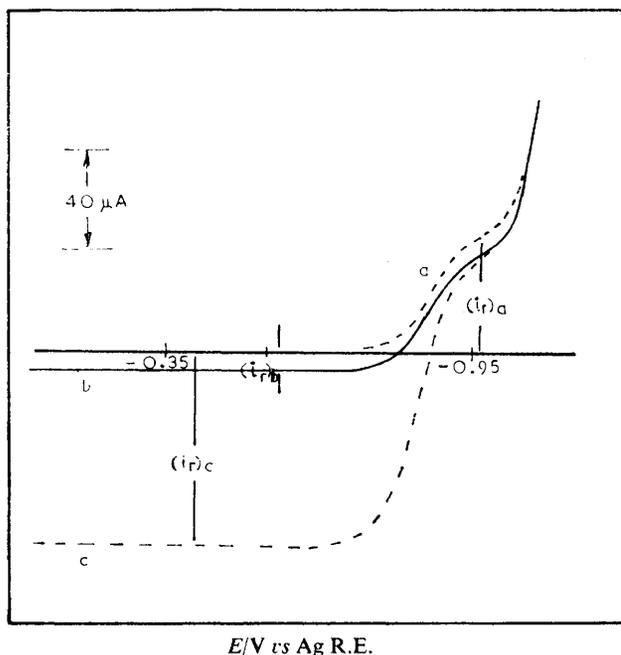


FIG. 5.—RRDE voltammograms of diethyl maleate (3 mM) with small (5-8 %) diethyl fumarate impurity in TBAP (0.15 M) DMF at a rotation rate of 98.6 s^{-1} and (a) $E_d = 0$ V, (b) $E_d = -0.9$ V, (c) $E_d = -1.4$ V vs Ag R.E.

caused by impurity DEF (i_r)_a followed by the main DEM reduction wave. When E_d is held at -0.9 V vs Ag R.E., corresponding to DEF reduction at the disc, the ring voltammogram shows collection of DEF⁻, (i_r)_b, and shielding of the ring in DEF reduction (curve *b*). When $E_d = -1.4$ V vs Ag R.E., corresponding to DEF and DEM reduction at the disc, (curve *c*) the ring current, (i_r)_c, shows a large increase at potentials where DEF⁻ is oxidized, but only a very slight decrease in the potential region where oxidation of any DEM⁻ that reached the ring would occur; oxidation of DEM⁻ in this region (-0.9 to -1.0 V vs Ag R.E.) would cause the total i_r to become less cathodic or even become anodic depending upon the relative fluxes of DEF and DEM⁻ to the ring. The observed behaviour again demonstrates the rapid isomerization of DEM⁻. An estimate of the relative rate of coupling of DEF⁻ and

DEM⁻ can be obtained by noting the collection efficiency ($N_k = |i_r/i_d|$) for DEF and DEM. For these concentrations and rotation rates for this RRDE, N_k for a solution of DEF is 0.55 ± 0.01 , essentially the value observed for collection of a stable species at this RRDE, and indicating negligible reaction of DEF⁻ on transit from disc to ring. For a DEM solution, however, N_k varied between 0.25 and 0.35 depending upon rotation rate and concentration. Similarly, for an equimolar mixture of DEF and DEM the collection efficiencies determined from i_r with E_r at potentials for DEF⁻ oxidation and i_d for DEF and DEM reduction are 0.45 and 0.36 respectively. These results show that the DEM⁻ undergoes reaction much more rapidly than DEF⁻ does, and this reaction competes with the isomerization of DEM⁻. Although coupling of DEM⁻ appears to be a possible reaction, determination of the rate and mechanism of reactions consuming DEM⁻ requires further study. The more rapid rate of reaction of DEM⁻ to non-electroactive products before isomerization is also shown in the dual electrode flow-cell experiments. In the experiments involving an initial solution of 1.4 mM DEF, the effluent following reduction and oxidation contained about one-half of the original amount of DEF. However, for experiments involving an initial solution of 1.2 mM DEM only about 5% of the original DEM was recovered as DEF following passage through the two electrodes, and this amount was even smaller when the flow rate was decreased.

Another experiment which illustrates the difference in reactivity of the trans- and cis-anion radicals is that involving the cross-coupling with acrylonitrile (AN).^{3b} Cyclic and RRDE voltammetry studies of the formation and reaction of DEF⁻ shows that addition of up to 0.2 M AN (which is reduced at more negative potentials)

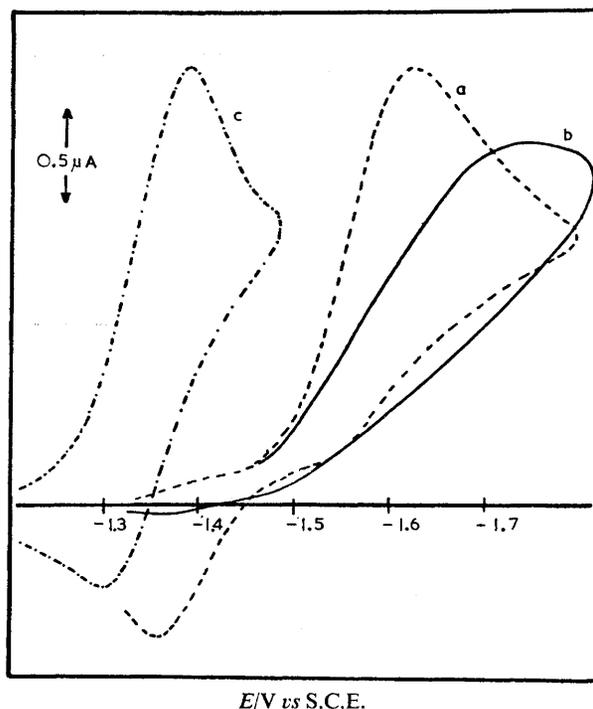


FIG. 6.—Cyclic voltammograms at 200 mV s^{-1} at a Pt electrode, (a) diethyl maleate (3.9 mM), TBAP (0.15 M), DMF; (b) DEM (3.9 mM) after addition of acrylonitrile (0.2 M); (c) dimethyl fumarate (3.7 mM) in the presence of DEM and AN.

causes little change in behaviour, indicating little or no reaction between AN and DEF^- under these conditions. The cyclic voltammetry of DEM in the absence and presence of AN is shown in fig. 6. The addition of AN causes disappearance of the DEF^- oxidation wave, showing that the DEM^- reacts with AN (presumably in an ECE reaction sequence leading to cross-coupled product) in a reaction which is fast compared to the rate of isomerization.

THE TRANS- AND CIS-1,2-DIBENZOYLETHYLENE SYSTEM

The cyclic voltammogram of TDBE in 0.1 M TBAI-DMF is shown in fig. 7. Two reduction waves with $E_{p1c} = -0.28$ and $E_{p2c} = -0.88$ V *vs* Ag R.E. are

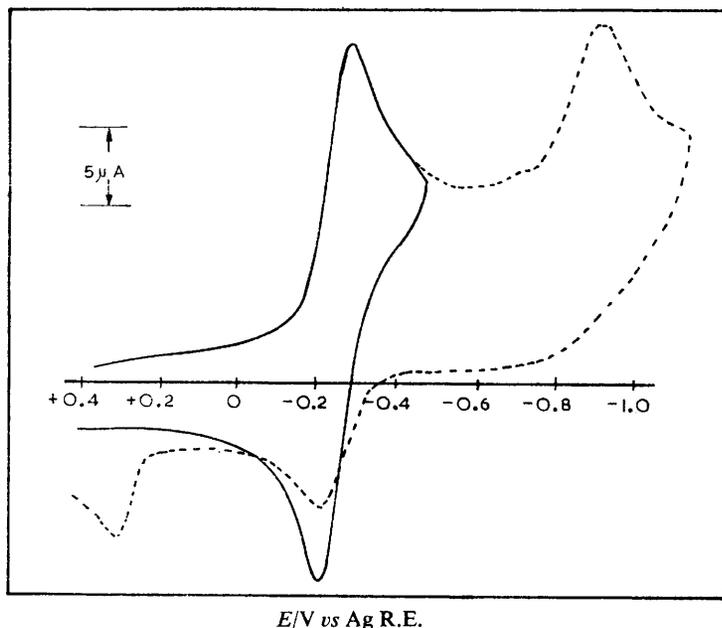


FIG. 7.—trans-1,2-Dibenzoyl ethylene (0.5 mM), TBAI (0.15 M), DMF cyclic voltammograms at 200 mV s^{-1} .

observed; the very small wave near -0.65 V is caused by some cis-compound impurity. The current function for the first wave, $i_{pc1}/v^{1/2}C$, is $85 \mu\text{A mM}^{-1} \text{V}^{1/2} \text{s}^{-1/2}$, characteristic of a one-electron reduction. The first reduction wave shows a reversal anodic wave, with $i_{pa}/i_{pc} = 1$. When the voltage scan is continued past the second reduction wave and then reversed, another anodic wave at $+0.27$ V appears. This wave is not present when scans to negative potentials only encompass the first reduction wave, even when the potential is held at potentials past the peak of the first wave for 10 s before reversal. The RRDE voltammogram shows two reduction waves in the plot of i_d *vs* E_d with E_d values of -0.22 and -0.88 V *vs* Ag R.E. The first wave shows an $i_d/\omega^{1/2}C$ of $5.4 \mu\text{A mM}^{-1} \text{s}^{-1/2}$ and the limiting current of the second wave is about one-half that of the first. A scan of i_r *vs* E_d with $E_r = +0.2$ V *vs* Ag R.E. shows a wave corresponding to the oxidation of the species produced at the first reduction wave with $N = 0.57$. This N -value is slightly higher than the value for a stable disc-produced species (0.55) because of a small amount of oxidizable impurity contained in the TDBE sample. At E_d -values corresponding to the second reduction

wave, i_r decreases to about two-thirds of its value at the first wave. For E_r held at 0.0 V, a larger drop in i_r is observed, since the product of the second reduction wave would not be oxidized.

The results can be interpreted as reduction of TDBE to a stable anion radical



with the reduction product in the second wave, probably the di-anion, decomposing rapidly, at least partially to the form the species oxidized at +0.27 V.

Attempts to study the cis-isomer, CDBE, with the usual methods of sample preparation in the light resulted in conversion of a large fraction of the starting material to the trans-isomer. For this reason, samples, once sublimed, were stored and studied in the dark. Cyclic voltammograms of CDBE are shown in fig. 8.

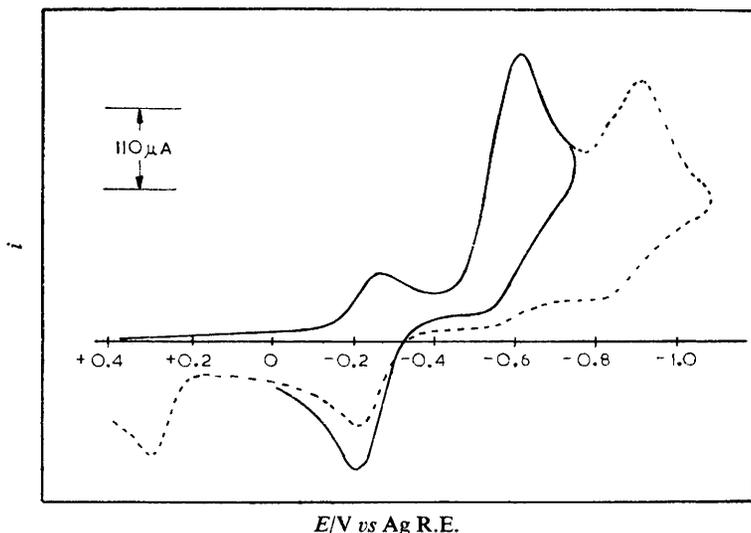


FIG. 8.—cis-1,2-Dibenzoyl ethylene (1.2 mM), TDBE (8-12 %), TBAI (0.15 M), DMF cyclic voltammograms at 200 mV s^{-1} .

The main reduction waves occur at -0.61 and $-0.91 \text{ V vs Ag R.E.}$ The small waves at -0.27 and -0.84 V can be attributed to some TDBE in the sample. The peak current function of the first reduction wave was $70 \mu\text{A mM}^{-1} \text{ V}^{\frac{1}{2}} \text{ s}^{-\frac{1}{2}}$, somewhat smaller than that of the trans-isomer. Neither of the CDBE reduction waves shows an associated oxidation wave on reversal; however, the wave attributed to oxidation of TDBE^- is enhanced when the potential is scanned over the first reduction wave. An additional oxidation wave appears at about $+0.28 \text{ V}$, similar to that observed in the voltammogram of TDBE. In this case, however, this wave appears when the scans to negative potentials only encompass the first reduction wave, although this small oxidation wave is larger when scans are made to -1.0 V , past the second reduction wave.

RRDE voltammograms for CDBE are shown in fig. 9. The description of the (i_d, E_d) curve follows the cyclic voltammetric behaviour. The curves of $i_r \text{ vs } E_d$ show anodic currents for oxidation of the trans-isomer radical anion. In this case the collection efficiencies were smaller than for TDBE, varying from 0.34 to 0.47 depending upon rotation rate and concentration. A plot of $i_r \text{ vs } E_r$ for different values of E_d is very similar to that of fig. 5, and can be interpreted in a similar manner. Some

RRDE data was obtained for mixtures of TDBE and CDBE. For a solution containing 0.42 mM TDBE and 0.21 mM CDBE, values of $N_{\text{TDBE}} = |i_r(E_r = 0 \text{ V})/i_d(E_d = -0.45 \text{ V})|$, (i.e., for TDBE reduction and oxidation) were between 0.52 and 0.57 and close to those for TDBE in the absence of CDBE. For a solution containing

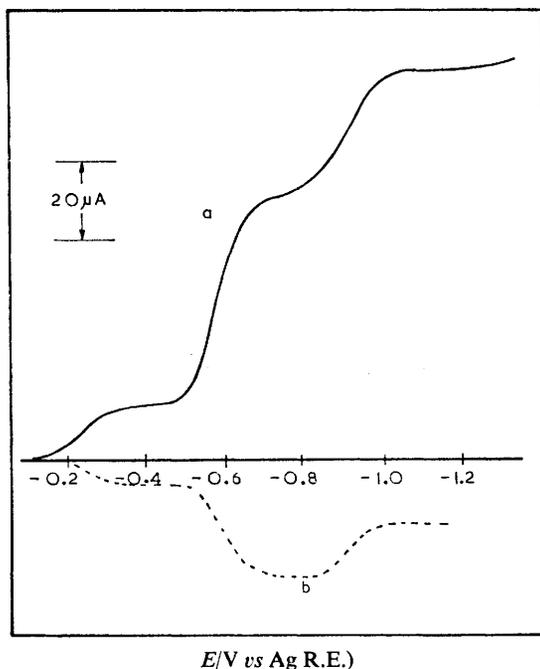
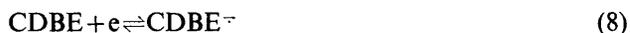


FIG. 9.—RRDE voltammograms of cis-dibenzoyl ethylene (1.2 mM) containing a small amount (8-12 %) trans-dibenzoyl ethylene, TBAI (0.15 M), DMF at 98.6 s^{-1} , (a) i_d vs E_d , (b) i_r vs E_d with $E_r = 0 \text{ V}$.

2.06 mM TDBE and 0.70 mM CDBE, N_{TDBE} varied between 0.28 and 0.40 for an ω of 202 to 27.6 s^{-1} . When bulk electrolysis of a solution containing both isomers at $-0.45 \text{ V vs Ag R.E.}$ (where only TDBE is reducible) was carried out, cyclic voltammograms showed that the reduction waves of both the trans- and cis- compounds decreased in magnitude after electrolysis. The behaviour of these isomers parallels that of the fumarate-maleate pair, and the reduction of CDBE can be described as



with the CDBE^- also undergoing reactions such as protonation, or perhaps coupling, at a rate which is fast compared to the isomerization rate. Again, the reactivity of CDBE^- is much greater than that of TDBE^- . Attempts to study cross-coupling of these radical anions with AN showed little difference between the isomers. Addition of AN did not perturb appreciably the cyclic voltammetric behaviour of either TDBE or CDBE, although the cis-isomer showed pronounced filming in the presence of AN while the trans-isomer did not.

E.S.R. OF THE DIBENZOYLETHYLENES

Intra muros electrolytic reduction of TDBE and CDBE in DMF at a platinum electrode was undertaken to compare the behaviour of these with that of the fumarate

and maleate. Il'yasov and co-workers⁷ reported that both TDBE and CDBE produce the same e.s.r. spectrum on reduction and showed a poorly-resolved spectrum obtained at -20°C . Winecoff, O'Brien and Boykin¹⁰ also mention a stable e.s.r. spectrum from TDBE. The e.s.r. spectrum obtained by electrolytic reduction of TDBE in 0.1 M TBAI-DMF in a non-flowing solution is shown in fig. 10a, while that

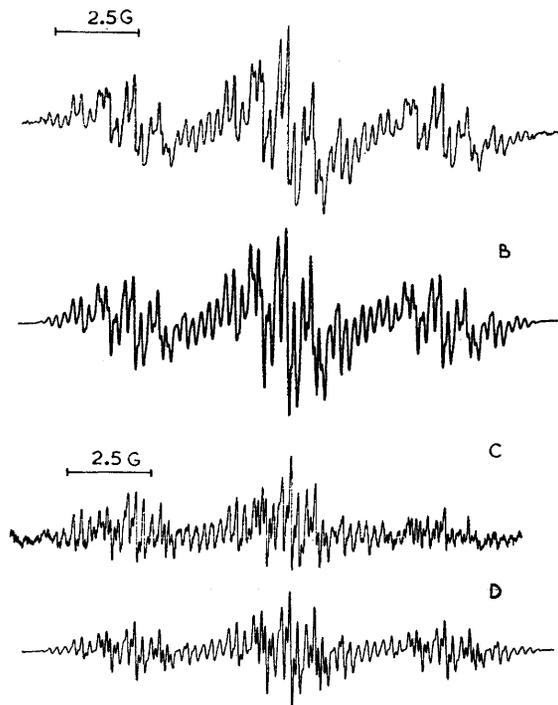


FIG. 10.—E.s.r. spectra of (a) radical anion generated from solution containing 3.1 mM TDBE, 0.1 M TBAI, DMF; (b) simulated spectrum using coupling constants in table 1 and linewidth of 0.11 G; (c) radical anion generated from solution containing 2.0 mM CDBE (+some TDBE), 0.1 M TBAI, DMF; (d) simulated spectrum as in (b), except line width was 0.08 G.

from a solution of CDBE (containing an appreciable amount of TDBE impurity) is shown in fig. 10c. The spectra are essentially the same, although that of the *cis* isomer shows a slightly narrower line width, and gives a less intense spectrum when electrolyzed in a similar manner. The simulated spectra shown in fig. 10b and d were obtained with the coupling constants shown in table 1 and line widths of 0.11 and 0.08 gauss, respectively. The assignment of the coupling constants to positions in the molecule was made on the basis of McLachlan molecular orbital calculations using the parameters: $\lambda = 1.2$; $\alpha_o = \alpha_c + 1.4 \beta_{cc}$; $\beta_{co} = 1.65 \beta_{cc}$.¹¹ For this molecule only a single conformation is found for the radical anion; the electrochemical results show that this is the *trans*-form and probably, from steric considerations in the conformation,

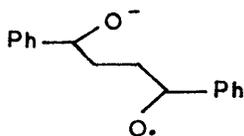


TABLE I.—COUPLING CONSTANTS OF 1,2-DIBENZOYLETHYLENE ANION RADICAL ^a

type of nuclei	no. of equivalent nuclei	^a H(G)	assignment	calculated ^b (G)
H	2	4.55	ethylenic	4.59
H	2	0.84	para	0.96
H	4	0.74	ortho	0.92
H	4	0.25	meta	-0.35

^a The solution was DMF containing 0.1 M TBAI and either 3.1 mM TDBE or 2.0 mM CDBE + TDBE. The SEESR cell used a Pt working electrode, W counter electrode and Ag reference electrode.

^b From McLachlan spin densities and $Q = 24.0$ G.

DISCUSSION

The results show that for these compounds the trans-form is more easily reduced than the cis-form. The measured difference in reduction potential for DEF and DEM is about 0.20 V at a platinum electrode from cyclic voltammetry, or 0.23 V from d.c. polarography, (compared to the difference of 0.15 V found for the methyl esters by Il'yarov *et al.*^{7a} by d.c. polarography). For TDBE and CDBE this difference from our results is 0.33 V (compared to 0.24 V found from d.c. polarography^{7a,10} and 0.27 V found by cyclic voltammetry at a mercury electrode¹⁰). The more difficult reduction of the cis-isomer can be ascribed to the repulsion of the carbonyl groups when a negative charge is added to the molecule making this configuration energetically less favourable. This difference in energy can be estimated by assuming a rate constant for isomerization of about 100 s⁻¹, which when coupled with the scan rate employed in the cyclic voltammetric experiments (e.g., 0.2 V s⁻¹) and the equation for the positive shift in potential for the wave for an electrode reaction with a fast following reaction,¹² yields a difference in reversible potentials of about 0.28 V for DEM and DEF. For stilbene, where this electrostatic repulsion of the carbonyl groups is absent, the $E_{1/2}$ -values of the trans- and cis-forms in DMF are almost identical, -2.15 and -2.18 V, respectively.¹³ The addition of the electron also decreases the bond order of the central ethylenic bond, which, when coupled with the carbonyl group repulsion, promotes rapid isomerization of the cis-form. This isomerization also occurs in stilbene, promoted by steric effects, but the rate is slower. For example, Dietz and Peover¹³ give the lifetime of the cis-stilbene radical anion as greater than 15 s. (In the presence of alkali metal ion the isomerization rate of cis-stilbene is apparently much faster, however.¹⁴) Finally, the cis-forms (DEM and CDBE) are more reactive than the trans-forms with respect to coupling or addition reactions. This can be rationalized as being caused by greater electron density residing on the central ethylenic carbons of the cis-radical ions because of the repulsion of the carbonyl groups or partial twisting around the central ethylenic bond. This effect has been noted before, for reaction of stilbene radical ions with water,¹³ but the difference in reactivity was not as striking as in the cases observed here. Finally, the cross electron transfer reactions, such as (6), explain how small amounts of radical ion catalyze the cis-trans conversion.

These results are also consistent with those previously found for the oxidation of cis- and trans-1,2-bis(p-N,N-dimethylaminopyrenyl)-1,2-diphenylethylene.¹⁵ For oxidation of either form to the stable di-cation, followed by reduction, a mixture of cis- and trans- parent results. In this case, oxidation weakens the central ethylenic bond, and steric effects cause rotation about it. Photo-isomerization has been a

subject of interest for many years. Isomerization upon electron transfer provides an interesting parallel to those studies.

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